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Tosyl-hydrazine, 4-nitrobenzoyl-hydrazine and terephthalyl-hydrazine as inhibitors for the corrosion of copper and aluminium in sulphuric acid

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The effect of tosyl-hydrazine (THy), 4-nitrobenzoyl-hydrazine (4-NBHy) and terephthalyl-hydrazine (terephthalyl-Hy) on the corrosion of copper and aluminium in sulphuric acid has been investigated. The inhibitive efficiency ranking of these compounds from both weight loss and polarization measurements was found to be terephthalyl-Hy > THy > 4-NBHy for Cu and THy > 4-NBHy for Al. Both THy and 4-NBHy were found to be much less efficient as inhibitors for the corrosion of aluminium when compared to the corrosion of copper in sulphuric acid. The inhibitors acted cathodically both in the case of copper and aluminium, by merely blocking the cathodic reaction sites in the former and by altering the course of the mechanism of corrosion in the latter. The relative inhibitive efficiency of these compounds has been explained on the basis of structure dependent electron donor properties of the inhibitors and the nature of the metal–inhibitor interaction at the surface.

1. Introduction

Hydrazine and derivatives of hydrazine have been found to act as inhibitors for the corrosion of metals [1–4]. In our investigations with substituted hydrazines as corrosion inhibitors for lead in acetic acid [5], it was found that tosyl hydrazine (THy) and 4-nitrobenzoyl hydrazine (4-NBHy) acted as very good inhibitors, impeding the corrosion of lead to the extent of 90% in acetic acid. The high inhibitive efficiency of these compounds was attributed to the presence of additional electron donor atoms such as S of the SO_2 group in THy and O of the CO group in 4-NBHy apart from N of the NH_2 group in the hydrazines which facilitates the strong binding of these compounds to the surface. In order to further explore the versatility of these compounds as inhibitors for the corrosion of other metals in acid as well as alkaline media we have, in this study, presented the results of our investigations on the effect of THy, 4-NBHy and terephthalyl hydrazine as inhibitors for the corrosion of copper and aluminium in sulphuric acid.

2. Experimental details

THy, 4-NBHy and terephthalyl-Hy were prepared, purified and characterized by nuclear magnetic resonance before use. The copper and aluminium samples were prepared from rectangular pieces of the respective metals by covering all but one 10 mm × 10 mm portion with lacquer. The surface to be exposed was mechanically polished with emery paper up to 4/0 grade, using alcohol as lubricant. After mechanical polishing the specimens were degreased, activated in 1 : 1 HNO_3, washed thoroughly with distilled water and then exposed to the aerated corroding medium. The corrosion rates were calculated by estimating the amount of metal dissolved in the solution colorimetrically.

The polarization measurements were carried out potentiostatically under aerated conditions using a Tacussel PRT 10-05L potentiostat and employing a three-electrode cell assembly. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes respectively.

3. Results

3.1. *Polarization measurements*

Potentiostatic anodic and cathodic polarization scans were carried out for Cu and Al in 0.1 M H_2SO_4 respectively and Tafel plots constructed. It was observed that both in the case of Cu and Al, the anodic Tafel lines were not altered in any way in the presence of inhibitors (Fig. 1). The cathodic Tafel lines on the other hand were shifted to higher potential regions without any appreciable change in slope in the case of Cu (Fig. 2) while in the case of Al, the cathodic Tafel lines were shifted to higher potentials accompanied by a change of slope (Fig. 3). The cathodic Tafel plots were extrapolated to the free corrosion potentials and exchange current densities determined. Inhibitive efficiencies, P' were calculated using the relation $P' = (i_0 - i)/i_0$, where i_0 and i are the exchange current densities in the absence and presence of inhibitors, respectively. The values of P' were found to be in good agreement with those of P obtained by the weight loss method (Table 1).

