The Influence of some Condensation Products of Aminobenzothiazoles and Salicylaldehyde on Corrosion Inhibition and Hydrogen Permeation in Sulphuric acid Solution

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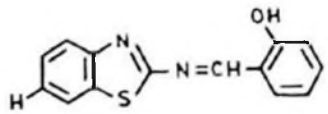
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2-Salicylidene aminobenzothiazole (SABT), 2-salicylidene amino-6-chloro-benzothiazole (SACLBT) and 2-salicylidene amino-6-methoxy-benzothiazole (SAMEOBT) - condensation products of aminobenzothiazoles and salicylaldehyde - have been synthesized and investigated for their efficiency as corrosion inhibitor for mild steel in 1N H_2SO_4 at different concentrations ranging from 100 to 500 ppm and at different temperatures ranging from 40 to 60°C. Of these compounds SABT gave the best performance - an inhibition efficiency as high as 99.9% even at a very low concentration at 40°C. Potentiodynamic polarization studies reveal that the inhibition of corrosion of mild steel in 1N H_2SO_4 in the presence of anils is under mixed control. These compounds are found to bring down the permeation of hydrogen through mild steel in 1N H_2SO_4 solution. The adsorption of these compounds on the mild steel surface follows Temkin's adsorption isotherm. Surface analysis of the mild steel surface exposed with SABT showed that the adsorption of this compound on the steel surface occurs through the interaction of lone pairs of nitrogen and sulphur atoms with the metal surface.

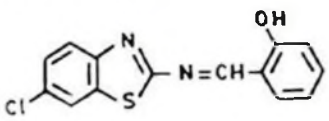
A perusal of literature [1-2] reveals that most of the commercial inhibitor formulations include aldehydes and amines as essential ingradients. Condensation products of carbonyls and amines (anils or schiff's bases) are more efficient inhibitors than the constitutent carbonyls and amines [3]. In the present investigation the influence of a few heterocyclic anils arising from salicyl aldehyde and substituted benzothiazoles on corrosion inhibition and hydrogen permeation through mild steel in 1N H_2SO_4 has been studied. The choice of these compounds as inhibitors is based on two considerations. Firstly, the presence of π bond of an azomethine group and π electrons of phenyl groups, in addition, the presence of a benzothiazole ring can induce greater adsorption of these inhibitor molecules on the metal surface. Secondly, the presence of an -OH group can increase the solubility of these inhibitors in test solutions, leading to a higher inhibition efficiency.

MATERIALS AND METHODS

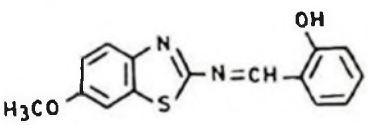
The folowing inhibitors were synthesised in the laboratory following the procedures reported elsewhere [4].



SABT



SACLBT



SAMEOBT

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2-Salicylidene aminobenzothiazole (SABT),
2-salicylidene amino-6-chloro-benzothiazole (SACLBT) and
2-salicylidene amino-6-methoxy-benzothiazole (SAMEOBT)

Aggressive solutions used were made from A.R. grade H_2SO_4 (MERCK). Appropriate concentrations of the acid were prepared using triply distilled water. Concentrations of compounds used range from 100 to 500 ppm in 1n H_2SO_4.

Mild steel (AISI 1070) strips of size 5x2x0.025 cm were used for weight loss and hydrogen permeation studies. A mild steel strip with an exposed area of 1 cm^2 was used for polarisation measurements. The chemical composition (wt %) of the mild steel is given in Table 1.

Specimens were mechanically polished first and then using different grades of emery papers successively. They were subsequently degreased with trichloroethylene and then dried at room temperature before use.

