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Adsorption of Some Aliphatic Carbonyl Compounds on Aluminium from Acidic Chloride Solution

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The adsorption of acetone, ethyl methyl ketone, diethyl ketone and disodium salt of ethylene diamine tetraacetic acid on aluminium from acidic chloride solution has been studied using the corrosion technique. The corrosion rates of aluminium in acidic chloride solution containing carbonyl compounds are measured by weight loss and hydrogen evolution as a function of carbonyl compounds concentration. The degree of surface coverage is used to calculate the protection efficiency and the free energy of adsorption of the carbonyl compounds.

INTRODUCTION

Aluminium is an industrially important metal and is corroded by several corrosive agents of which the aqueous acids are the more dangerous. Results on the corrosion of aluminium, reported in earlier work[1-7], make use of rough and etched surfaces. The inhibitive action during corrosion requires the knowledge of the adsorption of inhibitor at the electrode-solution interface[8]. Recent studies[9-12] on the adsorption isotherms of the inhibitors for the corrosion process have been made. This investigation examines the adsorption of carbonyl compounds on a polished aluminium surface from 2N hydrochloric acid solution.

The aim of the present work was to elucidate the inhibition mechanism of the corrosion of Al in 2N HCl by straight chain aliphatic ketones basing on experimental adsorption isotherms and results of hydrogen evolution measurements.

EXPERIMENTAL

All chemicals used were of A.R. quality and used without further purification.

The acid (2N HCl) solution and degreasing mixture were prepared as previously described[1].

Measurements of the corrosion rate were made by the gravimetric method. The value of coverage (θ) of the Al surface by adsorbed inhibitor molecules was determined by applying the known dependence:

$$\theta = 1 - \frac{U_i}{U} \tag{1}$$

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where U_i and U are the corrosion rates in solutions with and without the given inhibitor, respectively. Moreover, hydrogen evolution measurements were made.

RESULTS AND DISCUSSION

Figure 1 shows the dissolution rate of aluminium strips in 2N hydrochloric acid solution in presence of various concentrations (10^{-5}–10^{-1} M) of the carbonyl compounds studied at 27°C. As seen from Fig. 1 that the dissolution rate decreased gradually with the increase in concentration of

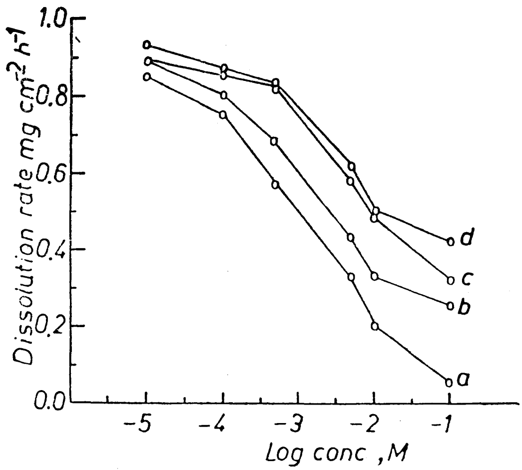

Fig. 1. Dissolution rate for aluminium in acidic chloride solution as a function of concentration of: (a) EDTA 2Na, (b) diethyl ketone, (c) ethyl methyl ketone, (d) acetone.

the inhibitors. The protection efficiency was calculated using the following equation:

$$\% P = \left(1 - \frac{U_i}{U}\right) \times 100 \quad (2)$$

where P is the protection efficiency, U_i and U are the corrosion rates in presence and absence of the inhibitor respectively. The maximum inhibitor efficiency (95.5%) was observed at 10^{-1} M EDTA 2Na.

The surface coverage (θ) was computed at different concentrations of all inhibitors using equation 1.

Increase of the protection efficiency with the increase of inhibitor concentration in solution suggests that inhibition is due to adsorption of these inhibitors on the surface of aluminium metal. A correlation between surface coverage (θ) and concentration of adsorbate (C) is given by the Langmuir adsorption isotherm[13]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

The experimental results (Fig. 2) are in good agreement with equation (3), showing that the adsorption of the tested compounds follows the Langmuir adsorption isotherm.

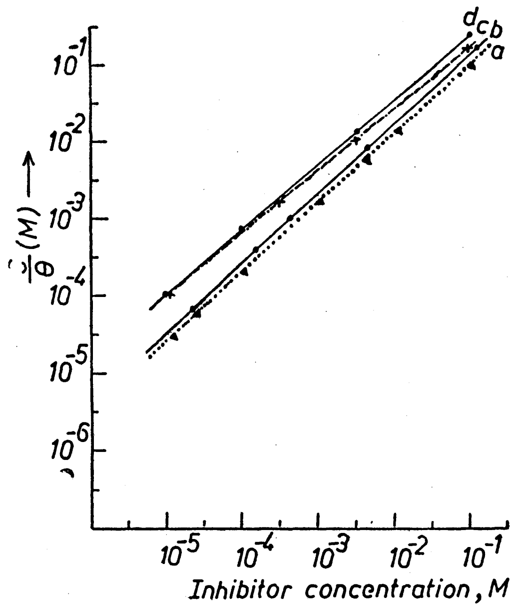

Fig. 2. Langmuir adsorption isotherm for adsorption of (a) EDTA 2Na, (b) diethyl ketone, (c) ethyl methyl ketone, and (d) acetone on aluminium in acidic chloride solution at 27°C.

It is clear that the adsorption of the organic compounds on the metal surface would take place through a functional group, essentially the cabonyl group (C═O) or the nitrogen atom, and would depend essentially on its charge density and the size of the molecules.

