The Effect of Bivalent Cations in the Adsorption of Phosphonic Acids on Iron Electrodes Studied by the Radiotracer Method

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The adsorption of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) on an iron electrode in neutral aqueous solution has been examined by the radiotracer method. The role of calcium and zinc cations in the adsorption mechanism has also been studied in order to understand the synergistic effect when HEDP is applied together with these cations.

Introduction

The chemicals used in the inhibition of metal corrosion in nearly neutral aqueous media can be classified, in general, as film forming inhibitors. These chemicals are capable of depositing on metal surfaces, thus forming a three dimensional (3 D) protective film. Film forming inhibitors are often termed as interphase inhibitors, to distinguish these from interface inhibitors. The effect of the latter is due to specific adsorption which forms a two dimensional (2 D) protective layer on the metal surface.

The 3 D inhibitors can further be divided into passivating and precipitation inhibitors [1]. Passivators function by shifting the electrochemical potential of the corroding metal into a region where an insoluble oxide or hydroxide forms. Chromates and nitrites are examples of this type of inhibitors.

Precipitation inhibitors form insoluble compounds on the metal surface. Inorganic and organic phosphorous compounds are probably the most widely used chemicals in this category.

The principle of operation is: by forming an insoluble iron, calcium or zinc phosphorus compound on the metal surface, this sufficiently thick layer constitutes a physical barrier hindering contact between solution and metal. Some surface active chelating agents with acidic (carboxylic, phosphonic, sulfonic) and/or basic (amine, alcoholic) functional groups are also efficient precipitation inhibitors. Successful chelate corrosion inhibitors require high surface activity and aqueous solubility.

During the past two decades, a number of phosphonates have been used in different inhibitor compositions [2]. Typical examples of these are 1-hydroxyethane 1,1-diphosphonic acid (HEDP), and aminotris(methylenephosphonic acid) (AMP). These compounds contain phosphorus-carbon (P–C) bonds contrary to phosphorus-oxygen bonds in inorganic phosphates. The P–C bonds are much more resistant to conversion into orthophosphate than are P–O bonds in inorganic phosphates.

It is also well known that the presence of cations as Zn^{2+} as well as Ca^{2+} ions in aqueous media synergistically increase the inhibitor efficiency of phosphonates. However, there still are open questions concerning both the mechanism of inhibition by phosphonates and the synergetic effect when phosphonates are applied together with the above cations. It has been shown that the inhibition of ferrous metal corrosion by organophosphorous compounds in the presence of Zn^{2+} or Ca^{2+} ions is due to the formation of a film on the metal surface which hinders the diffusion of species in the vicinity of the surface and retards the rate of both anodic dissolution and the cathodic oxygen reduction reactions [3, 4].

By surface analysis technique the presence of both phosphorous and zinc and/or calcium was detected, although the full composition of the film has not been determined. The aim of this study was to examine the adsorption of 1-hydroxy-ethylidene-1,1-diphosphonic

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acid (HEDP) on ferrous metal surface by the in situ radiotracer method. The efficiency of radiotracer methods for the investigation of adsorption phenomena has been clearly demonstrated by several authors [5].

Experimental

Electrochemical and radiochemical parameters were measured simultaneously. The new experimental technique was discussed in detail by Várallyai et al. [6, 7]. Adsorption measurement was carried out by the solution method. After the electrode is immersed in the solution under given conditions the decrease in activity of the solution due to the adsorption of radioactive species on the metal surface is measured and the amount of adsorption is determined.

The activity of substances labelled by β radiation was measured periodically and the activity of the substance labelled with γ radiation was recorded continuously, which ensured simultaneous labelling.

HEDP, calcium and zinc were labelled with ^{14}C, ^{45}Ca and ^{65}Zn isotopes, respectively. Characteristic values of the isotopes applied are given in Table 1. Activities were measured by liquid scintillation, and electrochemical parameters of the systems studied were controlled by a potentiostat. The measured data were stored in a computer. An iron electrode of 80 cm² geometrical surface area was used as an adsorbent with the following composition: Fe: 99.57%, Si: 0.05%, Mn: 0.3%, S: 0.01%, P: 0.02%.

The volume of the dilute aqueous sodium perchlorate solution (0.5 mol/dm³) was 80 cm² with pH = 7. To show the oxidation of Fe^{2+} ions, 10 µl ascorbic acid was added to the solution.

The time required for equilibration was determined by continuous measurement.

Equilibrium was attained in 30 minutes in all experiments, and this time period was applied in all experiments. For the determination of the effective inhibitor concentration, the corrosion potential as a function of

inhibitor concentration was measured. It has been found that a concentration of 10^{-6} mol/dm³ is already sufficient for substantial reduction of the corrosion rate of the metal electrode. However, $3 \cdot 10^{-4}$ mol/dm³ (or higher) HEDP concentration was applied in all experiments in order to perform simultaneous radiochemical and electrochemical measurements. The samples were first filtered through a colloid membrane filter (0.45 µ) and measured at different potentials in 30 minute intervals. The amount of adsorbed molecules on the electrode surface at each electrode potential was determined from the measured activities by the following relation:

$$\Gamma = \frac{I_0 - I_1}{I_0} \frac{c \cdot v}{s} \quad (\text{mol/cm}^{-2}),$$

where Γ is the amount of substances adsorbed per unit surface, I_0 and I_1 are activities of the solution before and after the adsorption process, c is the concentration and v the volume of the solution, and s is the geometrical surface of the working electrode.