Corrosion Weight loss Tests

Weight loss measurements were carried out as described earlier [5]. In brief, strips of mild steel specimens of 5 x 2 x 0.025 cm^3 (in triplicate) were immersed in 200 ml of corrodant media and allowed to stand for 2 hours. The inhibition efficiency (%IE) for different concentrations of compounds were calculated from the difference in weight loss values in the absence and presence of compounds in 1N H_2SO_4 solutions. Studies were carried out at three different temperatures ranging from 40 to 60°C.

Potentiodynamic Polarisation Studies

Both cathodic and anodic polarisation curves were recorded potentiodynamically at a scan rate of 1 $mV.sec^{-1}$ using EG & G PARC potentiostat/Galvanostat (model 173), Universal programmer (model 175) and with X-Y recorder (model RE 0089). The cell assembly consists of a mild steel working electrode, a plantinum foil of area 3 x 3 cm^2 as the counter electrode and a saturated calomel electrode (SCE) which served as the reference electrode. The solution was stirred using a magnetic stirrer. All the experiments were performed at 35±2°C.

Hydrogen Permeation Measurements

Hydrogen permeation studies were carried out at a temperature of 35±2°C using an adaptation of the modified Devanathan and Stachurski's two compartment cell as described elesewhere [6,7]. Hydrogen permeation currents were recorded usingan X-Y-T Rikadenki recorder in the presence and the absence of the inhibitors in 1N H_2SO_4.

Table 1

Composition of Mild steel AISI 1070

C	Mn	Si	S	P	Fe
0.14%	0.35%	0.17%	0.025%	0.03%	remainder

Auger Electron Spectroscopy

The Auger Electron Spectroscopic analysis was carried out using a Scanning Auger Microprobe (SAM PHI model 1590 A, USA). Specimens were polished using different grades of emery papers and dipped for 1.5 hours in inhibited acid solution containing 500 ppm SABT, rinsed with triply distilled water and dried at room temperature. They were fixed on a sample holder and introduced into the Fast Entry Air Lock (FEAL) chamber maintained at a vacuum level of 10^{-3} Torr. After allowing for degassing, the specimens were transferred into the preparation chamber, where degassing continued for long time. The specimens were then introduced into the analyser chamber. The area of interest is then selected with the help of SEM attached to the instrument and excited with a 3 keV electron beam. The area analysed is 200 A and depth resolution is 5-15 A.

RESULTS AND DISCUSSION

Different corrosion parameters such as percentage inhibition efficiency at corrosion rates obtained by weight loss method at different concentration and temperatures are given in Table 2. It can be noted from the Table that all compounds inhibit corrosion of mild steel in sulphuric acid at all concentrations used for the study. Maximum IE is achieved at 500 ppm concentration of each compound. It is also observed that the IE of SABT does not decrease much with increase in temperature (from 40 to 60°C) thereby indicating its stronger adsorption on the metal surface. Values of IE for different anils follow the order:

SABT > SACLBT > SAMEOBT

The differnece in their inhibitive performance can be explained on the basis of their molecular structure. Lesser inhibitive action of SACLBT may be attributed to the presence of electron withdrawing chlorine atom, which decreases the electron availability in the molecule and leads to less adsorption and hence less inhibition. Since SAMEBOT is a softer base as compared to SABT, it forms a weaker bond with metal ions which leads to less adsorption and less inhibition.

Organic molecules are known to inhibit corrosion by an adsorption mechanism [9-10]. The inhibition of corrosion of mild steel by anils can be explained on the basis of adsorption. In acidic solutions, the inhibitors can exist as neutral molecules or as cations. They may adsorb on the metal surface in the form of a neutral molecules through chemisorption mechanism [11]. The adsorption of inhibiors can also take place through interaction between π electrons of azomethine group (-C=N-), benzothiazole ring and the metal surface [12].

Adsorption isotherm

The degree of surface covrage (θ) for different concentrations of inhibitors in 1N H_2SO_4 has been evaluated from the value of inhibition efficiency and they are tested graphically for fitting a suitable adsorption isotherm. The plots of θ *vs.* log C for all the compounds in 1N H_2SO_4 at 40°C fits to Temkin's adsorption isotherm. A straight line (Fig.1) was obtained in all the cases proving the fact that the adsorption of these compounds on the mild steel surface obeys Temkin's adsorption isotherm.

