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Benzenethiols as inhibitors for the corrosion of copper

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The effect of benzenethiol (BT) and some substituted benzenethiols – {o-methyl benzenethiol (o-MBT), o-amino benzenethiol (o-ABT), p-amino benzenethiol (p-ABT) and m-methyl benzenethiol (m-MBT)} – on the corrosion of copper in H_2SO_4 and NaOH solutions has been investigated by means of spectrophotometric measurements, potentiostatic polarization studies, cyclic voltammetry and potential stepping experiments. In acid solutions, under ordinary conditions, the thiols are adsorbed onto the metal surface in their molecular forms through their thiol (–SH) moiety and when the potential is made more noble oxidative dimerization of the thiols takes place, and the dimer replaces the thiol. Both thiols and their dimers are not effective as inhibitors. In alkaline solutions *in situ* polymerization of thiol takes place to yield polythiol which is a very effective inhibitor both in acidic and alkaline media.

1. Introduction

Because of the stringent requirement for stable ring formation, the reactions of organic chelating agents are extremely metal specific. Two mechanisms can be responsible for metal stabilization by surface chelation. The chelating molecule may react with metal ions while they are still bound to the lattice of the metal surface as suggested by Hackermann [1]. In this case, the steric requirements for complex formation may be expected to be more stringent than those which apply in solution and only very specific molecular groupings will be able to provide effective corrosion inhibiton. The second possibility is that the ions of the metal surface dissolve and immediately react with the chelating agent forming a complex of high molecular weight and low solubility that precipitates on the metal surface. If this mechanism is applied, chelating agents of marginal solubility which are known to be effective in solution, may be expected to be good corrosion inhibitors.

The inhibiting action of benzenethiols on the corrosion of iron and steel in HCl solution was studied by Riggs *et al* [2]. They found that the methyl group increases the anodic inhibitor characteristics of thiols, while o-amino and o-carboxylic groups increase both anodic and cathodic inhibitor characteristics. Le Roy [3] studied the inhibiting action of possible chelating groups for the corrosion of zinc and galvanized steel in the pH range 2 to 10 and found that, although o- m- and p-amino substituted phenols and benzenethiols are capable of chelating with zinc, none of these compounds were sufficiently effective. Abdel *et al.* [4] have studied the inhibition action of benzenethiols and thioglycollic acid on the corrosion of zinc in solutions of some acids whose anions have different adsorbability and/or complexation with the electrode surface and found that various thiols behave differently in the acids studied.

Needless to say none of these reports have unambiguously dealt with the mechanism of thiols and the effect of the ring substituents on the inhibition behaviour. It is assumed that thiols inhibit corrosion by adsorption on the metal surface. However, it is also possible that *in situ* polymerization [5–8] of thiols may take place resulting in a diffusion barrier protective film.

In this paper an attempt is made to elucidate the mechanism of inhibition of the corrosion of copper by benzenethiol (BT), o-methyl benzenethiol (o-MBT), o-aminobenzenethiol (o-ABT), p-aminobenzenethiol (p-ABT) and m-methyl benzenethiol (m-MBT) in H_2SO_4. This study also includes the behaviour of copper in NaOH solutions containing thiols for comparison.

2. Experimental details

The benzenethiols were prepared by known methods and were purified and characterized by nmr before use. The copper samples were prepared from rectangular pieces of commercial grade sheets. The surface to be exposed were successively mechanically polished with emery paper up to 4/0 grade using alcohol as lubricant, degreased, activated in 1 : 1 HNO_3 and washed thoroughly with distilled water. An area of 1 cm^2 was exposed to the corrosive medium, whereas the remaining surface was covered with Araldite. The specimens were exposed to the aerated corrosive medium for a set period. The corrosion rates were calculated from spectrophotometric measurement of the copper ions in the solution using sodium diethyldithiocarbamate.

The polarization studies were carried out potentiostatically employing a three electrode cell assembly. A saturated calomel electrode and platinum electrode were used as reference and auxillary electrodes, respectively.

