

Inhibition of corrosion of α -brass (Cu-Zn, 67/33) in acid chloride solutions by some amino pyrazole derivatives

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The inhibition of corrosion of commercial 67/33 brass in 0.1 M HCl acid solutions by some amino pyrazole derivatives was tested using polarization, capacitance and weight-loss measurements. The amino pyrazole derivatives were 3(5)-amino, 5(3)-phenyl pyrazole; 3(5)-amino, 5(3)[4⁻-chlorophenyl] pyrazole; 3(5)-amino, 5(3)[4⁻-methoxy phenyl]pyrazole; 3(5)-amino, 5(3)[4⁻-methyl phenyl]pyrazole; 3(5)-amino, 5(3)-cyano pyrazole; and 3(5)-amino, 4-phenyl-5(3)-methyl pyrazole. The results showed that these compounds predominate as cathodic inhibitors and inhibition efficiencies up to 91% can be obtained. The inhibition was assumed to occur via chemisorption of the inhibitor molecules fitting a Temkin isotherm. The influence of the substituent group on the inhibition efficiency of the inhibitor was explained in terms of the density of the electron cloud on the pyrazole ring and the mode of adsorption. Although increase in temperature was found to decrease the corrosion in the absence of the inhibition, it increased in the presence of inhibitor, probably via desorption of the inhibitor molecules.

1. Introduction

Nitrogen-based heterocyclic compounds have been proved to be effective inhibitors for the corrosion of copper, as well as many other metals and alloys in aqueous solutions. Compounds such as benzotriazole [1-10], benzimidazoles [11, 12] and 1,2,4-triazole derivatives [13, 14] were reported to effectively inhibit the corrosion of copper and its alloys. In previous work, some amino pyrazole derivatives were found to be effective inhibitors for the corrosion of copper [15] and Zn [16] in acid chloride solutions. The aim of this paper is to describe an investigation of the inhibition of corrosion of commercial 67/33 brass in 0.1 M HCl solutions by some amino pyrazole derivatives using polarization, capacitance and weight-loss measurements.

2. Experimental details

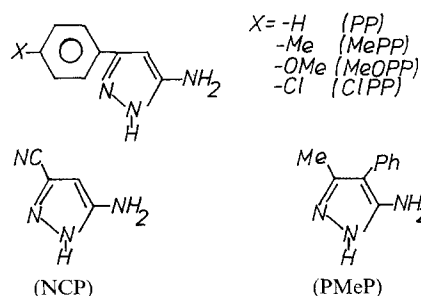
The brass electrodes were manufactured from local commercial grade α -brass (Helwan Company of Non-Ferrous Industries, Egypt) with the following composition (%): Cu, 67.28; Pb, 0.029; Fe, 0.002; Zn, 32.689.

Brass specimens were cooled and annealed in an electric oven maintained at 600°C. After annealing, the specimens were quenched in air to reach the ambient room temperature.

The electrode preparation for polarization and capacitance measurements, the electrolytic cell, the electrical circuits and the experimental details were described elsewhere [18, 19]. For weight-loss measure-

ments, 0.08-cm-thick sheets of area ca 10 cm², were immersed in 50 ml 0.1 M HCl solutions in the absence and presence of various inhibitors at different concentrations for 235 h. All solutions used were prepared from AnalaR grade HCl and doubly distilled water. All potentials were measured versus a saturated calomel electrode (SCE) and the capacitance was measured at 1 kHz. All experiments were carried out in an air thermostat at the desired temperature $\pm 0.2^\circ\text{C}$.

The inhibitors used were PP, MePP, MeOPP, ClPP, NCP and PMeP with chemical structures shown in Scheme 1.



Scheme 1.

The organic compounds were prepared, purified and identified according to the recommended method [19].

