JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 505–510

Substituted tertiary arsine and phosphines as interfacial adsorption inhibitors for corrosion of zinc in perchloric acid

H. B. RUDRESH, S. M. MAYANNA

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

Received 20 August 1979

The effect of triphenylarsine, triphenylphosphine and tri-*p*-tolylphosphine on the corrosion of zinc in $HClO_4$ at 30° C was studied. A significant decrease in the corrosion rate of zinc is obtained by the addition of these compounds. The corrosion rate is a function of the temperature, pH of the medium and the concentration of the inhibitors. The percentage protection calculated from weight loss and polarization methods are in good agreement. The apparent free energies of adsorption of inhibitors for different possible modes of adsorption are evaluated. The experimental data obtained are in agreement with the corrosion inhibition of zinc by interfacial adsorption of inhibitors.

1. Introduction

The study of adsorption during corrosion has been exciting from early days. The adsorption of organic compounds on the electrode surface is studied by measuring interfacial tension, the electrode charge and the differential capacitance of the double layer, together with the quantities associated with these parameters, for example, the dependence of contact angle and hardness or boundary friction at the surface on the electrode potential [1–3]. The study of adsorption of organic compounds on the dropping mercury electrode has been correlated to the adsorption on other metals [4, 5].

Adsorption of organic compounds at the electrode–solution interface can be directly studied by determining the decrease in the amount of adsorbant in dilute solutions. Information regarding adsorption can also be obtained indirectly from kinetic data, since any change in the double layer structure is shown to have an effect on the rate of an electrochemical process, if the process is not under diffusion control [6].

In the present investigation, the effect of substituted arsine and phosphines (triphenylarsine, triphenylphosphine and tri-*p*-tolylphosphine) on the corrosion of zinc in acidic solution is studied. The adsorption of these compounds on the zinc surface is discussed.

2. Experimental

The preparation of the solutions, the electrode surface and the general procedure have been described earlier [7].

3. Results

3.1. *Weight loss measurements*

The free dissolution of zinc in stirred 0.1 M $HClO_4$ with and without different concentrations of triphenylarsine (TPA), triphenylphosphine (TPP) and tri-*p*-tolylphosphine (TTP) was studied at 30° C. From the weight loss data, the corrosion rate ($mg\,cm^{-2}\,h^{-1}$) was calculated. The corrosion rate of zinc in $HClO_4$ decreased in the presence of TPA, TPP and TTP. At a given concentration of inhibitor, the extent of corrosion inhibition was in the order: TTP > TPP > TPA.

The corrosion rate varied with the inhibitor concentration up to 2×10^{-4} M. The corrosion rate of zinc in 0.1 M $HClO_4$ was found to be $2.16\,mg\,cm^{-2}\,h^{-1}$, which reduced to 1.10, 0.99 and $0.82\,mg\,cm^{-2}\,h^{-1}$ in the presence of 2×10^{-4} M TPA, TPP and TTP, respectively. From the corrosion rate data, with and without inhibitors, the percentage production of zinc was calculated using the equation

0021–891X/80/040505–06$02.60/0

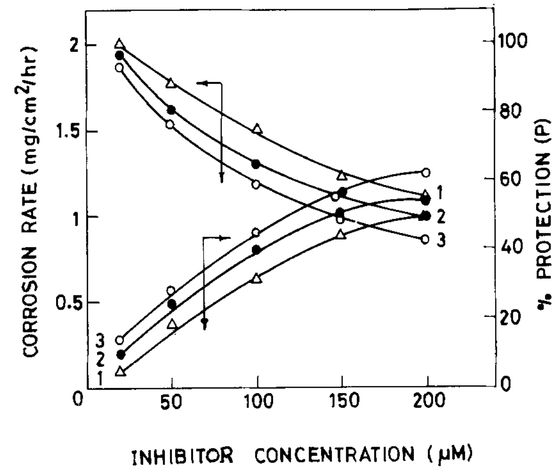

Fig. 1. Variation of corrosion rate and percentage protection of zinc with the concentration of inhibitors. 1. TPA; 2. TPP; 3. TTP.

$$\text{percentage protection } (P) = \frac{W_0 - W}{W_0} \times 100$$

where W_0 and W are the weight losses of zinc without and with inhibitor, respectively. Fig. 1 shows the variation of corrosion rate and percentage protection of zinc with concentration of the inhibitors.

Zinc was dissolved for different periods of immersion in $HClO_4$ with and without inhibitors. The variation of weight loss with immersion time in the presence and absence of inhibitors is shown in Fig. 2.

