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Indirect radiotracer study of the adsorption of corrosion inhibitors on hematite

Abstract The specific adsorption of corrosion inhibitors (inorganic and organic compounds) was studied at a metal oxide (hematite) in 0.5 mol dm^{-3} NaClO$_4$ solution by an indirect radiotracer technique. This indirect radiotracer technique is based upon the application of labeled indicator species, which were sulfate species at a concentration of 2×10^{-4} mol dm^{-3}. The displacement of sulfate species was found in all the cases studied. The order of the inhibition efficiency of the corrosion inhibitor molecules is in good agreement with the order of their adsorbabilities.

Keywords Corrosion inhibitor · Adsorption · Metal oxides · Indirect radiotracer technique · Indicator species

Introduction

Corrosion processes occurring at a metal electrolyte solution interface are heterogeneous electrochemical reactions. One of the most economical and universal ways of protecting metals is by the application of corrosion inhibitors.

In neutral aqueous solutions, in the presence of oxygen a porous oxide layer generally covers the surface of the metal. The role of the inhibitor could be the reduction of the dissolution rate of the passivating oxide, repassivation of the surface with repair or reformation of the oxide film, repair of the oxide film by plugging pores with insoluble compounds, and the prevention of aggressive anions adsorption on the surface.

In previous communications [1, 2, 3, 4, 5] it had been shown that the radiotracer technique offers a unique possibility of studying the adsorption of anions on oxide surfaces. As a first step for solving the problem, the in-vestigation of adsorption of various species at the solution–oxide interface can be suggested. It was demonstrated that reliable results can be obtained in the case of adsorption of sulfate and chloride ions using powdered hematite and γ-Al$_2$O$_3$ adsorbents.

On the basis of these results a similar study with corrosion inhibitors can be suggested. The aim of the present work is to show that the application of the indirect version of the so-called "thin foil" method can furnish interesting information on the adsorption of some inhibitors.

Organophosphono compounds as corrosion inhibitors

A great variety of inhibitors are capable of providing a broad range of protection for metals under certain environmental conditions. One of the oldest and most effective inorganic inhibitor is chromate. Owing to its toxicity, chromate as a corrosion inhibitor should be replaced. Nowadays, strict environmental laws regulate the discharge of chemicals into rivers, lakes, or water reservoirs. Owing to eutrophication, environmental regulations have also been proposed to decrease the phosphorous content of natural water, which means that even the application of nontoxic inorganic phosphates should be reduced. One way to achieve this is given by the application of organic phosphono compounds instead of inorganic phosphono materials. The reason behind this is that C–P bonds are much more resistant to hydrolysis in comparison to C–O bonds [6]. A widely used example of organic phosphonic acid inhibitor is 1-hydroxyethane-1,1-diphosphonic acid (HEDP) [7, 8].

Phosphorus contamination of rivers and lakes may be diminished by decreasing the phosphorus content of anticorrosive molecules for water treatment while simultaneously retaining or increasing their inhibition effectiveness. Such investigations have involved the preparation of new molecules with lower phosphorus content. Phosphonate compounds containing the –CH$_2$PO$_3$H$_2$ fragment instead of, or together with, a

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carboxyl groups have a number of features that result from their distinctive stereochemistry, their greater electronegativity, and the greater potential of PO_4^{2-} than of COO^- for dentate formation. The important feature of phosphonates compared with aminocarboxyl chelates is their ability to form quite stable protonated MeHL complex [8].

A systematic study of the corrosion behavior of organic compounds was made to prove the importance of phosphonic and carboxyl groups in inhibitory processes and to optimize inhibitor concentration with minimum corrosion rate and maximum scale inhibiting activity [9]. The results of these studies were that a new class of environmentally friendly compounds was developed based on amino acids [10]. N,N-di(phosphonometyl)glycine (DPG) has been found to be an excellent potential corrosion inhibitor [11].