Results and Discussion

In our experiments attention was focused on three essential points. The first was to study the effect of Ca^{2+} and Zn^{2+} ions on the amount of adsorbed HEDP molecules on the metal surface. The second was the correlation between the adsorption and the reduction of corrosion rates for the metal, and the third was the composition of the film formed by HEDP and bivalent ions through precipitation on mild steel.
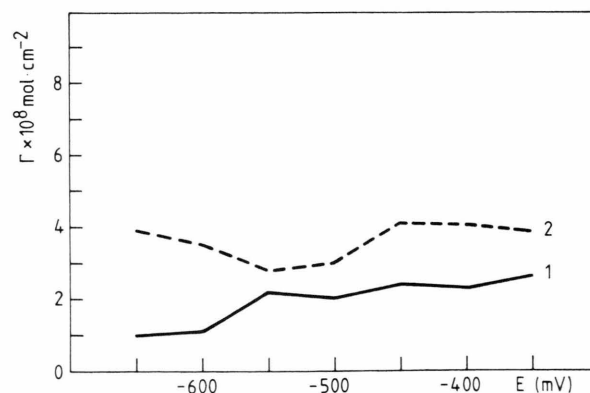
Isotope	Half-life	Energy (MeV)
^{14}C	5730 a	0.159 β
^{45}Ca	165 d	0.25 β
^{65}Zn	244 d	1.11 γ

Table 1.
Isotopes used in tracer adsorption studies.

Fig. 1. Potential dependence of the adsorption of HEDP in aqueous 0.5 mol dm⁻³ NaClO₄. (1) $c = 3 \cdot 10^{-4}$ mol dm⁻³, (2) $c = 6 \cdot 10^{-4}$ mol dm⁻³.
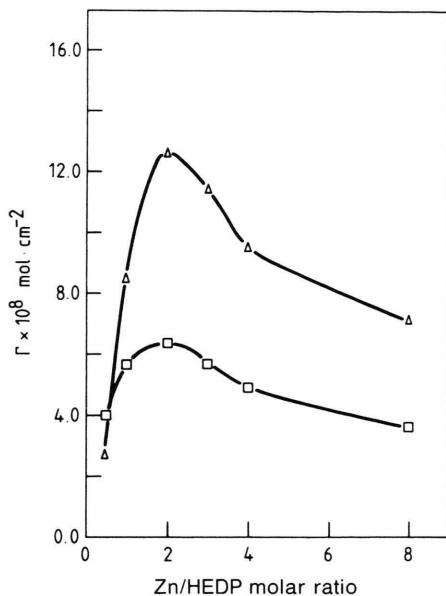
Fig. 2. Adsorption of labelled HEDP (^{14}C) and ^{65}Zn versus the Zn/HEDP molar ratio in aqueous 0.5 mol dm^{-3} NaClO$_4$. □ HEDP, △ Zn.
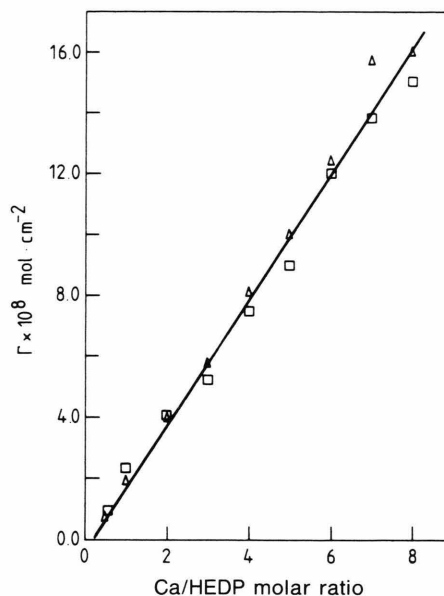

Fig. 4. Adsorption of labelled HEDP (^{14}C) and ^{45}Ca versus the Ca/HEDP molar ratio in aqueous 0.5 mol dm^{-3} NaClO$_4$. □ HEDP, △ Ca.
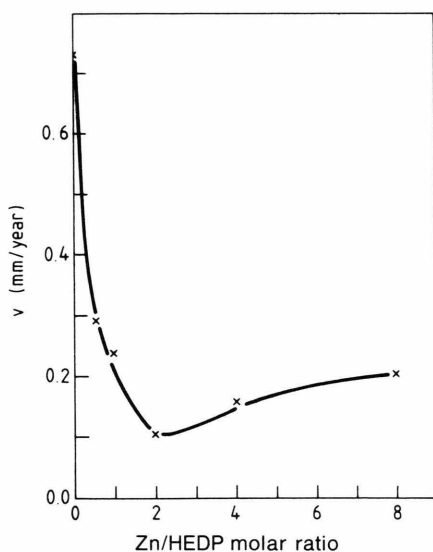

Fig. 3. Corrosion rate of iron electrode versus the Zn/HEDP molar ratio in aqueous 0.5 mol dm^{-3} NaClO$_4$.