Table 1. Corrosion rate (W) and inhibition efficiency (P) from weight loss measurements for copper in 1 M H_2SO_4 at 303 K as a function of inhibitor concentration

Inhibitor concentration	*o-MBT*		*0-ABT*		*p-ABT*		*BT*		*m-MBT*	
	*W**	*P*	*W**	*P*	*W**	*P*	*W**	*P*	*W**	*P*
Nil	162	–	162	–	162	–	162	–	162	–
1×10^{-3}	80	50.6	92	43.2	93	42.6	105	35.2	103	36.4
1×10^{-4}	105	35.2	112	30.9	113	30.2	120	25.9	118	27.2
1×10^{-5}	121	25.3	130	19.8	126	22.2	140	13.6	140	13.6
1×10^{-6}	150	7.4	154	4.9	153	5.6	160	NIL	162	NIL

* $\mu g\,cm^{-2}h^{-1}$

In the cyclic voltammetric study and potential stepping experiments the potential was controlled by a Tacussel potentiostat (PRT-10-0, 5) commanded by a Tacussel signal generator (GSTP-3) and the current-time transients were recorded using a *X–Y–t* recorder (Sefram).

3. Results and discussion

3.1. *Weight loss measurements*

Copper samples were exposed for 5 h in aerated 1 M H_2SO_4 with and without benzenethiols (1×10^{-3} to 1×10^{-6} M). From the amount of weight loss the corrosion rates were calculated. The inhibition efficiency, p, at each inhibitor concentration was calculated using the equation,

$$p = \frac{w_0 - w}{w_0} \times 100$$

where w_0 and w are the corrosion rates of copper in the absence and presence of the inhibitors. The results are collected in Table 1. It is clear from these results that the inhibition efficiency ranking is o-MBT > o-ABT ≈ p-ABT > BT ≈ m-MBT.

These results reveal that all thiols studied inhibit corrosion and this impedance of corrosion by thiols can be a result of either the adsorption of thiols (as such or as their oxidized and/or reduced product) on the electrode or to *in situ* polymerization on the electrode. In the former case the nature (leading in some cases to surface chelation) and mode of adsorption and, in the latter case, the conductivity of the polymer formed and its porosity, govern the efficiency of the inhibitor.

3.2. *Potentiostatic polarization measurements*

Data obtained for the electrochemical behaviour of copper in 1 M H_2SO_4 in the presence of thiols are given in Table 2. That the thiols act as inhibitors is evident from the shift of steady corrosion potential towards the more noble direction in their presence. The inhibition may be due to blocking of anodic or cathodic sites by adsorption or chelation of thiols on the surface or due to an alteration in anodic or cathodic partial processes in their presence. In the former case, the Tafel plots for the respective processes would be shifted to higher potential regions and in the latter their slopes would be altered.

The shift of anodic Tafel plots towards the high potential region with slight variation in slope and no change of any kind in cathodic Tafel plots in the presence of thiols in the present study suggest that the inhibitors act only at the anodic sites.

The inhibition of corrosion may be either due to the adsorption of thiols, as such, on the anodic sites or due to the *in situ* formation of a dimer or polymer on the electrode.

3.3. *Cyclic voltammetry*

The two basic mechanisms of anodic oxidation of thiophenolic compounds are [9–11] as follows. In neutral and acidic solutions, a two electron removal from the neutral and nonionized thiol occurs to give a

Table 2. Effect of benzene thiols on the electrochemical behaviour of copper in 1 M H_2SO_4 solution at 303 K (inhibitor concentration = 0.001 M)

Inhibitor	*Electrochemical Properties*			
	Ex. Curr. Density /mA cm^{-2}	*Steady Corr. Pot.* /mV	*Tafel slope (anodic)* /mV $decade^{-1}$	*Tafel slope (cathodic)* /mV $decade^{-1}$
Nil	0.088	−59 ± 5	40 ± 5	150 ± 5
O-MBT	0.068	+10 ± 5	55 ± 5	150 ± 5
o-ABT	0.070	−10 ± 5	58 ± 5	150 ± 5
p-ABT	0.070	−02 ± 5	50 ± 5	150 ± 5
BT	0.074	−16 ± 5	46 ± 5	150 ± 5
m-MBT	0.075	−30 ± 5	50 ± 5	150 ± 5

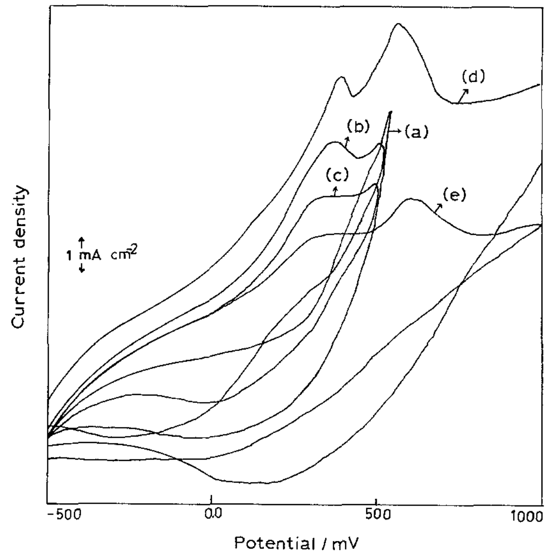


Fig. 1. CV patterns for Cu in 1 M H_2SO_4. Scan rate = 50 mV s^{-1}. Curves: (a) Cu/H_2SO_4 (1st cycle); (b) as (a) + 10^{-3} M 0-MBT (cycle I); (c) as (b) 10th cycle; (d) as (b) up to 1 V; and (e) as (c) up to 1 V.