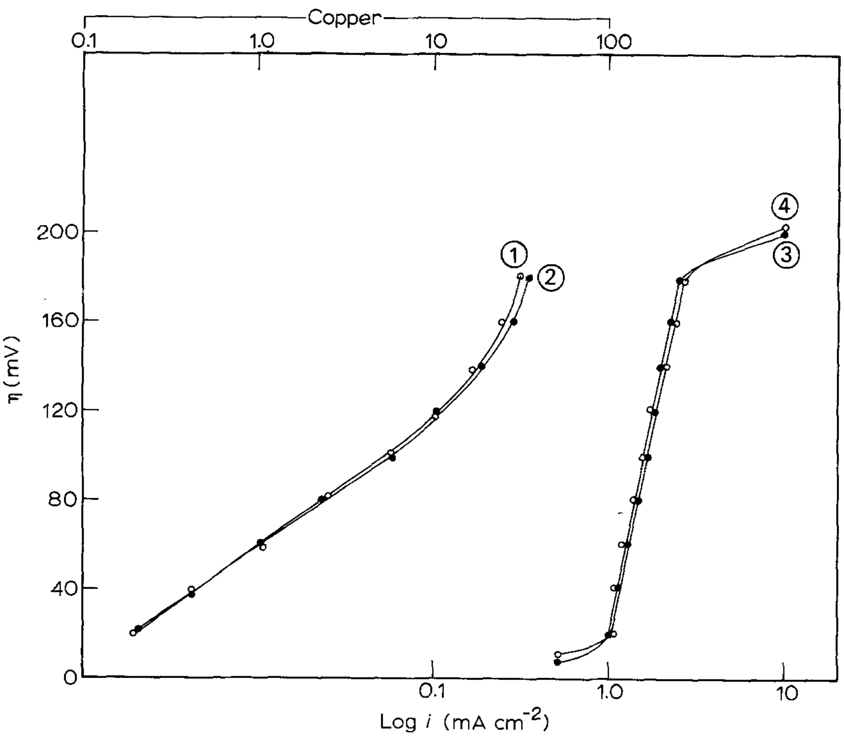

Fig. 1. Anodic Tafel curves for copper and aluminium in 0.1 M H_2SO_4 containing various inhibitor additions at 300 K. (1) Pure acid (copper), (2) pure acid + terephthalyl-hydrazine (copper), (3) pure acid (aluminium), and (4) pure acid + terephthalyl-hydrazine (aluminium).

3.2. *Weight loss measurements*

The Cu and Al samples were exposed for 5 h in 0.1 M H_2SO_4 both without additions and containing various concentrations (10^{-8}–10^{-1} M) inhibitor. From the calculated corrosion rates the inhibitive efficiency P (%) was calculated using the equation $P = 100(w_0 - w)/w_0$, where w_0 and w are the weight losses in the absence and presence of inhibitors, respectively.

The weight loss varied linearly with immersion period both in the presence and absence of inhibitors for the corrosion of Cu in H_2SO_4 (Fig. 4). In the case of Al, however, the weight loss against time of exposure plot underwent a change of slope after about 1.5 h in plain acid and after 1 h in the inhibited acid indicating the onset of a film formation.

The values of P for various concentrations of the inhibitors are given in Table 1 from which it is evident that, at any specific concentration, the efficiency ranking of the inhibitors is: terephthalyl-Hy > THy > 4-NBHy for Cu and THy > 4-NBHy for Al. In the case of Cu, an optimum value of 87–88% P is achieved with 4-NBHy and THy at a concentration of 1×10^{-3} M. Although at any specific concentration,

Table 1. Inhibitive efficiency determined from weight loss (P) and polarization (P′) measurements for Cu and Al in 0.1 M H_2SO_4 at 303 K as a function of inhibitor concentration

Inhibitor concentration (M)	*Cu*						*Al*			
	THy		*4-NBHy*		*Terephthalyl-Hy*		*THy*		*4-NBHy*	
	P (%)	P' (%)	P (%)	P' (%)	P (%)	P' (%)	P (%)	P' (%)	P (%)	P' (%)
0	–	–	–	–	–	–	–	–	–	–
1×10^{-9}	–	–	–	–	6.1	–	–	–	–	–
5×10^{-9}	–	–	–	–	–	–	–	–	–	–
1×10^{-8}	–	–	–	–	6.1	–	–	–	–	–
5×10^{-8}	7.4	–	5.0	–	14.2	–	–	–	–	–
1×10^{-7}	17.9	–	14.2	–	28.4	–	–	–	–	–
5×10^{-7}	25.3	–	22.8	–	43.8	–	–	–	–	–
1×10^{-6}	32.1	32.5	30.9	30.0	57.4	49.8	–	–	–	–
5×10^{-6}	35.2	–	43.2	–	65.6	–	–	–	–	–
1×10^{-5}	50.6	50.0	52.5	50.0	67.3	60.3	–	–	–	–
5×10^{-5}	61.7	–	63.0	–	72.8	–	–	–	–	–
1×10^{-4}	71.6	75.0	72.2	72.5	76.5	74.0	–	–	–	–
5×10^{-4}	82.7	–	82.7	–	84.0	–	–	–	–	–
1×10^{-3}	88.3	87.5	87.0	86.0	–	–	–	–	–	–
5×10^{-3}	88.3	–	87.0	–	–	–	13.3	–	5.9	–
1×10^{-2}	88.3	87.5	87.0	–	–	–	24.9	20.0	17.6	18.6
5×10^{-2}	88.3	–	87.0	–	–	–	42.2	–	29.4	–
1×10^{-1}	88.3	–	87.0	–	–	–	52.9	48.7	41.2	45.3
5×10^{-1}	88.3	–	87.0	–	–	–	52.9	–	41.2	–

