The Role of Surface Properties of Electrodeposited Cadmium in its Corrosion and Inhibition

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IT was found that potassium nitrate, potassium dichromate, glycine, L-leucine and L-valine have an acceleration effect while chloral hydrate, aniline, P-anisidine and thiosemicarbazide seem to act as inhibitors on the corrosion of electrodeposited cadmium in 1.0 M acetic acid. On the other hand, it was noticed that potassium permanganate possesses both acceleration and inhibition effects, while increasing temperature of the corrosive medium and cathodic current density of cadmium deposition was accompanied by a corresponding increase in the corrosion rate of electrolytic cadmium.

BECAUSE of the wide spread use of cadmium and its alloys in industrial applications as coatings for steel and aluminium, the study of the corrosion of cadmium is of a special interest. The effect of additives on the corrosion rate of cadmium in acid solutions has been the subject of numerous investigations[1-5].

In the present work the dissolution of electrodeposited cadmium in acetic acid solution in absence and presence of organic and inorganic additives was investigated using weight-loss technique [6].

EXPERIMENTAL

Cadmium sheets were prepared by electrodeposition on a platinum sheet of 25 cm^2 surface area from the following bath :

$CdSO_4$. 8/3 H_2O	0.25M	C.d.	0.25-1.5 A/dc^2.
$(NH_4)_2$ SO_4	0.25M	Temperature	25°C
$Al_2(SO_4)_3$	0.125M	PH	3-5

The electrodeposited metal was throughly washed with distilled water, ethyl alcohol and acetone then air dried and finally weighed and then immersed in the corrosive medium.

All chemicals used were of analar grade.

RESULTS AND DISCUSSIONS

In the present work weight-loss technique[6] for determining the corrosion rate of electrolytic cadmium expressed in mg./sq.dc/hr. was used. This was checked by polarographic technique which gave identical results, hence the former was used.

Effect of acetic acid concentration : The dissolution rate of electrolytic cadmium (cathodic current density 0.5 A/dc^2). expressed in mg./sq. dc./hr. was found to depend on acetic acid concentration, as recorded in table 1. It is seen that the corrosion rate increases with concentration. However, at concentrations > 3.0M, the corrosion rate attains a fairly constant value.

Effect of cathodic current density of cadmium plating : The effect of cathodic current density of cadmium deposition ranging from 0.25 to 1.5 A/dc^2. on the corrossion rate of cadmium in 1. M acetic acid solution ws investigated. The obtained data are recorded in table 2 and represented graphically in fig. 4. From table 2 and the graph in fig. 4 one can conclude that the corrosion rate of electrolytic cadmium increases with cathodic

TABLE 1

Variation of $V_{corr.}$ of electrolytic cadmium with acetic acid concentration

$V_{corr.}$ mg/sq.dc./hr	9.53	29.7	40 22	45.5	55.3	62 4	77.8	78.2	78.4	78.45
[CH_3COOH] M	0.25	0.5	0.75	1.0	1.5	2.0	3.0	6 0	9 0	12.0

TABLE 2

Variation of $V_{corr.}$ of electrolytic cadmium with its cathodic current densities in 1.0 M acetic acid solution

$V_{corr.}$ mg/sq.dc./hr	30.22	45.50	52.49	57.53	65.33	76.12
C.d. A/dc^2.	0.25	0.50	0.75	1.0	1.25	1.50

current density of cadmium deposition. This behaviour can be explained on the basis of the surface properties of the deposited metal. It is well known that at low current densities, the grain size of the metal deposits is coarser than at higher currents[7]. So the high corrosion rate of electrolytic cadmium at high current densities may be attributed to the spongy character of the metal deposits where its real surface area is more than the apparent one. Another factor of significant contribution is the deposition of the hydroxide and basic salts together with the metal deposits at high current densities[8].

Effect of organic and inorganic additives : The effect of concentration of the additives on the dissolution rate of electrolytic cadmium (0.5 A/dc².) in 1.0M acetic acid is shown in figs. 1 and 2. It is

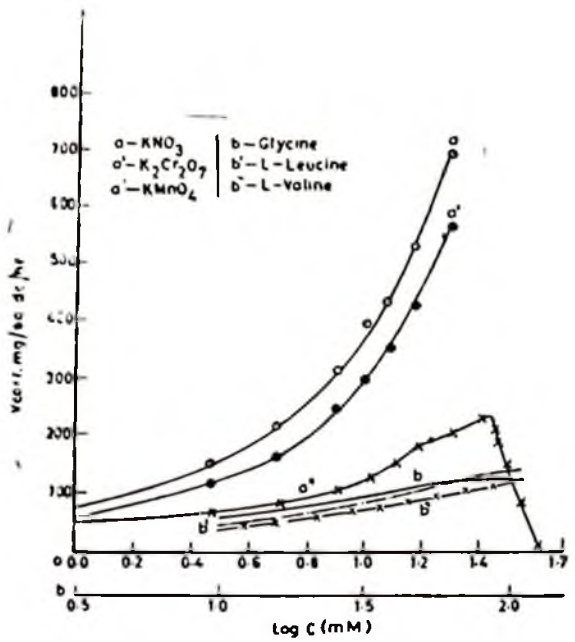


FIG.1 Effect of accelerators on the dissolution rate of Electrolytic cadmium in 1.0M HOAc

seen that potassium nitrate, potassium dichromate, glycine, L-leucine and L-valine accelerate while aniline, chloral hydrate, P-anisidine and thiosemicarbizide retard dissolution. Figure 1 shows that potassium permanganate accelerates up to concentrations of 27 mM and inhibits at higher concentrations.