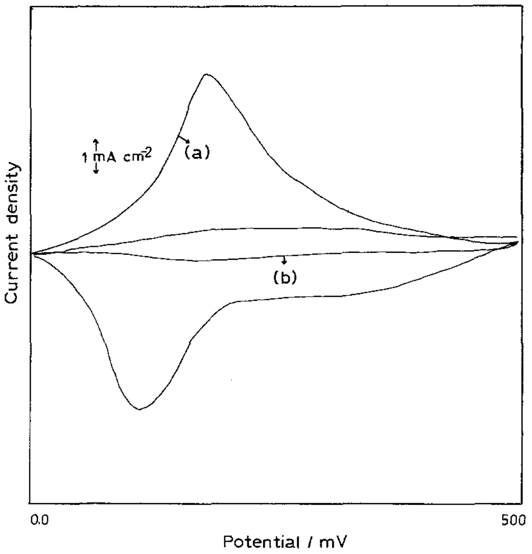
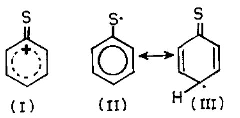


Fig. 3. CV patterns for Cu. Scan rate = 50 mV s^{-1}. Curves: (a) precycled in H_2SO_4 containing 10^{-3} M of o-MBT; (b) precycled in NaOH containing 10^{-3} M o-MBT.

thiophenoxonium ion (I). In a strongly alkaline solution a one electron removal from thiophenoxide anion occurs to give a thiophenyl free radical (II) and (III), (Scheme 1).



Scheme 1.

The cyclic voltammograms (CVs) for thiols were obtained in 1 M H_2SO_4 solution and also in 1 M NaOH solution for comparison. Typical CVs are presented in Figs 1 and 2.

In acidic solutions irreversible anodic peaks were obtained when scanned between -0.5 V to 1.0 V. Comparison of Fig. 1a and b indicates that the first anodic peak of Fig. 1b may be ascribed to inhibitor oxidation and the second to copper oxidation. Successive runs in the same solutions caused a slow decrease of the peak value, corresponding to inhibitor oxidation (Fig. 1c). Further, when the potential range was extended to 1.5 V the decrease in peak height was rapid (Fig. 1d and 1e).

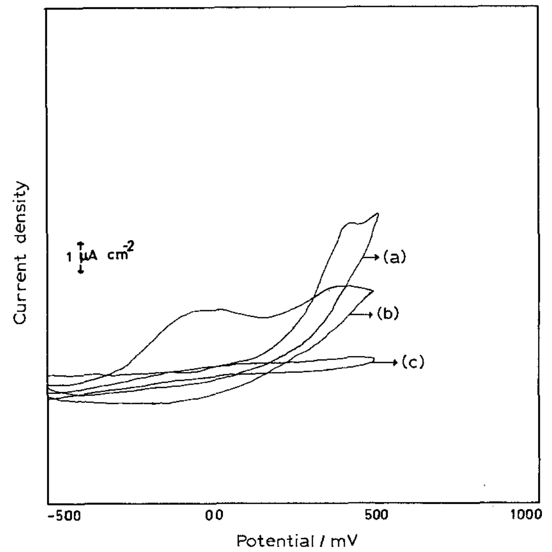


Fig. 2. CV patterns for Cu in 1 M NaOH. Scan rate = 50 mV s^{-1}. Curves: (a) Cu/NaOH (1st cycle); (b) as (a) + 10^{-3} M o-MBT (1st cycle); and (c) as (b) + 10th cycle.

On the other hand, the CV behaviour of copper in 1 M NaOH (Fig. 2a–c) was different from that in 1 M H_2SO_4 in that (i) the anodic peak potential of the benzenethiol oxidation reaction was more negative than in acidic solution; (ii) the anodic peak currents decreased significantly after the first cycle and after the second cycle the anodic currents were hardly visible. Further, a visible pale yellow film was observable on the working electrode and also the electrolyte in the vicinity of the working electrode developed a yellow colour.