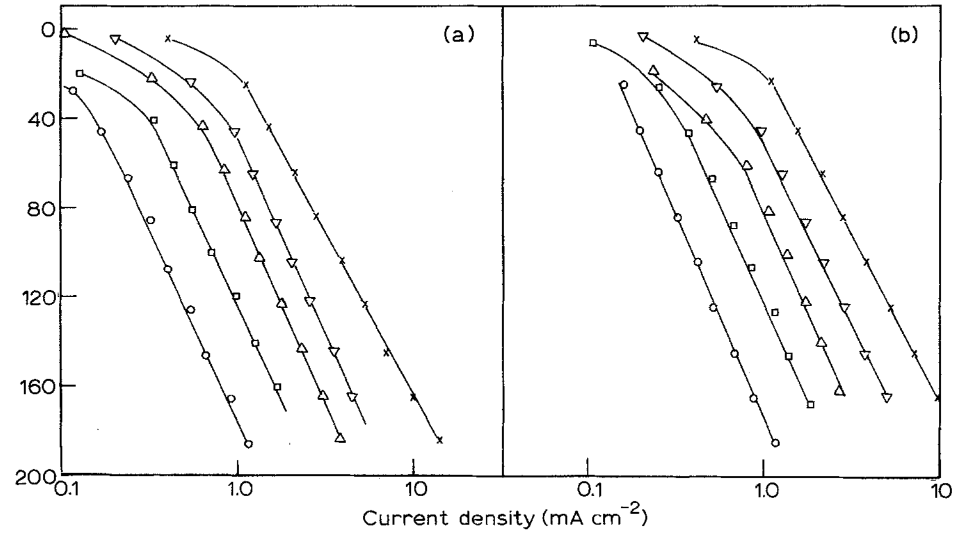

Fig. 2. Cathodic Tafel curves for copper in 0.1 M H_2SO_4 containing various inhibitor additions at 303 K. (x) 0.1 M H_2SO_4 alone and with (a) THy: (▽) 1 × 10^{-6}, (△) 1 × 10^{-5}, (□) 1 × 10^{-4}, (○) 1 × 10^{-3} M; and with (b) 4-NBHy: (▽) 1 × 10^{-6}, (△) 1 × 10^{-5}, (□) 1 × 10^{-3}, (○) 1 × 10^{-2} M.

terephthalyl-Hy is the more efficient of the three, yet the optimum efficiency achievable with it is only 84% at a concentration of 5 × 10^{-4} M beyond which it was not soluble. In the case of Al, an optimum value of 53% *P* is achieved with THy at a concentration of 5 × 10^{-1} M and a value of 41% *P* with 4-NBHy at the same concentration. It can be seen that both THy and 4-NBHy are much less efficient as inhibitors for the corrosion of Al when compared to corrosion of Cu in H_2SO_4. As the solubility of terephthalyl-Hy is low in H_2SO_4 (max. concentration obtainable, 5 × 10^{-4} M) and the fact that a comparatively higher concentration (10^{-1} M) of hydrazines is required to effect any inhibition in the case of Al, it was therefore found that terephthalyl-Hy is not a suitable inhibitor for the corrosion of Al in H_2SO_4.