The acceleration effect of the amino acids on the dissolution rate may be ascribed to the complexation of cadmium ions with the amino acids which may catalyse the dissolution process.

The acceleration effect of potassium dichromate, potassium nitrate, and potassium permanganate on the corrosion rate of electrolytic cadminm

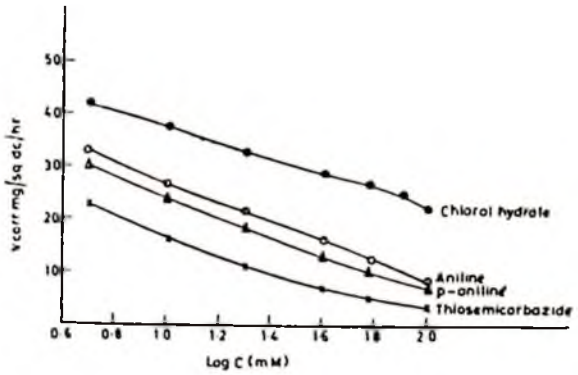


FIG.2 Effect of inhibitors on the dissolution rate of Electrolytic Cadmium in 1.0M HOAc

in 1 M acetic acid may be due to the high reducibility of dichromate, nitrate and permanganate anions, as shown by the following equations :

$$Cr_2O_7^{--} + 14\,H^+ + 6e = 2\,Cr^{+++} + 7H_2O \quad \text{.....(1)}$$

$$NO_3^- + 4\,H^+ + 3e = NO + 2\,H_2O \quad \text{.....(2)}$$

$$MnO_4^- + 8\,H^+ + 5e = Mn^{++} + 4\,H_2O \quad \text{.....(3)}$$

$$2MnO_4^- + Mn^{++} + 2\,H_2O = 5\,MnO_2 + 4H^+ \quad \text{.....(4)}$$

According to this mechanism, the first three anions can be considered as electron-acceptors and consequently the dissolution process will be largely affected.

For Figure 1 the acceleration efficiency of the three compounds in the sequence : $NO_3^- > Cr_2O_7^{--} > MnO_4^-$ which is in a good agreement with their reducibility. Another contributory factor is the pentration of the nitrate ion.

It is seen from fig. 1 that the curve of $KMnO_4$ consists of two ascending and one descending sections. The slope of the first section (up to 15.0 mM) is more than that of the second (from 15.0 to 25.0 mM). This can be explained as due to formation of a partially protective layer of MnO_2 preventing to some extent the accelerated dissolution due to permanganate ions. On the other hand, the third descending section shows the inhibition due increase of parmanganate ion concentration (more than 25.0 mM). The inhibition effect of potassium permanganate at high concentration (more than 27.0 mM) may be due to the blocking of the whole surface of the corroding metal with a complete layer of MnO_2.

From fig. 2 the inhibition efficiency is seen to as : thiosemicarbazide > p-anisidine > aniline > chloral hydrate.

It is well known that the bonding between the metal surface and oxygen, nitrogen and sulphur is in the sequence : S> N> O which is in accordance with the data of the inhibition efficiencies observed. On the other hand, the relatively high steric hinderence of chloral hydrate is probably responsible for lowering its adsorbability. This in turn must lead to its lower inhibition efficiency. The high inhibition efficiency of P-anisidine in comparison with aniline may be attributed to the presence of two pairs of lone electrons on oxygen atom which facilitate the protonation of amino group in P-anisidine since these compounds are thought to adsorbed via the protonated amino group on the cathodic sites of the metal surface.

Effect of temperature : The corrosion rates of electrolytic cadmium (0.5 A/dc.^{2}) in 1.0 M acetic acid at different temperatures are recorded in table 3. This table and the figure 3 show that the corrosion rate increases with rising temperature of the corroding medium. The corrosion rate in the range 0-60°C obey the Vant Hoff's and Arrhenius laws as can be seen from figure 3.