After cycling the electrode under conditions of the experiment of Figs. 1c and 2c, the electrodes were removed washed thoroughly with water and transferred into fresh 1 M H_2SO_4 containing no thiols and scanned between 0 to 0.5 V. For the electrode obtained from acidic solution a reversible oxidation–reduction peak was observed (Fig. 3) while for the electrode precycled in alkaline solution no such redox couple was noticed.

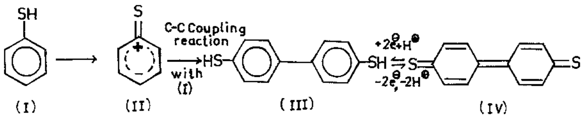
Further, the corrosion rates of the copper electrodes were obtained in 1 M H_2SO_4 containing no thiols, after having precycled them (under the conditions of Fig. 1c and 2c) in 1 M H_2SO_4 and 1 M NaOH containing 1×10^{-3} M thiols. The corrosion rates were found to be far less than for the uncycled case (directly exposed) and also the one precycled in the alkaline solution exhibited less corrosion than that precycled in acid solution (Table 3).

Similar results were obtained with all thiols studied. In the light of the above results and earlier observations [8–13] concerning the anodic oxidation of

Table 3. Corrosion rate (W) and inhibition efficiency (P) of copper in 1 M H_2SO_4 at 303 K as a function of the state of the electrode

State of the electrode	$W/\mu g\,cm^{-2}h^{-1}$	*P*
Freshly polished	162	-
Preexposed to 1 M H_2SO_4 containing o-MBT (1×10^{-3} M)	80	50.6
Precycled in 1 M H_2SO_4 containing o-MBT (1×10^{-3} M)	40	75.2
Precycled in 1 M NaOH containing o-MBT (1×10^{-3} M)	trace	100.0

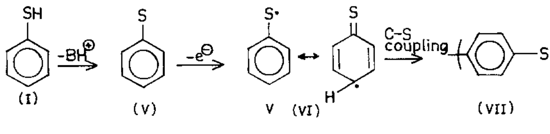
phenols and benzenethiols the following scheme may be proposed.



Scheme 2. In acid solutions

In acid solutions, the -SH group is undissociated (I). A two e^- anodic oxidation occurs with the simultaneous removal of hydrogen ion forming the thiophenoxonium ion (II) [9]. In general ions like (II) are expected to be reactive electrophiles and a coupling reaction between (II) and (I) occurs to form the dimer (dithiol). As can be seen from Figs. 1c and 3 this dimer can be oxidized to species (IV) (dithiophenoquinone) at potentials considerably negative of the anodic peak potential corresponding to the oxidation of thiols to species (II).

Thus, in acid solutions the inhibition of corrosion is mainly due to the molecular adsorption of thiols at the anodic sites on the copper electrode (the high potential shift of the anodic Tafel plot with slight variation of Tafel slope corroborates this fact). Such adsorption of thiols in the molecular form shifts the potential in the anodic direction (Table 2). However, this shift may not be sufficient to make the potential sufficiently positive for thiol dimerization (Fig. 1b) to take place. Thus, under normal conditions thiols inhibit corrosion primarily by adsorbtion onto the metal surface in molecular form. But when the potential is made more noble, the oxidative dimerization of thiols takes place in acid solution and the dimer formed replaces the adsorbed thiols. The dimer covers more area and is more effective as an inhibitor (Table 3). However, as a consequence of the existence of the electroactive redox couple (III $\rightleftharpoons$ IV) in Scheme 2), the dimer is also not sufficiently effective as an inhibitor



Scheme 3. In alkaline solutions

In alkaline solutions, on the other hand thiols are dissociated into thiophenoxide ions (V) [11] Scheme 3. In this case, the primary anodic product is a thiophenoxy radical (VI) formed via a one e^- removal. These thiophenoxy ions formed, undergo C–S coupling primarily to form polythiols (VII). The yellow powder formed at the copper electrode was subjected to spectral analysis after purification (i.r. and n.m.r.) and the structure was confirmed. However, the exact molecular weight could not be determined.

The oxidative polymerization reaction occurs at sufficiently less anodic potential in alkaline solutions (Fig. 2) and this value may be reached by shift of potential in the anodic direction as a result of adsorption of thiols on the copper electrode. As a consequence, polythiols are formed and cover the metal surface rapidly. This process is complete within one cycle (no anodic peak is observed during the second cycle in alkaline solution, Fig. 2). This film, being electro inactive and pore free (Fig. 3), completely insulates the underlying metal and effects greater inhibition (Table 3).