The dissolution rate of Cu and Al was then determined in different concentrations (0.1–4 M) of H_2SO_4 at constant concentration of each inhibitor (Table 2). The corrosion rate of Cu in plain acid decreased gradually from 0.1–1 M beyond which it remained almost constant. In inhibited acid, the corrosion rate of Cu remained almost constant up to a concentration of 1 M and then increased with the acid concentration. The value of *P* showed a very small decrease up to a concentration of 1 M. Above 1 M, there was a large decrease in *P* which eventually became zero at a higher concentration of the acid. This behaviour is attributed to the fact that the inhibitors undergo decomposition at a higher concentration of the acid. In the case of Al, the corrosion rate increased with increasing concentration of acid (plain or inhibited) whereas the value of *P* decreased and became zero beyond 2 M (Table 2).

The effect of temperature in the range 283–323 K on the corrosion rates of Cu and Al was also studied. The corrosion rate of copper increased with increasing temperature in plain acid but decreased with increasing temperature in the inhibited acid whereas the corrosion rate of Al increased with increasing tem-

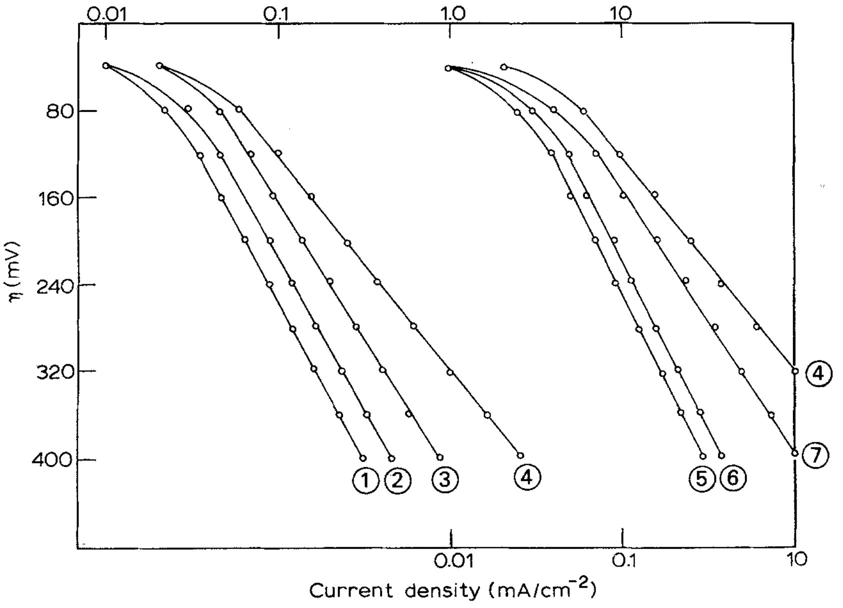

Fig. 3. Cathodic polarization of aluminium in 0.1 M H_2SO_4 containing various inhibitor additions at 303 K. With (1) 1 × 10^{-1}, (2) 5 × 10^{-2} and (3) 1 × 10^{-2} M THy; (4) 0.1 M H_2SO_4 alone; with (5) 1 × 10^{-1}, (6) 5 × 10^{-2} and (7) 1 × 10^{-2} M 4-NBHy.