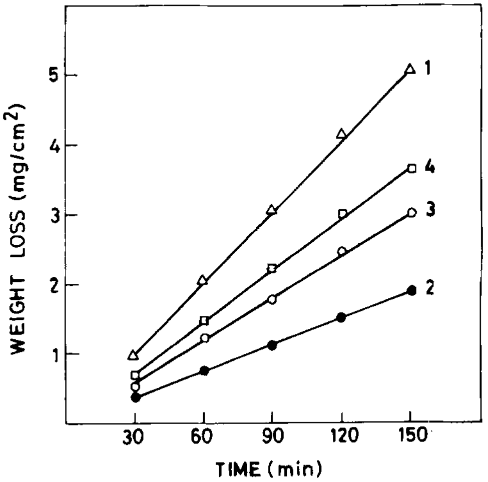

Fig. 2. Variation of weight loss of zinc with immersion time in perchloric acid with and without 10^{-4} M inhibitors. 1. 0.1 M $HClO_4$ only; 2. TTP; 3. TPP; 4. TPA.

Table 1. Percentage protection of zinc by inhibitors at different concentrations of acid

Concentration of acid (M)	pH	Percentage protection at 10^{-4} M TPA	TPP	TTP
0.05	2.30	30	36	44
0.10	2.00	31	40	45
0.25	1.60	50	54	59
0.50	1.30	60	66	69

Zinc was dissolved for one hour in different concentrations of $HClO_4$ with and without 10^{-4} M inhibitors in order to study the effect of pH on percentage protection of zinc. It was found that the percentage protections of TPA, TPP and TTP increased with the increase in the concentration of acid (Table 1). The effect of temperature on percentage protection was also studied (Table 2).

3.2. *Polarization studies*

Galvanostatic anodic and cathodic polarization studies were made on zinc in perchloric acid without and with 10^{-4} M inhibitors. Figs. 3 and 4 show the anodic and cathodic polarization diagrams for zinc in perchloric acid with and without inhibitors. Anodic and cathodic slopes were evaluated and were found to be 30 ± 5 mV/decade and 120 ± 10 mV/decade, respectively. These values did not change with the addition of inhibitors. However, the anodic and cathodic Tafel lines shifted to higher potential regions in the presence of inhibitors. The extent of shift in Tafel lines by the addition of inhibitors was in accordance with the decrease in corrosion rate.

Table 2. Effect of temperature on the percentage protection of zinc by inhibitors (10^{-4} M)

Temperature (° C)	Percentage protection TPA	TPP	TTP
20	34	46	50
30	31	40	45
40	28	33	39

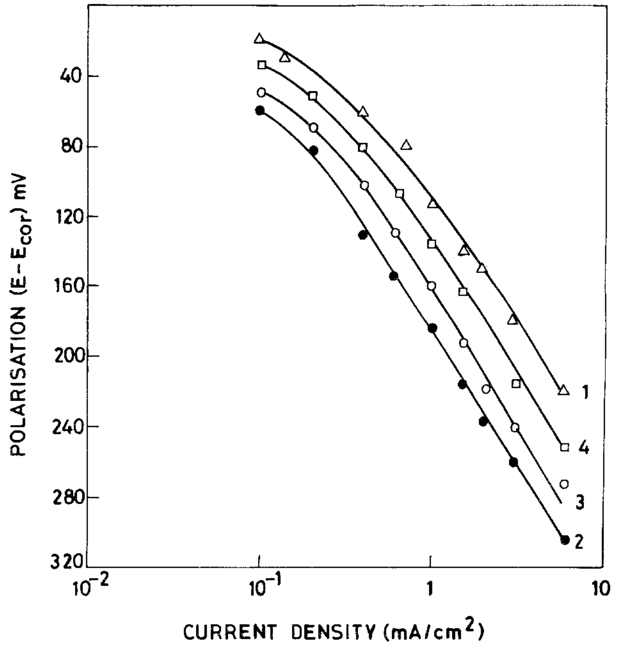

Fig. 3. Anodic polarization diagrams for zinc in perchloric acid solution with and without 10^{-4} M inhibitors. 1. 0.1 M $HClO_4$ only; 2. TPP; 3. TTP; 4. TPA.