In a previous study [12], a coupled application of the in situ radiotracer "foil" method and voltammetry was used, which provided information on the time, potential, concentration, and pH dependence of HEDP adsorption on a polycrystalline gold electrode. It has been stated that the adsorption of HEDP on polycrystalline gold is highly dependent on the electrode potential, as well as on the composition, concentration, and solution pH. In the course of corrosion processes, oxidized metal surfaces are formed and it is not easy to distinguish separately the adsorption phenomena occurring on the metal surface and on the layer or submonolayer of oxides and hydroxides formed by corrosion; therefore, it would be of some interest to get independent information about the sorption phenomena taking place on the oxide layer, i.e., on corrosion products themselves.

Radiotracer techniques

As to the role of the labeled species in the radiotracer study of adsorption phenomena, two different versions of the method may be distinguished. The first one, used in our previous work [1, 2, 3, 4], is the direct method. In this case the species to be studied is labeled and the radiation measured gives direct information on the adsorption of this species; however, this method cannot be used in several cases owing to the technical restrictions connected with the very nature of the radiotracer method (limitations in the available concentration range, no possibility of distinguishing between the adsorption of the labeled compound studied and that of a product formed from it, limitation in the number of commercially easily available labeled compounds).

Considering all these problems the use of so-called indirect radiotracer methods was suggested [5]. Instead of labeling of the species to be studied, another adequately chosen labeled species (indicator species) is added to the system and the adsorption of this component is followed by the usual radiotracer measuring technique. Obviously, the sorption of the indicator species should be in relation with that of the species to

be studied. The nature of this link could be different in different systems. For instance, in some cases the competitive adsorption with the labeled species may furnish information about the adsorption behavior of a given molecule, while in other cases induced adsorption of the labeled species plays a role. The principle of the study in the former case can be demonstrated by Scheme 1.

In the following, the results obtained from the indirect study of inhibitor adsorption on hematite are reported. As the adsorption of labeled sulfate ions at hematite was studied in detail in our previous communication [3] and a reversible adsorption was found ^{35}S labeled sulfate ions could be used as an ideal indicator species.

Experimental

The experimental technique and setup for the radiotracer study of sorption processes (involving powdered sorbents) are described in Refs. [1, 2, 3, 4, 5].

The very principle of the method used in the present study is the measurement of radiation intensity originating from labeled adsorbed species on a powdered oxide layer sprinkled on a thin plastic foil that serves simultaneously as the window for the radiation measurement. The measurements were carried out at ambient temperature in an Ar atmosphere, Ar was bubbled in the solution phase and was let through the gap between the bottom of the measuring cell and the detector. Labeled H_2SO_4 was used (Amersham, specific activity: 200 MBqmmol^{-1}) for the preparation of the solutions, mostly with perchlorate supporting electrolyte.

A commercial hematite powder (Reanal, analytical grade) characterized by its X-ray diffraction pattern was used (ATOMKI/Siemens horizontal θ–2θ X-ray diffractometer with Cu Kα radiation).

The specific surface area of the oxide powder, 0.15 ± 0.05 m^{2}g^{-1}, was estimated from the particle size distribution according to a microscopic method based on measurements with a Bürker chamber.

DPG and HEDP were chosen as model compounds representing the class of inhibitors. The adsorption of the latter compound on polycrystalline gold was studied recently [12].

Results and discussion

The fundamental relationships for the evaluation of experimental data

Denoting by A the inhibitor species by B the indicator sulfate species, and considering that according to the
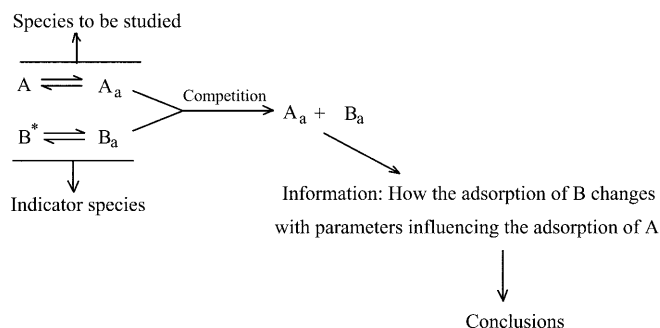
Scheme 1