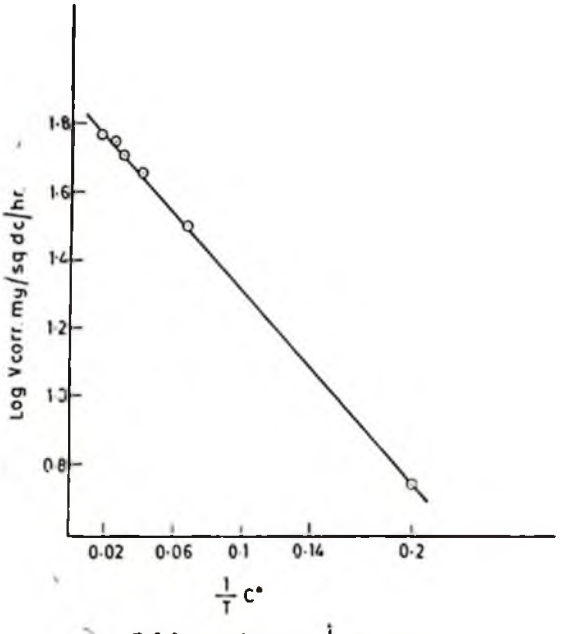


FIG 3 Log Vcorr $-\frac{1}{T}$ Relation

In order to emphasize the role played by surface properties of electrolytic cadmium, experiments were made to test the dissolution rate of cadmium deposited at different current densites (0.25-1.25 A/dc.^{2}) in presence of five concentrations of two inhibitors. The selective additives were potassium nitrate, aniline and thiosemicarbazide. Representative curves are shown in figs. 4 and 5 in presence of 10 mM of accelerators and 50 mM of inhibitors respectively. The other four concentrations reveal the same picture and trend.

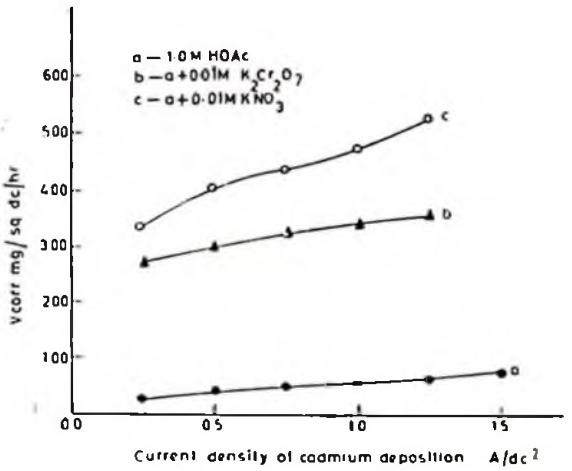


FIG. 4. Variation of Vcorr of cadmium with its cathodic current density in absence and presence of 0.01M $K_2Cr_2O_7$ or KNO_3 in 1.0 M OAc

The stimulation of corrosion process expressed in the form of η are recorded in table 4. η values can be calculated as follows :

$$\eta = \frac{V_1 - V_2}{V_1} \cdot 100 \qquad \text{.....(5)}$$

where V_1 and V_2 are the corrosion rates of electrolytic cadmium in absence and presence of additives respectively.

TABLE 3

Variation of $V_{corr.}$ of electrolytic cadmium with temperature in 1.0 M acetic acid solution

$V_{corr.}$ mg/sq. dc./hr.	5.62	31.61	45.5	52.48	56.23	50.57
Temperature °C	5.0	15.0	25.0	35.0	45.0	60.0

It is seen from figs. 4 and 5 that both acceleration and inhibition effects increase as the cathodic current density of cadmium deposition increases although the values of η decreases with increasing cathodic current density of cadmium deposition as can be seen from table 4. This behaviour can be explained on the basis of surface properties of electrolytic cadmium. It is well known that the real surface area of metal deposits at high cathodic current densities are much greater than the apparent ones. So it seems that at the same concentration surface coverage compact deposits is better and poor on spongy deposits indicating again the role played by surface properties of electrolytic cadmium in its corrosion and inhibition.

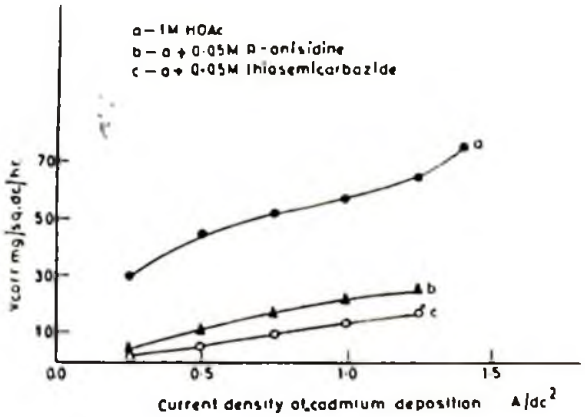


FIG 5 Variation of Vcorr of cadmium with its cathodic current density in absence and presence of 0·05M of p-anisidine and thiosemicarbazide

TABLE 4

Values of η in presence of 10 mM of potassium nitrate or potassium dichromate and 50 mM of P-anisidine or thiosemicarbazide

Current cadmium deposition A/dc².	η			
	pot. nitrate	pot dichromate	P-anisidine	thiosemi-carbizide
0.25	−1016.8	−800.0	83.45	97.93
0.50	−790.1	−576.9	73.36	86.81
0.75	−732.4	−519.0	65.71	80.95
1.0	−726.0	−491.0	61.73	75.65
1.25	−707.6	−450.0	61.53	72.31

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