The apparent free energy of adsorption ($\Delta G^0 a$) of the inhibitors was calculated using weight loss method from θ-values using the equation[14]

$$\log C = -\frac{\theta}{1-\theta} - \log B \tag{4}$$

$$\log B = -1.74 - (\Delta G^0 a/2.303 \text{ RT}) \tag{5}$$

where C is the concentration of the inhibitor in the bulk of the solution. The values of the free energies of adsorption at different concentrations of inhibitors are given in Tables 1–4, showing that the free energy of adsorption is negative irrespective of the concentration of the inhibitors. The results show that EDTA 2Na which gives maximum efficiency shows more negative free energy of adsorption indicating that it is strongly adsorbed on the metal surface.

The high order of inhibitor efficiency (Tables 1–4) supports the strong interaction between the metal surface and the inhibitors, also the negative free energy of adsorption which is the characteristic features of strong interaction.

TABLE 1

EFFECT OF EDTA 2Na CONCENTRATION ON PROTECTION SURFACE COVERAGE (θ) AND FREE ENERGY OF ADSORPTION

Concentration, M	Protection efficiency, %	θ from hydrogen evaluation methods	θ from weight loss method	Free energy of adsorption, $-\Delta G^{o}a$ KJ mol^{-1}
1×10^{-5}	23.88	0.21	0.24	35.8227
1×10^{-4}	34.91	0.33	0.35	31.4120
5×10^{-4}	49.25	0.50	0.49	28.8425
1×10^{-3}	55.22	0.54	0.55	27.7145
5×10^{-3}	70.15	0.71	0.70	25.3136
1×10^{-2}	82.09	0.78	0.78	24.6286
1×10^{-1}	95.52	0.95	0.96	23.6557

TABLE 2

EFFECT OF DIETHYL KETONE CONCENTRATION ON PROTECTION EFFICIENCY, SURFACE COVERAGE (θ) AND FREE ENERGY OF ADSORPTION

Concentration, M	Protection efficiency, %	θ from hydrogen evaluation method	θ from weight loss method	Free energy of adsorption, $-\Delta G^{o}a$ KJ mol^{-1}
1×10^{-5}	20.89	0.20	0.21	35.3933
1×10^{-4}	25.36	0.24	0.25	30.2162
5×10^{-4}	38.81	0.40	0.39	27.8269
1×10^{-3}	52.24	0.46	0.46	26.8143
5×10^{-3}	61.19	0.60	0.61	24.3163
1×10^{-2}	70.15	0.69	0.68	23.3522
1×10^{-1}	77.62	0.77	0.78	19.0032

TABLE 3

EFFECT OF ETHYLMETHYL KETONE CONCENTRATION ON PROTECTION EFFICIENCY, SURFACE COVERAGE (θ) AND FREE ENERGY OF ADSORPTION

Concentration, M	Protection efficiency, %	θ from hydrogen evaluation method	θ from weight loss method	Free energy of adsorption, $-\Delta G^0 a$ KJ mol^{-1}
1×10^{-5}	10.56	0.10	0.11	33.4837
1×10^{-4}	11.88	0.12	0.12	27.9875
5×10^{-4}	26.87	0.26	0.27	26.2971
1×10^{-3}	40.30	0.33	0.34	25.5602
5×10^{-3}	47.76	0.49	0.50	23.2009
1×10^{-2}	56.72	0.57	0.57	22.1755
1×10^{-1}	71.64	0.72	0.72	18.0863

TABLE 4

EFFECT OF ACETONE CONCENTRATION ON PROTECTION EFFICIENCY, SURFACE COVERAGE (θ) AND FREE ENERGY OF ADSORPTION

Concentration, M	Protection efficiency, %	θ from hydrogen evaluation method	θ from weight loss method	Free energy of adsorption, $-\Delta G^0 a$ KJ mol^{-1}
1×10^{-5}	9.83	0.10	0.10	33.2182
1×10^{-4}	12.39	0.12	0.12	27.9875
5×10^{-4}	25.37	0.23	0.25	26.2030
1×10^{-3}	32.84	0.30	0.31	25.2191
5×10^{-3}	44.78	0.44	0.45	22.7006
1×10^{-2}	55.22	0.51	0.50	21.4728
1×10^{-1}	62.69	0.60	0.63	17.0584

Mechanism of Inhibition

The order of inhibition was found to increase in the order: EDTA 2Na > diethyl ketone > ethyl methyl ketone > acetone. This can be explained on the basis of chain length and the basicity of the carbonyl group. It is known that the inductive effect of ethyl radical is more than that of methyl radical, so that the inductive effect of these compounds increases in the order: diethyl ketone > ethyl methyl ketone > acetone and meanwhile the charge density on the carbonyl group increases in the same order.

The results of the surface coverage (θ), protection efficiency and free energy of adsorption ($\Delta G^0 a$) confirm this mechanism.

Conclusion

The inhibitive efficiency of EDTA 2Na, diethyl ketone, ethyl methyl ketone and acetone increases with inhibitor concentration. At all concentrations, the efficiency is found to increase in the order: EDTA 2Na > diethyl ketone > ethyl methyl ketone > acetone. The inhibitive efficiency was found to increase with the increase in the chain length of the inhibitors and with the increase in charge density on the carbonyl group. The free energies of adsorption are found to be high (-36 KJ mol^{-1} to -17 KJ mol^{-1}); this explains the strong interaction between the inhibitors and surface of aluminium metal.

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