Table 2

Corrosion Parameters from Weight loss Mmethod for Mild steel
Media 1 N Suphuric acid with Different Concentration of Inhibitors

Inhibit. conc (ppm)	40°		50°		60°	
	Corr	%IE	Corr	%IE	Corr	%IE
	SABT					
500	0.05	99.9	0.02	99.9	3.51	98.0
400	0.36	99.4	1.73	98.1	10.35	94.1
300	1.84	97.0	5.30	94.2	33.00	81.2
200	3.07	95.0	28.90	68.4	66.18	62.3
100	9.65	84.3	42.44	53.6	110.7	36.8
	SACLBT					
500	1.10	98.2	9.51	89.6	34.33	80.4
400	1.59	97.4	11.89	87.0	43.58	75.2
300	2.27	96.3	20.12	78.0	60.91	65.3
200	3.38	94.5	27.71	69.7	104.8	40.3
100	5.90	90.4	63.85	30.2	122.5	30.2
	SAMEOBT					
500	8.97	85.4	19.94	78.2	55.64	68.3
400	9.95	83.8	27.35	70.1	57.75	67.1
300	12.48	79.7	36.22	60.4	91.63	47.8
200	15.25	75.2	51.86	43.3	108.5	38.2
100	23.18	62.3	59.00	35.5	122.0	30.5

Potentiodynamic Polarisation Studies

Table 3 gives corrosion parameters such as E_{corr}, I_{corr} and Tafel slope values obtained from potentiodynamic polarisation curves for mild steel in 1N H_2SO_4 containing different concentration of inhibitors. It is found that these compounds do not cause appreciable change in E_{corr} values and Tafel slope values thereby suggesting that all these inhibitors are of mixed type.

Hydrogen Permeation Studies

In acidic solutions hydrogen permeation in metals takes place as follows

$$M + H_3O^+ + e^- \longrightarrow H_2O + MH_{ads} \quad \ldots (1)$$

Table 3

Eectrochemical Corrosion Parameters
Mild steel in 1 N H_2SO_4 in absence & presence of Inhibitors

conc ppm	E_{corr} mV	I_{corr} µA	b_c mV/decade	b_a mV/decade	IE %
nil	-581	320	110	50	-
SABT					
500	-576	12	96	40	96.25
400	-572	18	92	45	94.37
300	-574	20	90	48	93.75
SACLBT					
500	-568	13	104	44	95.93
400	-568	20	100	42	93.75
300	-570	25	90	45	92.18
SAEOBT					
500	-588	20	95	40	93.75
400	-588	20	92	45	93.75
300	-586	30	90	48	90.62

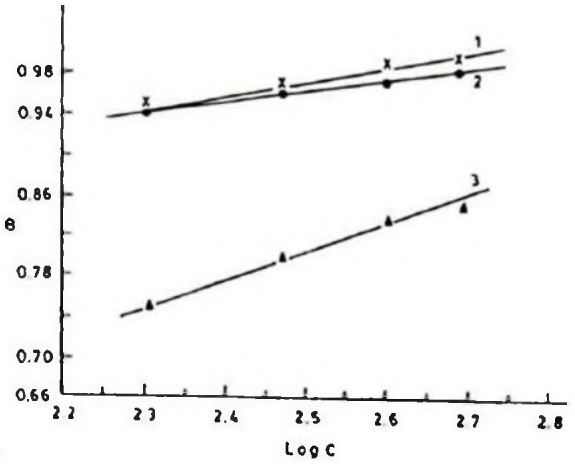


Fig.1. Temkin's adsorption isotherm plot for mild steel in IN H_2SO_4 containing different anils at 40°C.