3. Results

3.1. Effect of inhibitor derivatives

The stable values of corrosion potential of brass were

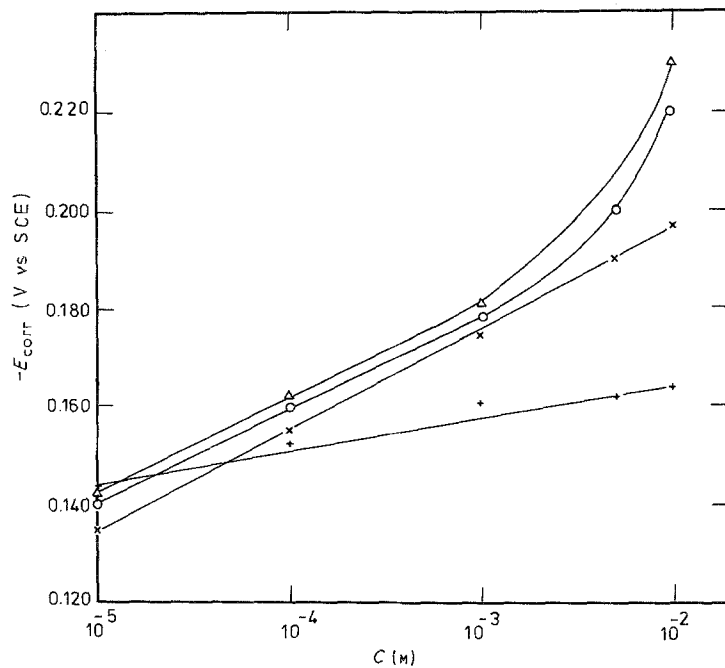


Fig. 1. Corrosion potential of 67/33 brass in 0.1 M HCl solutions containing various concentrations of: (Δ) MeOPP; (\circ) CIPP; (\times) MePP; ($+$) PP.

found to shift to more negative values in the presence of each of the tested compounds and the magnitude of such shifts increased with increase of the inhibitor concentration as can be seen in Fig. 1. This indicates that the compounds predominate as cathodic inhibitors [20].

Figure 2 shows the galvanostatic polarization of brass in 0.1 M HCl solutions in the presence of MePP of various concentrations. As can be seen, both the cathodic and the anodic reactions are inhibited and the inhibition increases as the inhibitor concentration increases. Similar results were obtained by using the other compounds.

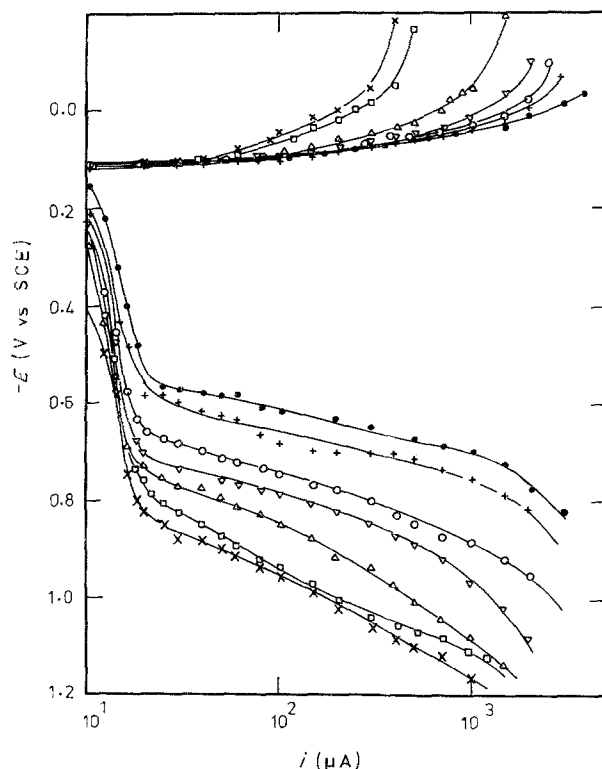


Fig. 2. Galvanostatic polarization of 67/33 brass in 0.1 M HCl solutions containing various concentrations of MePP. Electrode area = 0.300 cm².