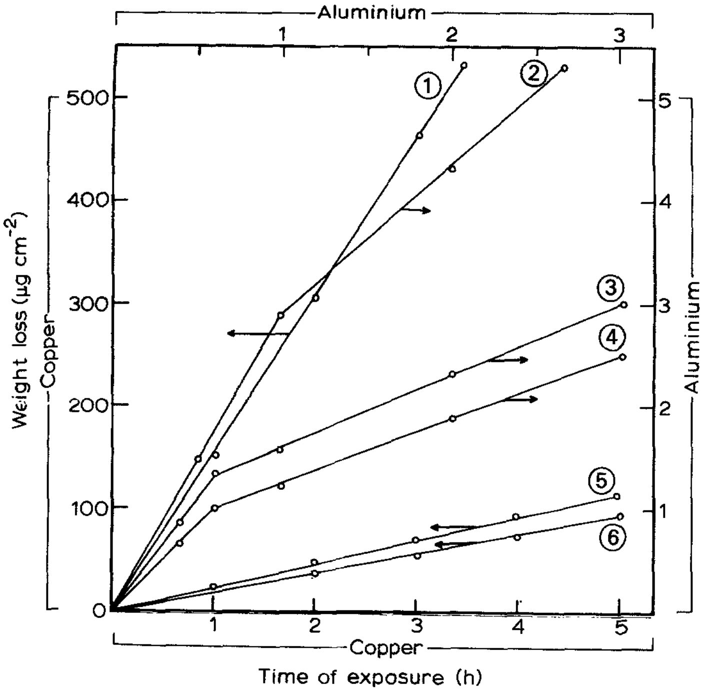

Fig. 4. Variation of weight loss of copper and aluminium with immersion time in 0.1 M H_2SO_4 containing various inhibitor additions at 303 K. With (1) Copper in 1.0 M H_2SO_4 (alone); (2) aluminium in 0.1 M H_2SO_4 (alone and (3) with 0.1 M 4-NBHy and (4) with 0.1 M THy; copper is 0.1 M H_2SO_4 (5) with 1×10^{-3} M 4-NBHy and (6) with 1×10^{-3} M THy.

perature in both plain and inhibited acid. However, the values of P increased with increasing temperature for all the inhibitors in the case of Cu as well as in the case of Al (Table 3). The apparent energies of activation, E_a, for the corrosion process in plain and inhibited acid for both Cu and Al were evaluated from the slopes of log(corrosion rate) against T^{-1} Arrhenius plots. The values obtained are given in Table 4.

Free corrosion potentials were recorded once steady values had been attained. The free corrosion potentials shifted to less noble values in the presence of inhibitors and the extent of this shift was found to be a function of the nature and concentration of the inhibitor. In the case of Cu, the value shifted from -59.0 mV in pure solution to ~ -75.0 mV in the inhibited solution and in the case of Al, the value shifted from -676.0 mV in pure acid to ~ -820.0 mV in the inhibited acid.

4. Discussion

The corrosion of Cu in aerated acidic solution is a result of the reactions [6, 7]:

$$\text{Anodic:}\quad Cu \rightleftharpoons Cu^+ + e^-$$

$$Cu^+ \xrightarrow{\text{r.d.s.}} Cu^+ + e^-$$

$$\text{Cathodic:}\ O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The linear variation of weight loss with time in plain and inhibited 0.1 M H_2SO_4 (Fig. 4) indicates the absence of insoluble surface films during corrosion. In the absence of any pre-existing film, the inhibitors are first adsorbed onto the metal surface and thereafter impede corrosion either by merely blocking the reaction sites or by altering the course of anodic or cathodic partial processes. In this instance, the unaltered cathodic and anodic Tafel slopes (Figs 1 and 2), the increase in cathodic overpotential (Fig. 2) and the

Table 2. Variation of inhibitive efficiency (P) of THy, 4-NBHy and terephthalyl-Hy with H_2SO_4 concentration at 303 K for the corrosion of Cu and Al

Acid concentration (M)	*P* (%)				
	Cu			*Al*	
	1×10^{-3} M *THy*	1×10^{-3} M *4-NBHy*	1×10^{-4} M *terephthalyl-Hy*	1×10^{-1} M *Thy*	1×10^{-1} M *4-NBHy*
0.1	88.6	88.6	85.8	52.9	41.1
0.2	86.1	86.1	85.0	–	–
0.3	86.1	85.4	79.1	–	–
0.4	85.5	84.1	72.5	–	–
0.5	80.8	80.8	61.5	–	–
1.0	80.0	79.0	2.0	51.6	41.9
2.0	50.0	48.1	(0)	48.8	39.5
3.0	(0)*	(0)*	–	17.3	28.8
4.0	(0)*	(0)*	–	(0)*	(0)*

* Absorbance value almost identical with that for uninhibited acid.

Table 3. Dependence of inhibitive efficiency (P) for the corrosion of Cu and Al on temperature in 0.1 M H_2SO_4

Temperature (K)	Cu (P, %)			Al (P, %)	
	THy	4-NBHy	Terephthalyl-Hy	THy	4-NBHy
283	65.0	63.2	60.0	–	–
293	76.0	75.0	75.0	50.0	37.5
303	89.0	88.1	85.8	52.9	41.2
313	93.0	95.0	92.4	67.9	58.5
323	–	–	–	78.0	71.0

shift of steady corrosion potential to a less noble direction in the presence of inhibitors indicates that the inhibitors are acting cathodically. The cathodic inhibitors in acid solution restrict the electronation reaction (dissolution) either by interfering with the hydrogen discharge reaction or by influencing the reduction of oxygen. The latter mechanism appears to be operative in the case of copper. Since the functioning of cathodic inhibitors involves their interaction at electron source areas, they are usually positively charged ions. Hydrazines being weakly basic are protonated in acid solutions and are in the form of cations. These are therefore transported to the cathodic sites where they are adsorbed, blocking the cathodic sites. At the same time hydrazines being good scavengers of oxygen, probably control the access of oxygen to the surface, thereby further inhibiting the cathodic reaction.