3.4. *Potential stepping experiments*

In order to further investigate the relative performance of thiol, dithiol and polythiol, potential stepping experiments were conducted. The cleaned electrodes were introduced to the electrolytic cell at potentials where the respective species are adsorbed (at 0 mV for thiol, and at +400 mV for dithiol in acidic solutions and at 0 mV for polythiol in alkaline solutions) and maintained at that potential for one hour when it was assumed that the adsorption of the respective species was complete. The electrodes were then stepped to a more positive potential and the current–time transients were recorded. (For polythiol the electrode was stabilized in alkaline solutions and introduced to acid solution for the stepping experiments).

The results are depicted in Fig. 4. The electrodes stabilized at potentials corresponding to both thiol

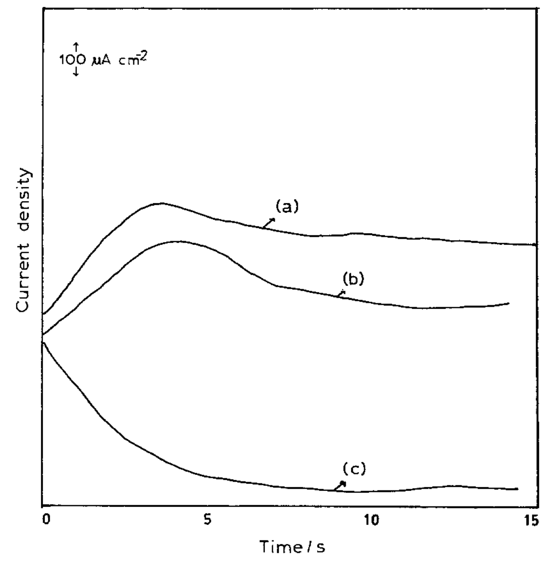


Fig. 4. Current transients for Cu in 1 M H_2SO_4. Stepped potential = 1.5 V. Curves: (a) stabilized at 0 V in 1 M H_2SO_4; (b) stabilized at 4 V in 1 M H_2SO_4; and (c) stabilized at 0 V in 1 M NaOH.

Table 4. Dependence of inhibition efficiency, P, for the corrosion of copper with temperature in 1 M H_2SO_4

Temperature	$W/\mu g\,cm^{-2}h^{-1}$			
	Plain	*o-MBT*	*o-ABT*	*BT*
303	162	80(50.6)	92(43.2)	105(35.2)
313	230	74(67.8)	87(62.2)	100(56.5)
323	300	69(77.0)	80(73.3)	95(68.3)

and dithiol adsorption exhibited an increasing current transient while that stabilized at potential corresponding to polymer formation showed a decreasing transient. These results clearly indicate that the polymer is efficient both in acidic and alkaline media, while thiol and dithiol have only limited efficiency. These *i–t* data are consistent with nucleation and growth of a surface phase [14]. However, since other processes probably occur at the same time, more detailed information cannot be obtained.

3.5. *Nature of adsorption*

Since the first step for any electrolytic process is the adsorption of the species on the electrode, information was collected regarding the nature and mode of adsorption.

In order to elucidate the nature of adsorption of thiols (chemisorption or physical adsorption) the effect of temperature on the corrosion rate of copper in plain and inhibited acids was studied. The corrosion rate increased with increasing temperature in plain acid but decreased with increasing temperature in inhibited acid. the value of P, however, increased with increasing temperature (Table 4). The energies of activation, E_a, for the corrosion process in plain and inhibited acids evaluated from the slopes of log corrosion rate against T^{-1}. Arranenius plots are given in Table 5.

The surface coverage (θ) of the absorbed inhibitors was calculated assuming no change in the mechanism of both the anodic and the cathodic reactions (approximately constant values of both anodic and cathodic Tafel slope) using the equation $\theta = P/100$.

The values of free energies of adsorptions as calculated from Langmuir type adsorption isotherm [4] (Fig. 5) are given in Table 5. The large negative values of the free energies of adsorption are usually characteristic of strong interaction. The decrease in energy of activation in the presence of inhibitors and the increase in P in the presence of inhibitors with temperature are suggestive of chemisorption of the inhibitors on the metal surface.

