

# Corrosion inhibition by some organic compounds of mild steel in synthetic and natural seawater

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**SIX ORGANIC** compounds, *N*-1-naphthylethylene diamine dihydrochloride (A), *N,N*-diethyl-*P*-phenylenediamine sulphate (B), ethylene diamine tetra-acetic acid (C), hexamethylenetetramine (D), sulphanilamide (E), and 1-naphthylamine (F), were assessed for corrosion inhibition of mild steel using potentiodynamic polarization. The concentrations required to achieve maximum inhibition varied with the type of organic compound and the electrolyte. The differences observed are due to the chemical nature of the compounds and the electrolyte. In general, the six compounds were all found to control the anodic process more than the cathodic process, suggesting that they may be mixed-type inhibitors. Compound E was found to be a weak inhibitor in synthetic seawater, whereas in natural seawater it acted as a very-efficient inhibitor. The corrosion-inhibition efficiency of the compounds in synthetic seawater was in the order  $A > D > C > B > F > E$ , whereas in natural seawater their efficiency was in the order  $E > C > A > F > B > D$ .

## Introduction

Many organic compounds have been reported to serve as corrosion inhibitors, in particular azoles, thiols, thiourea, amines, and their derivatives [1-14]. Most of the experimental work on these compounds was for the purpose of recommending inhibitors for the control of corrosion in industries which are dealing with acids. However, little is known about the use of corrosion inhibitors in industries using seawater for various purposes. In view of this, an attempt has been made to identify the efficiency of corrosion inhibitors for mild steel in seawater.

In this investigation six amines, which are readily available in the market, have been assessed for their inhibition efficiency in synthetic and natural seawater. The standard electrochemical techniques have been used for the purpose. The choice of the two seawater media was intended to provide results which can be compared with each other, and extrapolated. The variation in the corrosion rates is discussed in relation to the degree of surface coverage of mild steel by the inhibitors.

## Experimental details

Coupons (2cm x 2cm) of commercial-grade mild steel (C - 0.2%, Si - 0.05%, Mn - 0.26%, P - 0.05%, S - 0.04% and Fe - rest) were used for the polarization studies. The surface of each coupon was first cleaned with 5% HCl to remove mill scale, mechanically polished on zero emery paper, and finally degreased in acetone. Electrochemical studies were performed by using a computer-controlled potentiostat. Corrosion software from EG & G PARC was used to determine the corrosion current from the Tafel extrapolation method. The coupons were potentiodynamically polarized at a scan rate of

0.2mV/sec over the range of -300mV to +300mV relative to the corrosion potential in the synthetic [15] and natural seawater containing 0, 0.1, 1, 10, 50, 100 and 200ppm concentration of the compounds. A standard flat-cell consisting of mild steel (MS) as working, platinum as counter, and a calomel electrode (SCE) as reference electrode, was used for the purpose. The area exposed to the electrolyte was 1sqcm. For each compound concentration, experiments were conducted in duplicate. The corrosion-current densities were used to calculate the percentage inhibition using the equation,

$$\%I = \{(i_0 - i) \times 100\} / i$$

where  $i_0$  is the mean corrosion-current density in the blank solution, and  $i$  is the corrosion-current density in the test solution.

The surface coverage of each inhibitor at a given concentration was calculated using the following equation [16]:

$$Q = (1 - i/i_0)$$

where  $Q$  is the surface coverage,  $i$  is the corrosion-current density in the test solution, and  $i_0$  is the corrosion-current density in the blank.

The compounds used in the present investigation were *N*-1-naphthylethylene diamine dihydrochloride (A), *N,N*-diethyl-*P*-phenylenediamine sulphate (B), ethylene diamine tetra-acetic acid (C), hexamethylenetetramine (D), sulphanilamide (E) and 1-naphthylamine (F) (Table 1).

Stock solutions of all the compounds were prepared in distilled water, except that for B which was first dissolved in concentrated HCl and diluted with distilled water. Series of concentrations were

DESIGNATION	COMPOUND	FORMULA
A	N-1-Naphthylethylene diamine dihydrochloride	<chem>NCCN</chem> attached to a naphthalene ring, $\cdot 2\text{HCl}$
B	N,N-Diethyl-P-phenylenediamine Sulfate	<chem>CCN(CC)Cc1ccc(N)cc1</chem> , $\cdot \text{H}_2\text{SO}_4$
C	Ethylene diamine tetra-acetic acid disodium salt	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa}))_2$
D	Hexamethylenetetramine	<chem>C1CN1CN1CN1</chem>
E	Sulfonamide	<chem>NC(=O)c1ccc(S(=O)(=O)N)cc1</chem>
F	1-Naphthylamine	<chem>Nc1ccc2ccccc2c1</chem>

Table 1. Chemistry of the compounds under investigation.

made in either synthetic and/or natural seawater.