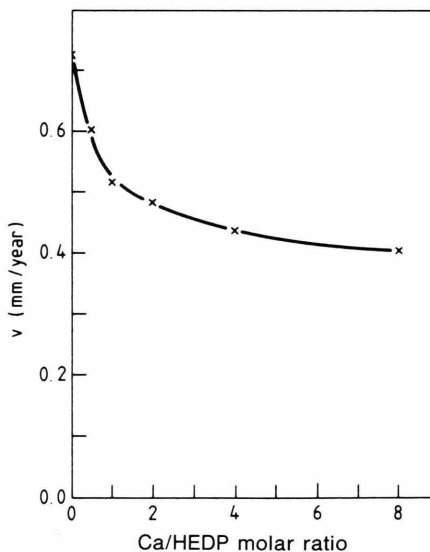

Fig. 5. Corrosion rate of iron electrode versus the Ca/HEDP molar ratio in aqueous 0.5 mol dm^{-3} NaClO$_4$.

The potential dependence of the adsorption of HEDP for $3 \cdot 10^{-4}$ mol/dm^3 and $6 \cdot 10^{-4}$ mol/dm^3 HEDP concentration in a 0.5 mol/dm^3 NaClO$_4$ solution is shown in Figure 1. It is clearly observable that the potential dependence of adsorption in the studied region is very weak, however, surface coverage of the metal surface increases with increasing HEDP con-

centration in the solution. In both cases the corrosion potential was at about -410 mV (SHE). To study the role of Zn^{2+} and Ca^{2+} ions in the adsorption of HEDP molecules, experiments with ion/HEDP molar ratios 0.5–8 were carried out in 0.5 mol/dm^3 NaClO$_4$ solutions at equilibrium electrode potential. The adsorption of HEDP molecules was measured by ^{14}C

isotope substitutions while ion adsorption was followed by ^{45}Ca and ^{65}Zn isotopes, respectively.

The initial concentration of HEDP molecules in the solutions was in all cases $3 \cdot 10^{-4}$ mol/dm³.

The corrosion rate of metal under identical circumstances was measured by the weight loss method with specimens immersed in solution for 24 hours. The Figure 2 shows the amount of adsorbed HEDP molecules and Zn^{2+} ions as a function of the Zn/HEDP molar ratio in the solution. The enhancement of HEDP adsorption in the presence of Zn^{2+} ions is clearly demonstrated. An important observation is that the mol ratio in the film remains about the same from Zn/HEDP = 1 up to Zn/HEDP = 8. The maximum amount of adsorbed HEDP molecules is attained at Zn/HEDP = 2 in the solution, in correspondence with the minimum corrosion rate, as is shown in Figure 3. From the above data an overall mechanism of inhibition emerges: HEDP forms a protective film on the metal surface via formation of a Zn-HEDP complex compound. The decrease in HEDP adsorption with increasing amount of Zn may be due to a greater solubility of the Zn-HEDP complexes in the presence of a higher amount of zinc hydroxide (amphoter hydroxide) near the metal surface (increased local pH).

The behaviour of HEDP adsorption in the presence of Ca^{2+} ions is demonstrated in Figure 4. Contrary to Zn^{2+} ions, the enhancement of HEDP adsorption on the metal surface increases for the molar ratios in solution between 0.5 and 8, in correspondence with a monotonous decrease of the metal corrosion rate shown in Figure 5. The molar ratio of Ca to HEDP in the film is unity, indicating that the Ca-HEDP complex is the basic component in the film. In spite of the same amount of HEDP molecules adsorbed on the metal surface, the higher corrosion rates of metal indicate that Ca/HEDP films are more transparent than Zn-HEDP films.

Summary

The results obtained by ^{14}C labelled HEDP, ^{65}Zn and ^{45}Ca isotopes have shown that HEDP by itself forms a loosely bound adsorption layer on iron oxide surface, and that the presence of zinc or calcium ions in solution leads to an increased adsorption of HEDP molecules. The maximum value in the efficiency of HEDP-Zn mixtures is achieved at about Zn/HEDP = 2 in the solution. For higher values of this ratio the ratio in the protective film remains about the same.

The HEDP adsorption is monotonously enhanced with increasing amount of Ca^{2+} ions in the solution, Ca/HEDP on the metal surface being unity.

These results indicate a precipitation mechanism for inhibition in both cases. Different weakly soluble complex compounds with zinc or calcium ions which precipitates on the metal surface, providing a protective layer may be formed by HEDP.

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