The anodic dissolution of brass in 0.1 M HCl solutions in the absence and presence of different inhibitors of various concentrations was studied potentiodynamically (scanning rate = 5 mV s⁻¹). Tafel lines of nearly equal slopes were obtained as can be seen, for example, in Fig. 3. The percent inhibition efficiency, $I\%$, was calculated using Equation 1

$$I\% = \left(1 - \frac{i_{inh}}{i_0}\right) \times 100 \quad (1)$$

where i_0 and i_{inh} are the corrosion currents in the absence and presence of inhibitor and the results are summarized in Table 1. The highest efficiency is that of MePP followed by MeOPP, while the least efficient inhibitors are PMeP and NCP. The inhibition efficiencies of the homologous series follow the order MePP \approx MeOPP > CIPP > PP, assuming that the inhibition occurs through chemisorption of the inhibitor molecules and that the inhibition efficiency is a function of the surface coverage, θ_i , as can be seen in Fig. 4. The linear variations fit a Temkin isotherm at intermediate coverages [21, 22]. The data obey the

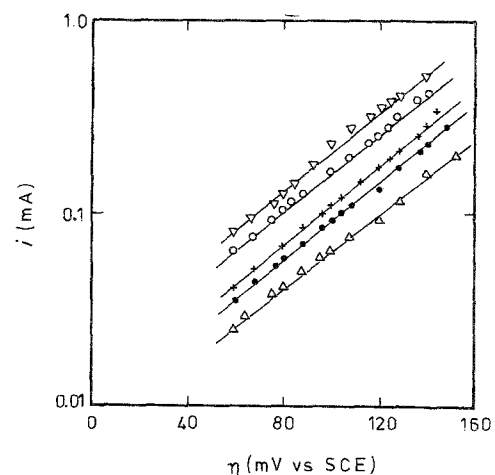


Fig. 3. Anodic dissolution of 67/33 brass in 0.1 M HCl solutions containing NCP of concentrations of: (∇) 10⁻⁴; (\circ) 10⁻³; ($+$) 2.5 \times 10⁻³; (\bullet) 5 \times 10⁻³; (Δ) 10⁻² M; electrode area = 0.105 cm².

Table 1. Corrosion currents, Tafel slopes and percentage of inhibition efficiency for 67/33 brass in 0.1M HCl solution in the absence and presence of different amino pyrazole derivatives of various concentrations at 30° C

Inhibitor	Concentration (M)	b_a (mV)	i_{corr} ($\mu A cm^{-2}$)	I%
Blank	0	77	13.9	-
PP	0.01	92	3.00	78.4
	0.005	95	4.30	69.0
	0.001	96	8.25	40.6
MeOPP	0.01	92	1.92	86.2
	0.005	96	2.15	84.5
	0.001	95	3.53	74.6
MePP	0.01	77	1.27	90.9
	0.005	80	1.41	89.9
	0.001	76	2.56	81.6
CIPP	0.01	79	2.77	80.1
	0.001	80	4.59	67.0
NCP	0.01	95	3.36	75.8
	0.005	95	4.95	64.4
	0.0025	95	5.72	58.8
	0.001	95	8.86	36.2
	0.0001	95	13.06	6.0
PMeP	0.01	92	6.06	56.4
	0.005	91	13.5	2.6
	0.001	92	18.2	-

equation

$$\theta_i = 1/f \ln l_0 C \quad (2)$$

where l_0 is the value of the Langmuir constant and f is a constant depending on intermolecular interactions in the adsorption layer and on the heterogeneity of the surface.

The capacitance of the 67/33 brass electrode in 0.1M HCl solutions in the absence and presence of the inhibitors of various concentrations was traced with time until steady state was obtained and an example is shown in Fig. 5. With increasing inhibitor concentration, the steady state capacitance decreased probably due to coverage of the electrode surface with a solid film and/or adsorption of the inhibiting species onto the metal surface [10, 16, 23]. The surface cover-

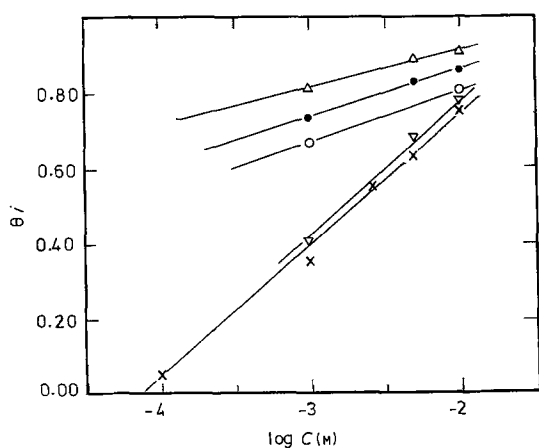


Fig. 4. Variation of surface coverage, θ_i , with the logarithm of the inhibitor concentration.