## Results and discussion

### Corrosion rate ( $I_{corr}$ )

Fig.1 shows the variations of corrosion current ( $I_{corr}$ ), and consequently the corrosion rate of mild steel (MS) in synthetic seawater containing different concentrations of compounds. The corrosion rate of MS in synthetic seawater decreased gradually with concentration of 0.1, 1, 10, and 50ppm of the compounds F, D, B and A, respectively; the  $I_{corr}$  values increased after the concentrations were enhanced. On the other hand, an increase in the corrosion rate was evident with concentrations up to 1ppm of the compounds C and E. Subsequently, the corrosion rate decreased with concentrations up to 50 ppm and increased thereafter up to 200ppm of these compounds. It is possible that the adsorption of amines from solutions of low concentrations may cause stimulation of corrosion by way of formation of organometallic complexes[2,3,17]. The results indicated that these compounds can be considered as corrosion inhibitors and were found to influence the corrosion of MS in synthetic seawater to a varying extent.

As a result of the differing characteristics of the inhibitors, the concentrations required for maximum inhibition varied (Table 1). However, higher concentrations in synthetic seawater promoted corrosion, suggesting that these compounds at higher concentrations might have acted as catalysts in the reactions.

The corrosion rate of MS in natural seawater decreased with increasing concentrations of the compounds A, B and E, up to 1ppm, whereas for the compounds D and F the corrosion rate decreased at the concentrations 10ppm and 0.1ppm, respectively (Fig.2). Thereafter, the corrosion rate was found to

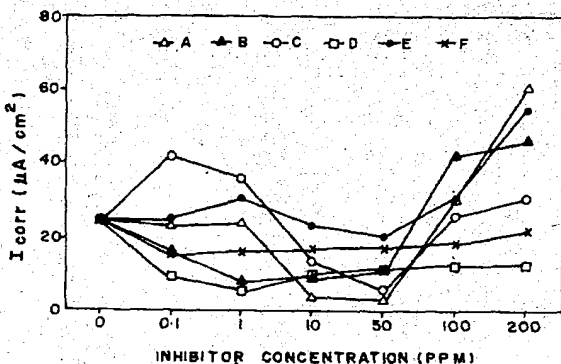


Fig.1. Variations of corrosion-current density in relation to inhibitor concentrations in synthetic seawater.

increase gradually with increasing concentration. On the other hand, the corrosion rate decreased with increasing concentration of compound C.

The compounds A, B and E at concentrations of 200ppm were found to accelerate the corrosion rate of mild steel in natural seawater. It is evident from these results that the compounds acted as corrosion inhibitors in natural seawater as well. However, the concentrations required for maximum inhibition varied with the compound. The difference in concentrations for maximum inhibition could be attributed to the difference in the chemical nature of the compounds (Table 1). At higher concentrations (200ppm) the compounds, except for C and F, were found to enhance the corrosion rate slightly higher than for the control. The possible reason for this could be the involvement of these compounds as catalysts in the anodic reaction, with a resulting enhancement of the corrosion process.

### Corrosion potential ( $E_{corr}$ )

Tables 2 and 3 show the dependence of the corrosion potential on the concentration of the inhibitors in synthetic and natural seawater,

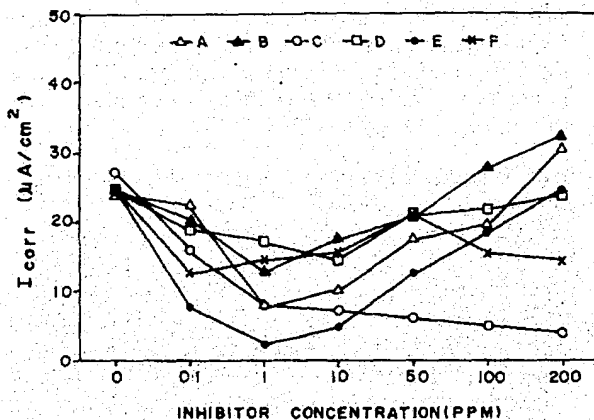


Fig.2. Variations of corrosion-current density in relation to inhibitor concentrations in natural seawater.