1. SABT 2. SACLBT 3. SAMEOBT

where M is the cathode metal surface, followed by either

$$MH_{ads} + MH_{ads} \longrightarrow 2M + H_2 \quad \text{... (2)}$$
(discharge step)

or

$$MH_{ads} + H_3O^+ + e^- \longrightarrow M + H_2O + H_2 \quad \text{—(3)}$$
(electrochemical desorption)

Hydrogen gas is liberated during the corrosion process. A part of the atomic hydrogen permeates through the metal (when the remainder is evolved as molecular hydrogen) and gets occluded in the crystal lattice. Later, they create some detrimental effects such as cracking, pitting, breakage etc., on the metal surface. Thus, the design of inhibitors should take into account this effect also. A good inhibitor must either prevent hydrogen adsorption or favour H-H recombination.

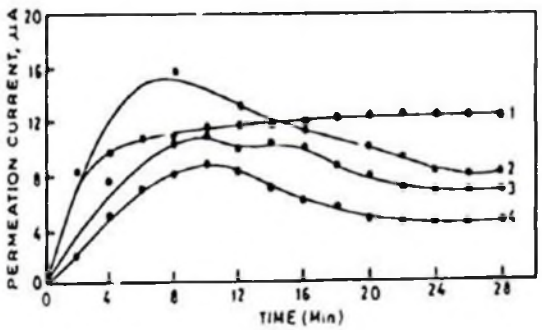


Fig.2. Hydrogen permeation current vs. time curves for mild steel in 1N H_2 in the absence and presence of anils

1. Blank 2. SABT 3. SACLBT 4. SAMEOBT

In the present study, hydrogen permeation studies have been carried out for mild steel in 1N H_2SO_4 alone and in the presence of anils and are shown in Fig.2. It is clear from this figure that, all the anils are able to reduce hydrogen permeation current effectively in 1N H_2SO_4 solution. The better performance of these compounds is due to the availability of more π-electrons and more surface area which leads to more adsorption, inhibition and also more reduction in permeation current.

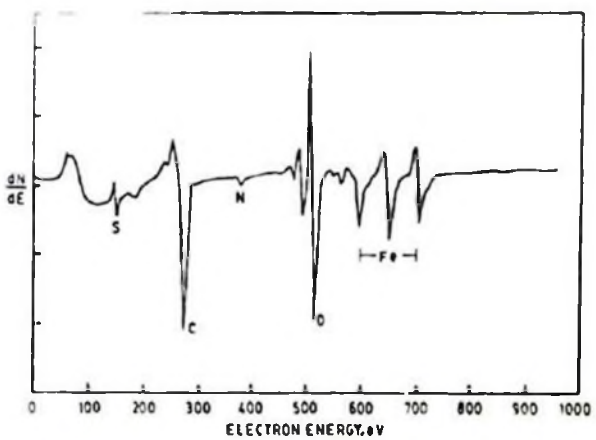


Fig.3. Auger Electron Spectrum for the mild steel surface exposed to 1N H_2SO_4 containing SABT.

Auger Electron Spectroscopy (AES)

The AES spectra for mild steel in 1N H_2SO_4 containing SABT at a concentration of 500 ppm is shown in Fig.3. The appearance of peaks for N and S atoms at 385 and 154 eV respectively indicates the adsorption of this compound on the metal surface through interaction betwen lone pairs of electron of the above atoms and the metal surface.

CONCLUSIONS

1. All anils studied in the present work have been found to perform well as corrosion inhibitors in 1N H_2SO_4.
2. The inhibition of corrosion of mild steel in the presence of these anils is under cathodic control.
3. The anils have been found to inhibit the corrosion of mild steel by getting adsorbed on the metal surface.
4. The anils bring down the permeation current considerably in 1N H_2SO_4.
5. The adsorption of anils on the mild steel surface from 1N H_2SO_4 obeys Temkin's adsorption isotherm.

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