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Materials Chemistry and Physics 93 (2005) 54–64

MATERIALS CHEMISTRY AND PHYSICS

www.elsevier.com/locate/matchemphys

meta-Substituted aniline-*N*-salicylidenes as corrosion inhibitors of zinc in sulphuric acid

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Received 1 December 2004; accepted 16 February 2005

Abstract

The corrosion of zinc in sulphuric acid containing different *m*-substituted aniline-*N*-salicylidenes has been studied with respect to inhibitor and acid concentration, period of exposure and temperature. 99% inhibitor efficiencies have been observed. It appears that the salicylidene part of the inhibitor including the iminic group in the molecule plays a dominant role in the inhibition. As far as the effect of exposure period and temperature is concerned, *m*-CNS has turned out to be the best one. For all the five inhibitors, the heats of adsorption and free energies of adsorption are negative, while the entropies of adsorption are positive. The free energies of adsorption are more negative in the case of very good inhibitors like *m*-TNS and *m*-CNS, indicating a strong interaction of the inhibitor molecules with the metal surface. The activation energies in the presence of these inhibitors are higher than that in plain acid. The adsorption of these inhibitors follows Langmuir adsorption isotherm. The conjoint effect of external cathodic current and the inhibitor is observed to be either synergistic or additive. Galvanostatic polarization studies indicate that these are mixed type inhibitors with predominant action on the local cathodes. Mechanism of the action of inhibitors has been provided.

Keywords: Acid inhibition; Cathodic protection; Schiff bases; Zinc

1. Introduction

Zinc is highly susceptible to attack by acids. Hence for scale removal and cleaning of zinc surfaces with acidic solutions, it becomes necessary to use inhibitors. In modern industry acids are used for the chemical cleaning of metals and alloys. Thus, to have inhibitors of the corrosion of these metals and alloys in acid solutions is not only beneficial but also at times indispensable. With this aim in mind the influence exerted by some Schiff bases on the corrosion rate of zinc in 0.25 M and 0.5 M sulphuric acid has been studied. Previously studied inhibitors for zinc in acids include alkaloids [1], thiourea [2], benzene-thiols and related derivatives [3], imidazole azo derivatives [4], quinoline derivatives [5], quaternary salts of pyridine bases [6], benzaldehyde and its derivatives [7], and Schiff bases of chloroanilines and toluidines [8]. Lin et al. have studied the effect of 2-mercapto-benzimidazole on the corrosion inhibition of zinc in phosphoric acid [9]. Some Schiff bases have been reported earlier for copper [10], aluminium [11] and aluminium alloy 3102 [11a]. Many of the commercial inhibitor formulations for acid solutions include aldehydes and amines [12]. Desai et al. [13] report that the inhibition efficiency of Schiff bases is much more than that of corresponding amines and aldehydes. This may be due to the presence of –CH=N– group in the molecule. In earlier work the inhibition of corrosion of zinc in sulphuric acid by Schiff bases of ethylenediamine [14], *ortho*-substituted aniline-*N*-salicylidenes [15] and *ortho*-, *meta*- and *para*-aminophenol-*N*-salicylidenes [15a] has been reported. In the present work the corrosion of zinc in sulphuric acid containing different *m*-substituted aniline-*N*-salicylidenes has been reported. Due to the presence of an imine (–CH=N–) group and conjugated double bonds, these should function as good inhibitors.

The effect of inhibitor concentration, exposure period, temperature, and externally applied cathodic current on the behaviour of these inhibitors has been investigated.

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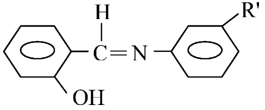
doi:10.1016/j.matchemphys.2005.02.004

2. Methodology

The Schiff bases were synthesized as per the procedure described by Jaeger [16]. All the five Schiff bases, namely, aniline-*N*-salicylidene, ANS, (mp., 50.5 °C; registry number, 779-84-0), *m*-toluidene *N*-salicylidene, *m*-TNS, (mp., 39.5 °C; registry number, 952-81-8), *m*-anisidine *N*-salicylidene, *m*-AnNS, (mp., 60 °C; registry number, 889-29-2), *m*-chloroaniline *N*-salicylidene, *m*-CNS, (mp 95 °C; registry number, 886-32-8) and *m*-aminophenol *N*-salicylidene *m*-APNS, (mp., 128 °C; registry number, 26213-36-5) are yellow crystalline products insoluble in water but soluble in ethanol. ANS has been used as an inhibitor for steel [17] and aluminium-56S [18–20] in hydrochloric acid. *m*-TNS, *m*-AnNS, *m*-CNS and *m*-APNS are all being reported for the first time as corrosion inhibitors. The general structure of these inhibitors may be represented by:



where $R' = H$ in ANS; $R' = CH_3$ in *m*-TNS; $R = OCH_3$ in *m*-AnNS; $R' = Cl$ in *m*-CNS; and $R' = OH$ in *m*-APNS.