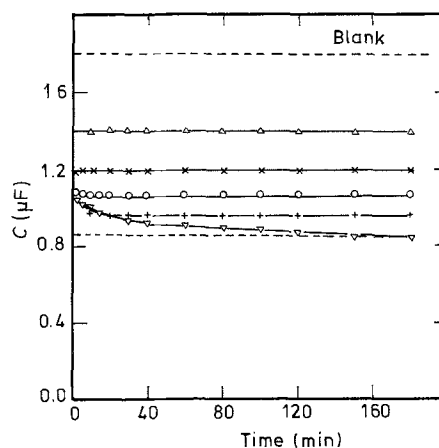


Fig. 5. Variation of brass electrode capacitance with time in 0.1M HCl solutions containing PP of concentrations of: (Δ) 10^{-5} ; (\times) 10^{-4} ; (\circ) 10^{-3} ; ($+$) 5×10^{-3} ; (∇) 10^{-2} M; electrode area = $0.105 cm^2$.

age, θ_c , was estimated from the following equation

$$\theta_c = \frac{C_0 - C_{inh}}{C_0 - C_m} \quad (3)$$

where C_0 and C_{inh} are the steady state capacitances in the absence and presence of inhibitor and C_m is the capacitance at $\theta_c = 1$. The data obtained from capacitance measurements were also found to fit a Temkin isotherm as can be seen in Fig. 6.

It should be mentioned that the electrode capacitance in the presence of inhibitor decreased with time during the first few hours until a steady state was attained. The magnitude of the decrease in capacitance depends on the inhibitor type and concentration as can be seen in Fig. 7.

3.2. Effect of temperature

Figure 8 shows the effect of temperature on the anodic

Table 2. Corrosion currents and percentage of inhibition efficiency for 67/33 brass in 0.1M HCl solutions in the absence and presence of different phenyl amino pyrazole derivatives at various temperatures

Inhibitor	Concentration (M)	Temperature ($^{\circ} C$)	i_{corr} ($\mu A cm^{-2}$)	I%
Blank		30	13.9	-
Blank		40	8.47	-
Blank		50	7.19	-
PP	0.01	30	3.00	78.4
		40	3.67	56.7
		50	6.06	15.7
MeOPP	0.01	30	1.92	86.2
		40	4.46	71.0
		50	3.32	53.8
MePP	0.01	30	1.27	90.9
		50	2.65	63.1
PP	0.005	30	6.62	52.4
		50	3.96	44.9
MeOPP	0.005	30	2.15	84.5
		40	2.98	64.8
		50	4.46	38.0
MePP	0.005	30	1.41	89.9
		50	2.42	66.3