Table 5. Free energies of adsorption (ΔG_{ads} and apparent free energy of adsorption for the inhibition of Cu in 1 M H_2SO_4)

Inhibitor	E_a/kJ mol^{-1}	ΔG_{ads}/kJ mol^{-1}
Plain	19.15	-
o-MBT	− 5.74	31.90
o-ABT	−55.74	31.23
BT	− 3.83	30.4

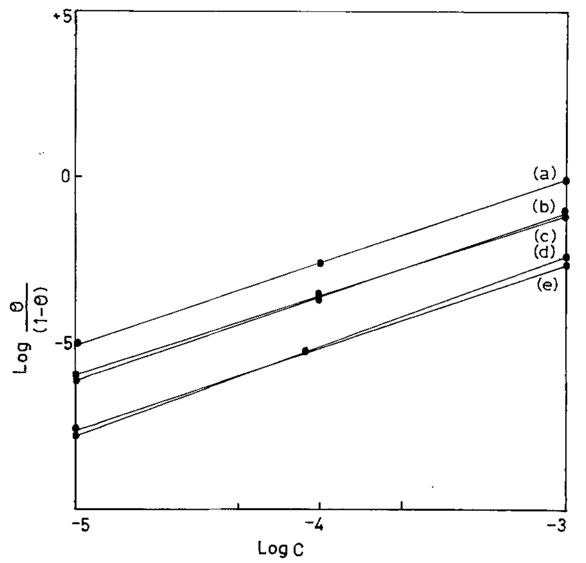


Fig. 5. Langmuirs isotherm for the adsorption of benzene thiols on copper from 1 M H_2SO_4 at 300 K. Curves: (a) o-MBT; (b) o-ABT; (c) p-ABT; (d) BT; and (e) m-MBT.

3.6. *Mode of adsorption*

Thiols can be chemisorbed as a bidentate surface ligand in which surface coordination is through both the sulphur and aromatic moieties [15] or solely through the -SH moiety. The two possible modes are depicted in Fig. 6. The mode of adsorption depends on the affinity of the metal towards the organic moiety. It has been proved that on platinum and gold [15], which have lesser affinity towards organic moieties, the thiols are adsorbed vertically only through the -SH moiety; while on irridium [16] and molybdium [17] which have more affinity for organic moieties, thiols are adsorbed in a tilted structure (Fig. 6a), with both -SH group and organic moiety involved in bond formation. For copper, which has less affinity for the organic moiety, it is reasonable to assume that the inhibitors are adsorbed vertically through the -SH group alone. Further, evidence for the vertical orientation of thiols on copper may be obtained indirectly from the effect of ring substituents on inhibition.

3.7. *Substituent effect on inhibition*

The inhibition efficiency ranking of studied thiols is (Structure given in Fig. 7) o-MBT > o-ABT ≈ p-ABT > BT ≈ m-MBT. BT is adsorbed vertically through the -SH group as described. In o-ABT and p-ABT the adsorption is likely either through the

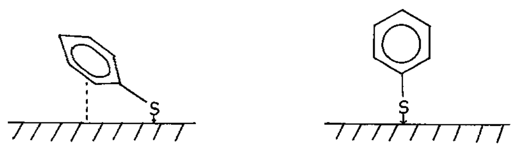


Fig. 6. Mode of adsorption of benzene thiol.

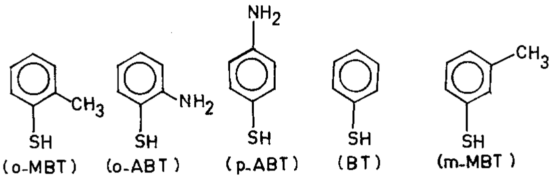


Fig. 7. Structures of benzene thiols.

$-NH_2$ or the -SH groups. The experimental results and properties of the groups involved favour a vertical mode of adsorption through -SH. Foremost among these is the tendency of S to form a stronger coordination bond compared to N on electronegativity grounds [18]. The easy oxidazability (chemical or electrochemical) of thiophenate group as compared to amine function [14] is a second supportive factor for adsorption through -SH. Finally the almost identical inhibition efficiency of o-ABT and p-ABT suggest that they are adsorbed vertically through -SH. For, if the thiols were adsorbed in the tilted form, the surface coverage by p-ABT would have been more and, consequently, the efficiency of p-ABT would have been more than that of o-ABT.

The high inhibition efficiency obtained with o-ABT, p-ABT, o-MBT when compared with BT may be explained in terms of the electron donating nature of the substituents. Since, the presence of a methyl group at meta position will not interact with -SH group, the m-MBT has the same inhibition efficiency as that of BT.

Acknowledgements

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