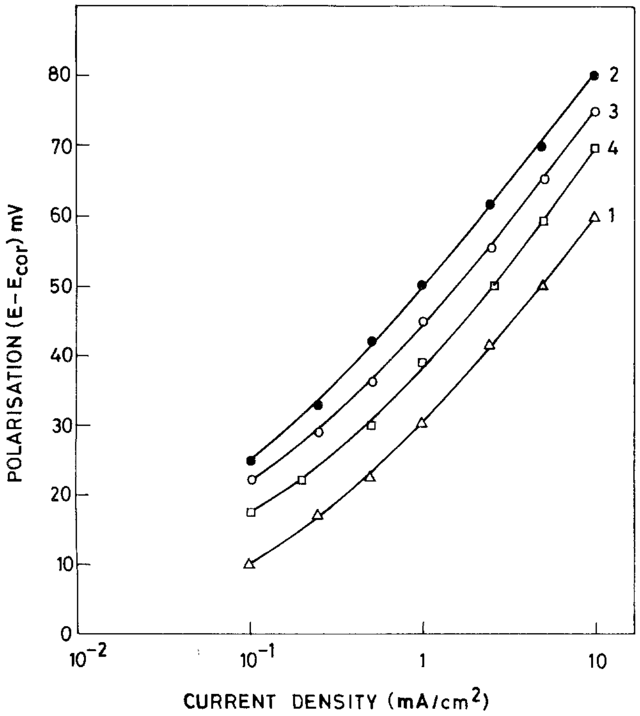

Fig. 4. Cathodic polarization diagrams for zinc in perchloric acid solution with and without 10^{-4} M inhibitors. 1. 0.1 M $HClO_4$ only; 2. TTP; 3. TPP; 4. TPA.

Table 3. Corrosion current density, and percentage protection (by weight loss and polarization methods) of zinc in perchloric acid in the presence of 10^{-4} M inhibitors

Bath solution	*Corrosion current density* (mA cm^{-2})	*Percentage protection* *Polarization method*	*Percentage protection* *Weight loss method*
0.1 M $HClO_4$ only	0.15		
+ 10^{-4} M TPA	0.10	33	31
+ 10^{-4} M TPP	0.09	40	40
+ 10^{-4} M TTP	0.08	47	45

The Tafel lines were extrapolated to the free corrosion potential value to find the corrosion current density. The percentage protection was calculated using corrosion current density values. The corrosion current density and percentage protection evaluated by weight loss and polarization methods are tabulated in Table 3.

4. Discussion

Compounds with a lone pair of electrons act as corrosion inhibitors by adsorption or by film formation. It has been shown that the dipolar organic molecules control the corrosion reaction by complexing with the surface atoms [8] and hence forming submonolayers of a surface species.

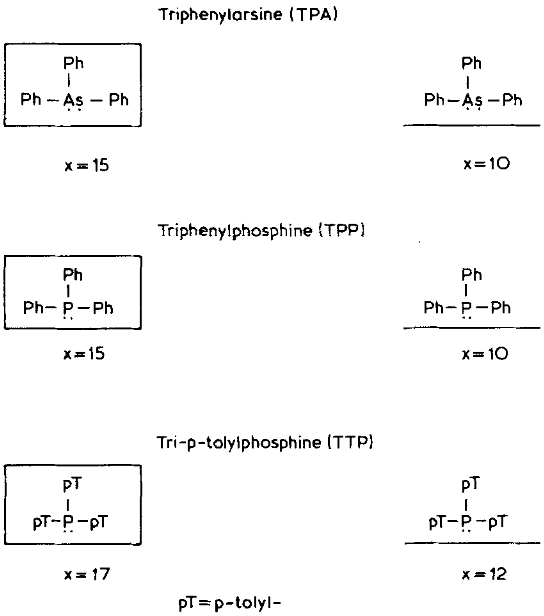

Fig. 5. Different possible modes of adsorption of arsine and phosphines with the corresponding x values.

In the present investigation, TPA, TPP and TTP are found to be effective corrosion inhibitors (Fig. 1). The values of Tafel slope and the parallel shift of anodic and cathodic Tafel lines to higher potential regions in the presence of inhibitors indicate that the corrosion inhibition is by blocking both the anodic and cathodic sites on the surface through adsorption [9, 10]. This type of adsorption is known to be a quasi-substitution process of water by organic molecules [11]. The isotherm for such a process is given by Bockris and Swinkle [12].

$$\Delta G_a^0 = -2.303\,RT$$
$$\times \log\left\{\frac{55.4\theta}{C_{org}(1-\theta)^x}\;\frac{[\theta + x(1-\theta)]^{x-1}}{x^x}\right\}$$

where ΔG_a^0 is the apparent free energy of adsorption, C_{org} is the concentration of inhibitor in the bulk of the solution, θ is the surface coverage and x is the size factor (i.e. the number of water molecules replaced by one molecule of inhibitor).