The high inhibitive efficiency achieved with the inhibitors in the case of copper suggests that these compounds strongly interact with the surface. The factors favouring strong interaction are: The potential of Cu on the ϕ scale being negative [8], its surface is negatively charged which may attract the inhibitors, which are present as cations in solution. Secondly, Cu being a transition metal could easily coordinate with the lone-pair electrons on the heterometal atoms in the inhibitor molecules, thereby strongly binding them to the surface. The large negative free energies of adsorption and positive value of heats of adsorption observed (Table 4) are usually characteristic of strong interaction. In addition the decrease in activation energy in the presence of inhibitors and the increase in P with temperature are suggestive of chemisorption of inhibitors onto the metal surface.

The experimental data for THy and 4-NBHy could easily fit the Bockris–Swinkels adsorption isotherm [9] (Fig. 5) whereas for the data on terephthalyl-Hy, the Frumkin isotherm [10] was found to be more appropriate (Fig. 6) for the evaluation of thermodynamic parameters. According to Bockris–Swinkels' isotherm

$$\frac{\theta}{(1-\theta)^n}\,\frac{\{\theta + n(1-\theta)\}^{n-1}}{n^n} = \left(\frac{C_{\mathrm{org}}}{55.4}\right)\exp\left(\frac{-\Delta G^0_{\mathrm{ads}}}{RT}\right)$$

where C_{org} is the concentration of the inhibitor, θ, the surface coverage (given by $\theta = (i_0 - i)/i_0$) and n, the number of water molecules displaced by the adsorbed inhibitor. The most probable value of n evaluated from a plot of LHS of the above equation against C_{org} was found to be 8 for THy and 9 for 4-NBHy.

The SO_2 group in THy and the C=O group in 4-NBHy provide additional centres for anchoring of these inhibitors onto the surface apart from the NH_2 groups in them. It is also probable that the π-orbitals of the phenyl group facilitate adsorption and thus increase the surface coverage. These factors lead one to visualize that these molecules lie flat or are adsorbed linearly as indicated in Fig. 7a. The fact that both the molecules have the same molecular length and that they displace almost the same number of water molecules suggests that their mode of adsorption is also identical and this accounts for the almost identical inhibitive efficiency achieved with the two.

The Bockris-Swinkels isotherm, which is a form of Langmuir adsorption isotherm, is usually applicable to adsorbed species which do not interact among themselves. The fact that the data on terephthalyl-Hy do not fit the Bockris–Swinkels isotherm and that they fit the Frumkin isotherm (Fig. 6) suggests that the mode of adsorption of Terephthalyl-Hy is different from that of THy and 4-NBHy and that the adsorbed molecules experience some kind of intermolecular interaction. It appears that the presence of two NH_2 groups in a molecule is most favourable for chelation.

Table 4. Thermodynamic parameters ($\Delta G^0_{\mathrm{ads}}$, $\Delta H^0_{\mathrm{ads}}$, $\Delta S^0_{\mathrm{ads}}$) and activation energy (E_a) for the inhibitors on Cu and Al in sulphuric acid

Metal	Inhibitor	f*	k*	E_a ($kJ\,mol^{-1}$)	n†	$\Delta G^0_{\mathrm{ads}}$ ($kJ\,mol^{-1}$)	$\Delta H^0_{\mathrm{ads}}$ ($kJ\,mol^{-1}$)	$\Delta S^0_{\mathrm{ads}}$ ($J\,K^{-1}mol^{-1}$)
Cu	Plain acid	–	–	33.3	–	–	–	–
	THy	–	–	25.5	8	−38.8	17.3	185.0
	4-NBHy	–	–	26.8	9	−40.2	21.3	203.0
	Terephthalyl-Hy	−0.79	2.5 × 10⁴	−14.2	–	−25.1	33.3	194.0
Al	Plain acid	–	–	9.4	–	–	–	–
	THy	−1.14	16.9	5.7	–	−3.1	0.23	11.0
	4-NBHy	−1.99	9.1	6.5	–	−2.4	0.17	8.5

* Constants in Frumkin isotherm.