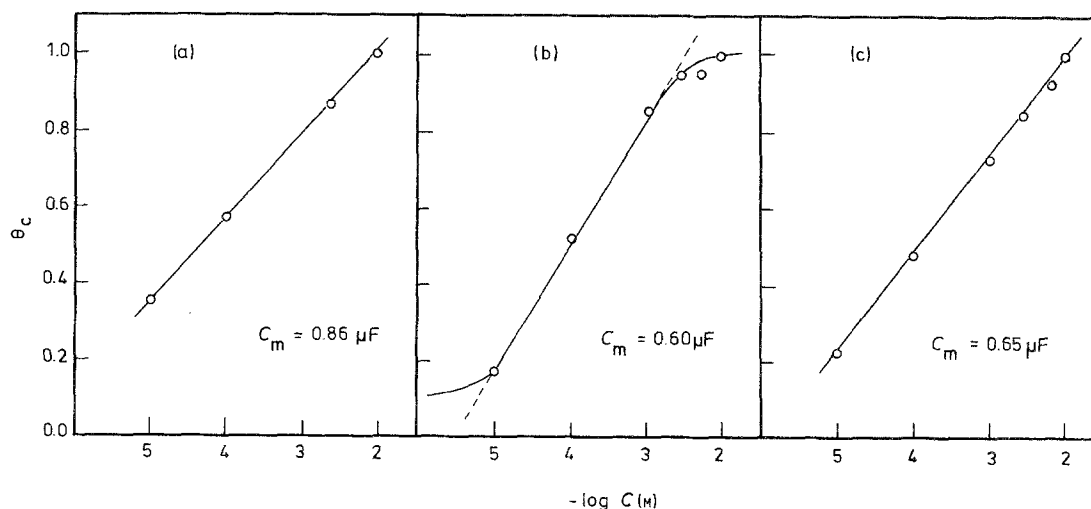


Fig. 6. Variation of surface coverage, θ_c , with the logarithm of the inhibitor concentration: (a) PP; (b) MeOPP; (c) MePP; electrode area = 0.105 cm^2 ; $C_0 = 1.70 \mu\text{F}$.

dissolution of 67/33 brass in 0.1 M HCl solutions in the absence and presence of 0.005 M MeOPP. In the absence of MeOPP, the anodic dissolution current decreases with increase of temperature. Such decreases in anodic current may be connected to the decrease of oxygen content within the polarization range used. In the presence of MeOPP, the variation of dissolution current with temperature is controlled by the extent of the adsorption process, i.e. increase in temperature decreases the adsorption and hence the dissolution current increases. Table 2 shows the same trend for the corrosion current.

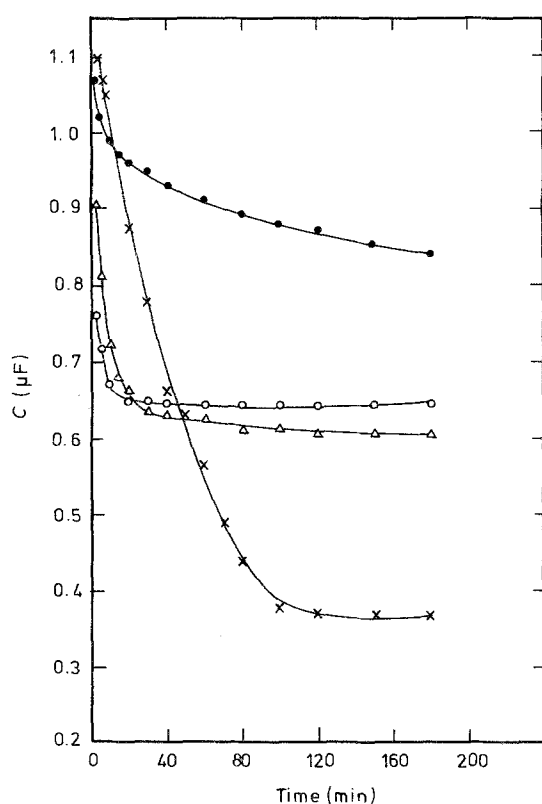


Fig. 7. Variation of brass electrode capacitance with time in 0.1 M HCl solutions containing 0.01 M of: (●) PP; (○) MePP; (△) MeOPP; (×) ClPP; electrode area = 0.105 cm^2 .

4. Discussion

The limited solubility of the tested amino pyrazole derivatives in pure water increases noticeably in acid solution via protonation of the amino group and hence, the inhibiting species include both free and protonated species. The inhibition process is assumed to occur via the adsorption of the inhibitor through the lone pair of electrons of the azole nitrogen or/and through the six delocalized π -electrons of the pyrazole ring. Previous studies on corrosion inhibition of copper [15] and zinc [16] by these pyrazole derivatives indicate the involvement of the two modes of adsorption. The nature of the substituent group of the phenyl pyrazole derivatives, whether electron-donating, e.g. CH_3 -, $\text{CH}_3\text{-O}$ -, or electron-withdrawing groups, e.g. NO_2 -, Cl -, affects the electron density on the pyrazole ring. It is expected that increase of the electron density on the pyrazole ring increases the inhibition efficiency. Using Hammett substituent constants [24] (for *p*-chloro-, methyl- and methoxy-derivatives they are +0.23,