The size factor depends on the mode of adsorption of inhibitor. Different possible modes of adsorption of TPA, TPP and TTP with corresponding x values are shown in Fig. 5.

ΔG_a^0 of inhibitors for different possible modes of adsorption at different concentrations are calculated and given in Tables 4–6. ΔG_a^0 varied with x for a given inhibitor. However, the trend in the variation of ΔG_a^0 with θ was the same for different x values.

The double layer potential is strongly influenced by the ionic strength of the electrolyte used. The potentials of inner and outer Helmholtz

Table 4. Surface coverage, and free energy of adsorption at different concentrations of triphenylarsine (TPA)

Concentration (M)	*Surface coverage* (θ)	$-\Delta G_a^0$, *free energy of adsorption* (kcal mol^{-1})	
		$x = 15$	$x = 10$
10^{-5}	0.056	6.04	6.24
5×10^{-5}	0.19	6.03	6.25
10^{-4}	0.31	6.09	6.35
1.5×10^{-4}	0.43	7.72	6.91
2×10^{-4}	0.49	7.92	6.61

Table 5. Surface coverage, and free energy of adsorption at different concentrations of triphenylphosphine (TPP)

Concentration (M)	*Surface coverage* (θ)	$-\Delta G_a^0$, *free energy of adsorption* (kcal mol^{-1})	
		$x = 15$	$x = 10$
10^{-5}	0.10	5.62	5.63
5×10^{-4}	0.25	5.99	6.51
10^{-4}	0.40	6.47	6.68
1.5×10^{-4}	0.48	6.55	6.80
2×10^{-4}	0.54	6.65	7.08

Table 6. Surface coverage, and free energy of adsorption at different concentrations of tri-p-tolylphosphine (TTP)

Concentration (M)	*Surface coverage* (θ)	$-\Delta G_a^0$, *free energy of adsorption* (kcal mol^{-1})	
		$x = 17$	$x = 12$
10^{-5}	0.12	5.65	6.87
5×10^{-5}	0.29	6.11	6.70
10^{-4}	0.45	6.42	6.92
1.5×10^{-4}	0.55	6.80	7.15
2×10^{-4}	0.62	6.13	7.33

layers have an effect on the corrosion rate. The extent of adsorption of the inhibitor molecule at the interface depends on the potential and charge at the interface. At higher concentrations of the electrolyte, the electrical double layer is sharply defined and hence the charge at the interface increases which facilitates adsorption.

The decrease of percentage protection at higher temperatures also supports the quasi-type of substitution process at the interface.

The percentage protection of Lewis-base type inhibitor will be affected by a slight change in electron donating or accepting capacity in a molecule. The relative percentage protection of TPA, TPP and TTP are in accordance with their basicity.

Acknowledgements

The authors are grateful to Professor G. K. Narayana Reddy, Head of the Department of Chemistry, Central College, Bangalore, for his encouragement. One of them (H.B.R.) thanks CSIR New Delhi, for the financial assistance.

References

[1] A. N. Frumkin and Levich, *Zh. Fiz. Khim* **21** (1947) 1135, 1183.

[2] Levich, Physiochemical Hydrodynamics, Prentice Hall, New Jersey (1962) p. 562.

[3] Krjukova and A. N. Frumkin, *Zh. Fiz. Khim.* **23** (1949) 819.

[4] N. Hackerman and A. A. Roebuck, *Industr. Eng. Chem.* **46** (1954) 1481.

[5] N. Subramanyan, *Proceedings of 13th Seminar on Electrochemistry* (1972).

[6] A. N. Frumkin, *Dodl. Akad. Nauk. SSSr* **85** (1952) 373.

[7] H. B. Rudresh and S. M. Mayanna, *Brit. Corr. J.* **12** (1977) 54.

[8] O. L. Riggs Jr., 'Corrosion Inhibitors' (edited by C. C. Nathan) (NACE, Houston, 1973) p. 7.

[9] T. P. Hoar and R. D. Holliday, *J. Appl. Chem.* **3** (1953) 502.

[10] C. A. Mann, *Trans. Electrochem. Soc.* **69** (1936) 115.

[11] H. B. Rudresh and S. M. Mayanna, *J. Electrochem. Soc.* **124** (1977) 340.

[12] J. O'M. Bockris and D. A. J. Swinkles, *J. Electrochem. Soc.* **111** (1964) 736.