Inhibitor	Conc. (ppm)	$E_{corr}$ (-mV)	$I_{corr}$ ( $\mu A/cm^2$ )	Inh. efficiency (I %)
A	0.0	400	24.9	-
	0.1	360	22.91	8.02
	1.0	460	23.92	8.06
	10.0	512	3.97	85.6
	50.0	465	2.58	89.64
	100.0	471	29.85	*
	200.0	513	60.32	*
B	0.0	441	24.8	-
	0.1	454	16.09	35.12
	1.0	450	7.66	69.11
	10.0	458	8.49	66.76
	50.0	473	10.56	57.41
	100.0	495	42.08	*
	200.0	550	45.95	*
C	0.0	369	24.0	-
	0.1	372	41.75	*
	1.0	386	36.04	*
	10.0	421	13.32	44.50
	50.0	461	5.46	77.24
	100.0	435	25.44	*
	200.0	494	30.51	*
D	0.0	410	24.0	-
	0.1	417	9.07	62.20
	1.0	433	5.34	77.75
	10.0	434	9.77	59.29
	50.0	429	11.14	53.28
	100.0	433	11.86	53.58
	200.0	439	12.09	50.58
E	0.0	440	24.86	-
	0.1	461	24.86	*
	1.0	479	30.51	*
	10.0	472	22.85	8.08
	50.0	489	20.09	19.18
	100.0	512	30.91	*
	200.0	552	54.36	*
F	0.0	482	24.86	-
	0.1	488	14.81	40.42
	1.0	487	15.60	37.24
	10.0	466	16.59	33.26
	50.0	496	16.69	33.86
	100.0	520	18.10	27.55
	200.0	541	21.64	13.11

Table 2. Effect of inhibitors on the electrochemical behaviour of mild steel in synthetic seawater.

\* indicates no inhibition

respectively. The corrosion potential ( $E_{corr}$ ) was shifted towards the less-noble direction for the concentrations at which maximum inhibition was observed for all the compounds, except B and E. The shift of  $E_{corr}$  towards the less-noble direction indicates that the anodic process is controlled more than the cathodic process [16]. Therefore, it can be considered that the compounds under study were mixed-type inhibitors [4].

#### Inhibition efficiency and degree of surface coverage

The maximum-percentage inhibition efficiency of these compounds varied between 19.1% and 89.6% in synthetic seawater. It is evident from Table 2 that compound A, giving 89.6% protection to mild steel (Fig.3), appears to be the most efficient inhibitor, followed in order by compounds D, C, B, F and E. The concentrations required to achieve maximum inhibition with each compound varied from one to another. These concentrations were 50ppm for compounds A, C, and E, only 1ppm for compounds B and D, and 0.1ppm for compound F.

The values for degree of coverage also agree closely with the percentage inhibition efficiency. The maximum degree of coverage varied between 0.18 and 0.89 (Table 4). The values of degree of coverage for 100ppm and 200ppm were negative except for the compounds C, D, and F, whereas at lower concentrations the values were positive except for compounds C and E. The positive values of degree of coverage suggest an adsorption process on the surface, whereas the negative values suggest desorption of molecules and, hence, acceleration of corrosion.

Regarding the inhibition efficiency of these compounds in natural seawater (Table 3), compound E was found to be the most efficient (90.9%) followed by the compounds C (86%), A (72.8%), F (50%), B (48%) and D (41%). The concentration required to achieve maximum efficiency varied with the compound. The values of degree of adsorption for each concentration agreed closely with the corresponding values of inhibition efficiency (Table 5). The negative values of adsorption are suggestive of promotion of corrosion. A maximum of (90.9%)

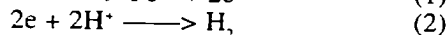
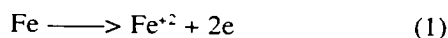
Inhibitor	Conc. (ppm)	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu A/cm^2$ )	Inh. efficiency (I %)
A	0.0	410	23.70	-
	0.1	481	22.70	4.21
	1.0	455	7.79	72.83
	10.0	501	9.95	58.01
	50.0	471	17.24	27.20
	100.0	484	19.19	19.00
	200.0	488	30.19	*
B	0.0	512	24.86	-
	0.1	510	20.20	18.74
	1.0	490	12.73	48.79
	10.0	500	17.60	29.20
	50.0	514	20.27	18.46
	100.0	505	27.68	*
	200.0	511	32.02	*
C	0.0	421	26.92	-
	0.1	430	15.92	40.86
	1.0	397	7.74	71.24
	10.0	404	7.12	73.55
	50.0	424	5.79	78.49
	100.0	392	4.76	82.31
	200.0	426	3.76	86.03
D	0.0	421	24.29	-
	0.1	475	18.72	22.93
	1.0	441	16.96	30.17
	10.0	491	14.33	41.00
	50.0	485	21.04	13.37
	100.0	483	21.53	11.50
	200.0	520	23.11	4.85
E	0.0	517	24.39	-
	0.1	453	7.66	68.59
	1.0	376	2.21	90.90
	10.0	422	4.76	80.48
	50.0	405	12.26	49.73
	100.0	466	18.01	26.73
	200.0	506	24.43	*
F	0.0	453	24.86	-
	0.1	450	12.38	50.20
	1.0	476	14.35	42.27
	10.0	495	15.36	38.21
	50.0	470	20.83	16.20
	100.0	478	15.18	38.93
	200.0	482	13.99	43.72

\* indicates no inhibition

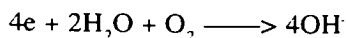
Table 3. Effect of inhibitors on the electrochemical behaviour of mild steel in natural seawater.

surface coverage was evident, as indicated by calculation in the case of compound E. followed by 86% surface coverage for compound C.