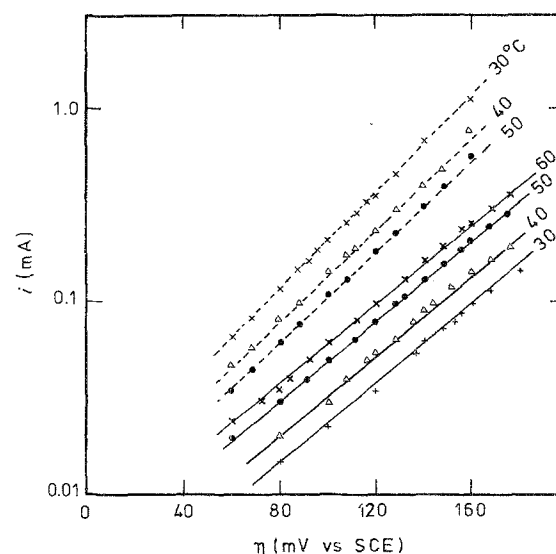


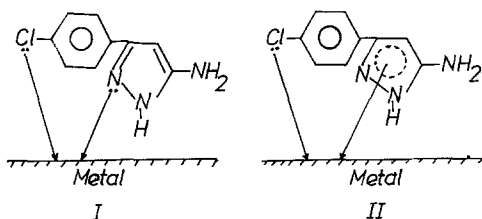
Fig. 8. Anodic dissolution of 67/33 brass in 0.1 M HCl solutions in absence (---) and presence (—) of 0.005 M PP at different temperatures; electrode area = 0.105 cm^2 .

Table 3. Weight loss and inhibition efficiency of corrosion of 70/30 brass in 0.1 M HCl solutions containing various inhibitors at 20°C

Inhibitor	Weight loss ¹ (g cm ⁻² h ⁻¹)	I%
Blank	4.51 × 10 ⁻⁵	—
0.01 M PP	1.19 × 10 ⁻⁵	73.6
0.0 M MeOPP	0.63 × 10 ⁻⁵	86.0
0.01 M MePP	0.51 × 10 ⁻⁵	88.7
0.01 M ClPP	0.65 × 10 ⁻⁵	85.7

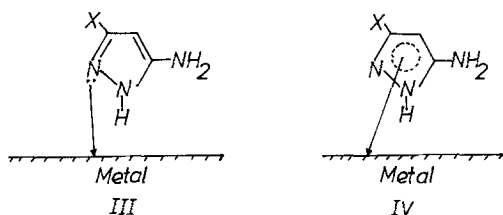
¹ Average of 3 experiments after 235 h immersion.

−0.17 and −0.27, respectively), the order of increase of the electron density on the pyrazole is CIPP < PP < MePP < MeOPP. The order of increase of inhibition efficiency, as observed from the results of this study, is NCP < PP < CIPP < MeOPP ≈ MePP. Table 3 shows the same order by using weight-loss measurements, i.e. PP < CIPP < MeOPP ≈ MePP. The discrepancy between the expected and the experimentally observed orders can be explained in terms of modes of the adsorption process through the pyrazole ring as well as the chloro group [15, 16]. The mode of adsorption may be as shown in Scheme 2.



Scheme 2.

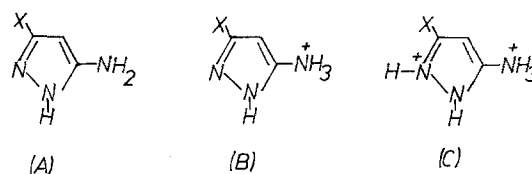
This is why the chloro-derivative efficiency is higher than that for PP. For other derivatives, the mode of adsorption is assumed to be as in Scheme 3.



Scheme 3.