† Term appearing in Bockris–Swinkel isotherm.

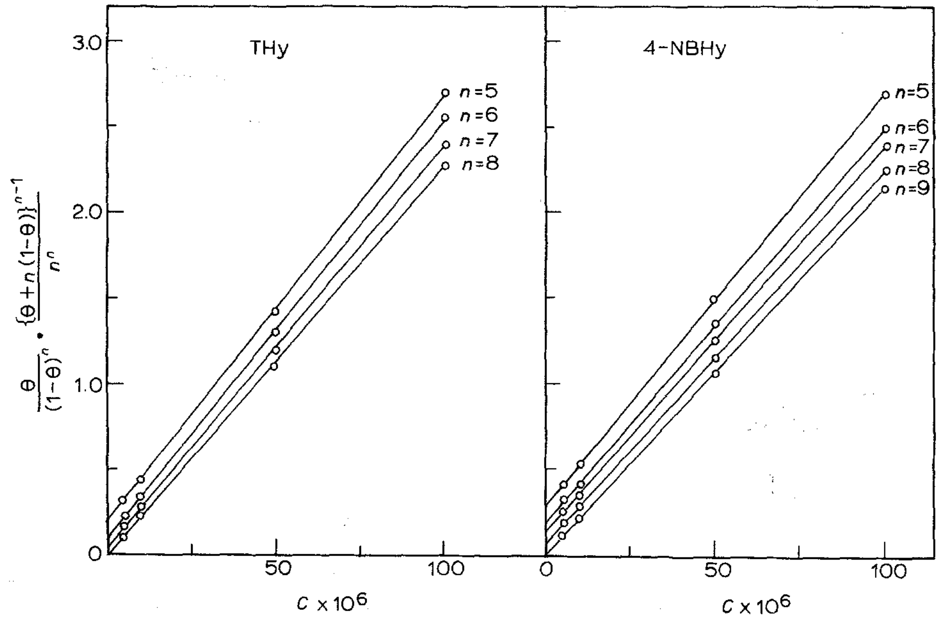

Fig. 5. Bockris–Swinkels isotherm for the adsorption of THy and 4-NBHy on copper in 0.1 M H_2SO_4 at 303 K.

The terephthalyl-Hy molecule may therefore not lie flat on the surface as in the case of THy and 4-NBHy; rather it may be adsorbed as shown in Fig. 7b (exaggerated). In this state, the C=O and NH groups in the molecule would be projected into the solution. There may therefore be feeble intermolecular hydrogen bonding between the C=O of one molecule with the NH of the neighbouring molecule, leading to stronger adsorption and, hence, to higher inhibitive efficiency as observed in this case. The constant *f* in the Frumkin isotherm is found to be −0.79 (Table 4) which is also suggestive of the attraction between adsorbed molecules.

The dissolution of Al occurs through the partial reactions [11]

$$\text{Anodic:}\quad \mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3e^-$$

$$\text{Cathodic:}\quad \mathrm{H}^+ + e^- \longrightarrow \mathrm{H(ads)}$$

$$\mathrm{H}^+ + \mathrm{H(ads)} + e^- \longrightarrow \mathrm{H_2(gas)}$$

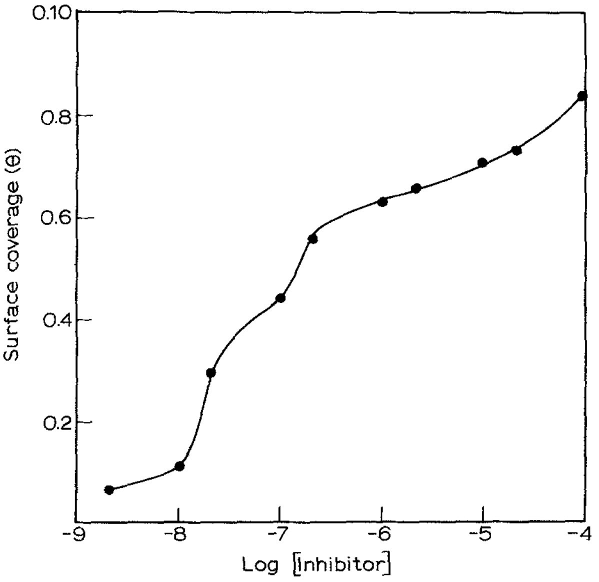

Fig. 6. Frumkin isotherm for the adsorption of terephthalyl-Hy on aluminium from 0.1 M H_2SO_4 at 303 K.