It has been reported that many of the aliphatic and aromatic amines are corrosion inhibitors[9-14]. The amine group is believed to be the donor of electrons[18], and hence it can be assumed that the amines can enhance the rate of cathodic reaction (equn.2, below) by providing electrons with resulting suppression of the anodic reaction (equn.1, below).



or



and the corrosive environment. The amines are believed to form chelates with the corrosion product, and remain adsorbed on the surface. The molecules of these compounds can penetrate through, and remain in, the interstices of the corrosion-product film, and thus block the anodic sites. The inhibition of corrosion is related to the adsorption displacement of activator (Cl<sup>-</sup>) by passivating ions[8,18].

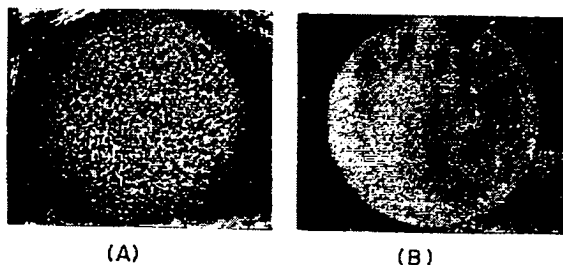


Fig.3. Photographs showing the extent of corrosion of polarized mild-steel samples in synthetic seawater (A) without, and (B) with, 50ppm of naphthylethylene diamine dihydrochloride.

Inhibitor	Concentration (ppm)					
	0.1	1	10	50	100	200
A	0.080	0.040	0.856	0.896	-0.190	-1.420
B	0.351	0.691	0.660	0.574	0.850	-0.890
C	-0.680	-0.450	-0.450	0.464	0.780	-0.230
D	0.450	0.677	0.410	0.327	0.330	0.270
E	-0.078	-0.220	0.080	0.180	-0.240	-2.000
F	0.360	0.327	0.280	0.280	0.211	0.060

**Table 4. Degree of surface coverage of mild steel with respect to the inhibitor concentrations in synthetic seawater.**

Inhibitor	Concentration (ppm)					
	0.1	1	10	50	100	200
A	0.063	0.730	0.580	0.272	0.190	-0.270
B	0.186	0.480	0.290	0.184	-0.110	-0.288
C	0.409	0.712	0.730	0.780	0.823	0.860
D	0.246	0.301	0.410	0.133	0.133	0.048
E	0.685	0.909	0.804	0.497	0.261	-1.690
F	0.500	0.422	0.380	0.160	0.389	0.436

**Table 5. Degree of surface coverage of mild steel with respect to the inhibitor concentrations in natural seawater.**

In the current investigation, maximum protection was achieved at the lowest concentration (0.1-1 ppm) used for most of the compounds in the study, in both types of seawater. It has been suggested that it is often adequate to cover the metal surface with a small amount of inhibitor to produce a passive surface [18]. According to Rosenfeld [18], the corrosion stops absolutely when approximately 4% of the surface is covered.

It is believed that the efficiency of inhibitors is dependent on the two opposing effects of inhibition by adsorbed molecular species, and an acceleration of corrosion by adsorbed protonation species. In this investigation, the accelerating effect of the compound at higher concentrations could be explained on this basis. The other possible reason for the enhanced corrosion rate at higher concentrations of the compounds could be due to the solubility factor of the compounds [11]. At higher concentrations, the solubility of the compound might have decreased with an accompanying increase in activity of Cl<sup>-</sup> ions and resulting depassivation of the metal surface. However, this particular point needs more work to explain the higher corrosion rate of MS with higher concentration of the compound in synthetic and natural seawater. The possibility of desorption of molecules at higher concentrations of the compounds cannot be ruled out as a possible cause of the enhancement of corrosion at higher compound concentrations. Adsorption and desorption of molecules are dependent on the bonding strength between the inhibitor species and the surface. This is, in turn, dependent on the nature of the functional groups in the inhibitor as well as on the structure of the rest of the inhibitor molecules.

### Conclusions

1. Compounds A, B, C, D, E and F were effective as corrosion inhibitors for mild steel in both synthetic and natural seawater.

2. The concentrations required to achieve maximum corrosion inhibition varied with respect to the compound and the type of electrolyte under study.

3. Electrochemical behaviour of these compounds in synthetic and natural seawater suggests that they are mixed-type inhibitors.

4. Compound E was found to be a weak inhibitor in synthetic seawater, but was very efficient in natural seawater.

5. The corrosion inhibition efficiencies of these compounds in synthetic and natural seawater were in the order A > D > C > B > F > E and E > C > A > F > B > D respectively.

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