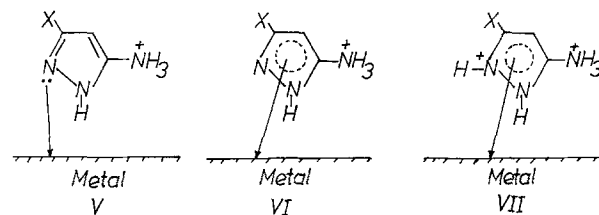
The higher efficiency of MePP and MeOPP may be attributed to the increased adsorption inhibition through the delocalized π -electrons of the pyrazole ring rather than that of the active adsorption nitrogen centers. Also, the inhibition through the formation of metal-inhibitor complexes cannot be excluded [15, 16].

In the corrosive acid solutions used (0.1 M HCl) the inhibitor takes place by the predominant species A, B and C [25, 26], i.e. unprotonated and protonated species with one and two hydrogen ions (Scheme 4).



Scheme 4.

The following modes of adsorption (V–VII) may be involved (Scheme 5).



Scheme 5.

In conclusion, the amino pyrazole derivatives inhibit the corrosion of 67/33 brass in 0.1 M HCl solutions via chemisorption of the inhibiting species onto the metal surface following Temkin isotherms. The inhibition efficiency increases in the order PMeP < NCP < PP < ClPP < MeOPP ≈ MePP.

References

- [1] I. Dugdale and J. B. Cotton, *Corros. Sci.* **3** (1963) 69.
- [2] J. B. Cotton, *Trans. Inst. Marine Eng.* **77** (1865) 165.
- [3] J. B. Cotton and I. R. Scholes, *Br. Corros. J.* **2** (1967) 1.
- [4] R. Walker, *Anticorros.* **17** (1970).
- [5] F. Mansfield, T. Smith and B. P. Parry, *Corrosion* **27** (1971) 289.
- [6] G. W. Poling, *Corros. Sci.* **10** (1970) 359.
- [7] G. Lewis, *Corrosion* **34** (1978) 424.
- [8] S. M. Mayanna and T. H. V. Setty, *Corros. Sci.* **15** (1975) 627.
- [9] D. Chadwick and T. Hashemi, *ibid.* **18** (1978) 39.
- [10] F. El-Taib Heakal and S. Haruyama, *ibid.* **24** (1984) 185.
- [11] G. Lewis, *ibid.* **22** (1982) 579.
- [12] N. K. Patel, S. G. Makwana and M. M. Patel, *ibid.* **14** (1974) 91.
- [13] P. G. Fox and P. A. Bradley, *ibid.* **20** (1980) 43.
- [14] J. W. Schultze and K. Wippermann, *Electrochim. Acta* **32** (1987) 823.
- [15] A. M. Bekheet, A. G. Gad Allah, M. W. Badawy and H. H. Rehan, submitted for publication.
- [16] A. G. Gad Allah, M. M. Hefny, S. A. Salih and M. S. El-Basiouny, *Corrosion*; accepted for publication.
- [17] W. A. Badawy, B. A. Sabrah and N. Hilal, *J. Appl. Electrochem.* **17** (1987) 357.
- [18] A. G. Gad Allah and H. A. Abd-Rahman, *ibid.* **17** (1987) 1065.
- [19] A. Takamizawa and Y. Hamashima, *Yakugaku Zasshi* **48** (1964) 1113.
- [20] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Plenum Press, New York (1976) Vol. 2, p. 1306.
- [21] M. I. Temkin, *Zh. Fiz. Khim.* **15** (1941) 296.
- [22] A. N. Frumkin, *Z. Phys. Chem.* **116** (1925) 466; **35** (1926) 792.
- [23] M. M. Abou-Romia and M. M. Hefny, *Electrochim. Acta* **136** (1982) 339.
- [24] L. P. Hammett, 'Physical Organic Chemistry', 2nd edn, McGraw-Hill, New York (1970).
- [25] R. A. Y. Jones, 'Physical and Mechanistic Organic Chemistry', Cambridge University Press, Cambridge (1979).
- [26] L. A. Paquette, 'Principles of Modern Heterocyclic Chemistry', W. A. Benjamin, Massachusetts (1974) p. 185.