3. Preparation of specimens

Rectangular specimens of electrolytic zinc, of size 3 cm × 3 cm (thickness 28 SWG), with a small hole of ∼2 mm diameter just near one end of the specimen were used for the determination of the corrosion rate. The specimens were polished using successively '0' to '0000' Oakey emery paper. The final polishing was done using jewellers rouge, which gave a mirror-like finish. The specimens were finally de-greased by A.R. carbon tetrachloride (sulphur free). The test specimens were exposed to 0.25 M and 0.5 M sulphuric acid solutions, containing controlled additions of various Schiff bases in the range of 0–1.0%. One specimen only was suspended by a Pyrex glass hook in each beaker containing 230 ml of the test solution which was open to the air at 35 ± 0.5 °C (unless otherwise specified) to the same depth of about 1.5 cm below the surface of the liquid.

4. Polarisation measurements

For polarisation studies, metal coupons of circular design, diameter 2.802 cm with a handle 3 cm long and 0.5 cm wide were used. The handle and the back of the coupon and of the auxiliary platinum electrode were coated with Perspex leaving only the circular portion of the specimen exposed of apparent surface area, 6.156 cm^2. The solution, 80 ml in each limb, was contained in a H-type Pyrex glass cell with the Luggin capillary as near to the electrode surface as possible and a porous partition to separate the two compartments. The potential was measured against a saturated calomel reference electrode (SCE). Galvanostatic polarisation data were obtained with Wenking Potentioscan POS 73. In these experiments, the current density was varied in the range of 1.62×10^{-3} to 32.5×10^{-3} A cm^{-2}. For cathodic protection studies, it was varied in the range 0.01624 A dm^{-2} to 3.492 A dm^{-2}.

5. Effect of inhibitor concentration

To study the effect of inhibitor concentration on inhibitive efficiency, weight losses were determined at 35 °C in 0.25 M and 0.5 M sulphuric acid containing 0.1–1.0% inhibitor for an immersion period of 30 min. The results given in Table 1 shows that a specimen of zinc suffers a weight loss of 8770 mg dm^{-2} in 0.25 M and 22977 mg dm^{-2} in 0.5 M uninhibited acid. In inhibited acid, the inhibitor efficiencies were found to increase with inhibitor concentration. *m*-CNS and *m*-APNS at lower concentrations accelerate the corrosion but at higher concentrations (>0.3%) they function as inhibitors. Thus at an inhibitor concentration of 0.5% in 0.25 M acid the inhibitive efficiencies were found to increase in the order: *m*-APNS (99.0%) < *m*-TNS (99.6%) < *m*-AnNS (99.7%) < ANS (99.8%) < *m*-CNS (99.9%).

In 0.5 M acid also the inhibitors were quite effective and the order of increase in efficiency was found to be: *m*-CNS (96.0%) < *m*-APNS (98.4%) < *m*-AnNS (99.8%) < *m*-TNS (99.9%) < *m*-ANS (99.9%).

When plots of $\log \theta$ versus $\log C_{\text{inh}}$ (Freundlich) and plots of θ versus $\log C_{\text{inh}}$ (Temkin) were drawn, they did not obey the above two isotherms. However, when the plots of $\log \theta/1-\theta$ versus $\log C_{\text{inh}}$ (inhibitor concentration) were drawn (Fig. 1), straight lines were obtained, indicating that the adsorption of the inhibitors takes place following Langmuir adsorption isotherm [21]:

$$C_{\text{inh}} = \frac{\theta}{K(1-\theta)} \tag{1}$$

where θ is the inhibitor efficiency.

From the results it appears that the presence of various substituent groups in the *m*-position do not have much significant effect on the inhibitive efficiency and that the salicylidene part of the inhibitor including the iminic group in the molecule plays a dominant role in conferring the inhibition.

6. Effect of exposure period

The effect of exposure period on the inhibitive efficiency of different inhibitors was studied at 35 °C in 0.25 M and 0.5 M sulphuric acid containing 1.0% (0.5% in the case of ANS and *m*-APNS) of inhibitor. The results given in Table 2 show that as the exposure period is increased from 30 to 180 min the loss in weight of zinc in plain acid increases from 8770 mg dm^{-2} to 17791 mg dm^{-2} in 0.25 M and from