The Al^{3+} in solution combines with oxygen forming a protective film of Al_2O_3 on the surface which accounts for the much lower rates of corrosion observed with Al when compared to Cu in H_2SO_4. However, a certain induction time is required for the onset of film formation as evident from Fig. 4 which may be explained as due to the requirement of a build-up of minimum concentration of Al^{3+} in solution to initiate the formation of the film.

The lack of any change in anodic Tafel lines (Fig. 1), the shift of cathodic Tafel lines to higher potentials (Fig. 3) and the shift of steady corrosion potential values in the less noble direction in the presence of inhibitors again indicate that the inhibitors act cathodically, but in this case the corrosion is checked by the inhibitors altering the mechanism of hydrogen discharge, as evidenced by a change in cathodic Tafel slope in the presence of inhibitors (Fig. 3).

The extent of inhibition achieved with 4-NBHy and THy in the case of Al (~50%) is much less when compared to that achieved with Cu (~90%). One of the reasons for this could be that the potential of aluminium being positive [8], its surface is positively

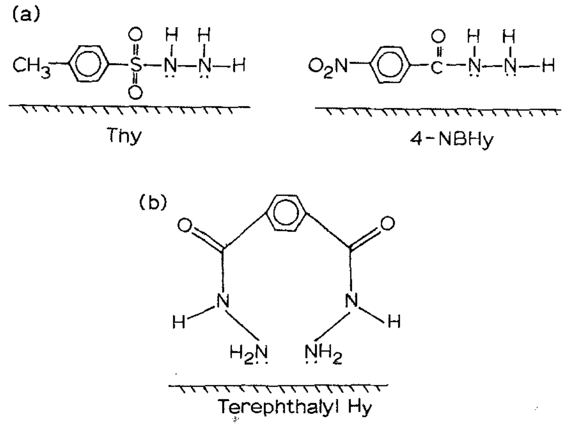

Fig. 7. Modes of adsorption of (a) THy and 4-NBHy on copper and (b) terephthalyl-Hy on copper.

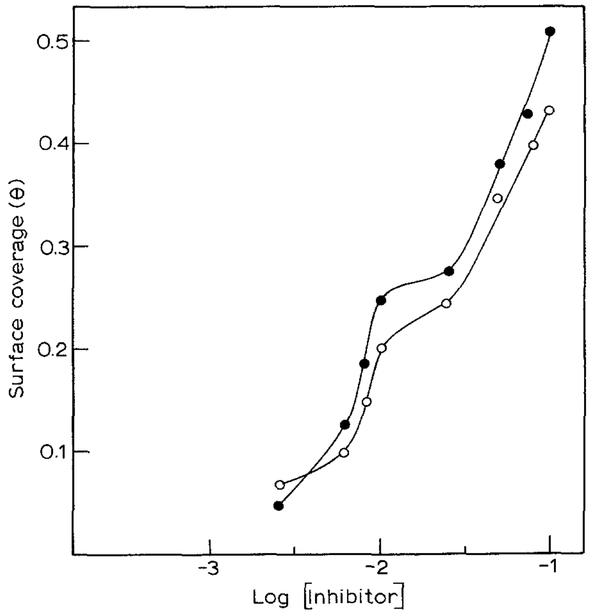

Fig. 8. Frumkin isotherm for the adsorption of (●) THy and (○) 4-NBHy on aluminium from 0.1 M H_2SO_4 at 303 K.

charged, which may not be very conducive to the strong adsorption of inhibitors which are present as cations in solution. Secondly, aluminium, not being a transition metal like copper, is not as amenable to stronger coordinate-bond formation with the lone-pair electrons on the heteroatoms in the inhibitors. The inhibitors probably therefore are not strongly adsorbed. The free-energy and heat of absorption values (Table 4) calculated by fitting the corrosion data to a Frumkin isotherm (Fig. 8) also corroborate this. Inhibitors of aluminium are less effective.

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