results reported in Ref. [3] the adsorption of sulfate ions can be described by a Langmuir isotherm in the case of both adsorbent studied, the following equations can be used:

$$\theta_A = \frac{b_A c_A}{1 + b_A c_A + b_B c_B} \tag{1}$$

$$\theta_B = \frac{b_B c_B}{1 + b_A c_A + b_B c_B}. \tag{2}$$

Transformation of Eq. (2) leads to the expression

$$\frac{1}{\theta_B} = 1 + \frac{1}{b_B c_B} + \frac{b_A c_A}{b_B c_B}. \tag{3}$$

At a fixed concentration of the indicator species and taking into account that θ_B is proportional to the radiation intensity measured (I)

$$\theta_B = qI, \tag{4}$$

where q is a proportionality factor, we obtain

$$\frac{1}{I} = D + Fc_A. \tag{5}$$

From Eqs. (1) and (2)

$$\frac{\theta_A}{\theta_B} = \frac{b_A}{b_B} \cdot \frac{c_A}{c_B} \tag{6}$$

and

$$\theta_A = F'Ic_A. \tag{7}$$

Results

Curve 2 in Fig. 1 shows the effect of the addition of DPG on the radiation intensity originating from adsorbed labeled sulfate species present at a concentration of 2×10^{-4} mol dm^{-3} in 0.5 mol dm^{-3} NaClO$_4$ supporting electrolyte at pH 2.5. It may be seen from this figure that a significant decrease in the adsorption of sulfate ions takes place at DPG concentrations commensurable with that of the sulfate species.

For the sake of comparison the displacement of the adsorbed sulfate species by phosphoric acid is shown by curve 2 in Fig. 1. Figure 1 clearly demonstrates that the adsorbability of DPG is higher than that of phosphoric acid. On plotting the $1/I$ values against the concentration of DPG, a linear relationship is obtained as expected on the basis of Eq. (5). (Fig. 2).

By using Eq. (7) for the calculation of the θ values in arbitrary units the adsorption isotherm of DPG (relative scale) can be obtained as shown in Fig. 3.

The results obtained with HEDP are very similar to those presented earlier. The effect of HEDP on the adsorption of the sulfate species is shown in Fig. 4. The corresponding $1/I$ versus c_{HEDP} points are shown in
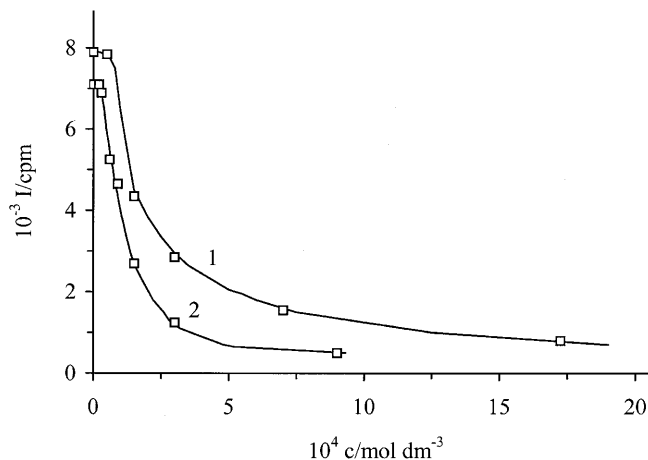

Fig. 1 The displacement of adsorbed labeled sulfate species by N,N-di(phosphonometyl)glycine (*DPG*) (*2*) and phosphoric acid (*1*) 2×10^{-4} mol dm^{-3} labeled H$_2$SO$_4$ in 0.5 mol dm^{-3} NaClO$_4$; pH 2.5 (2 mg Fe$_2$O$_3$/cm^2 referred to the geometric surface area of the bottom of the measuring cell)
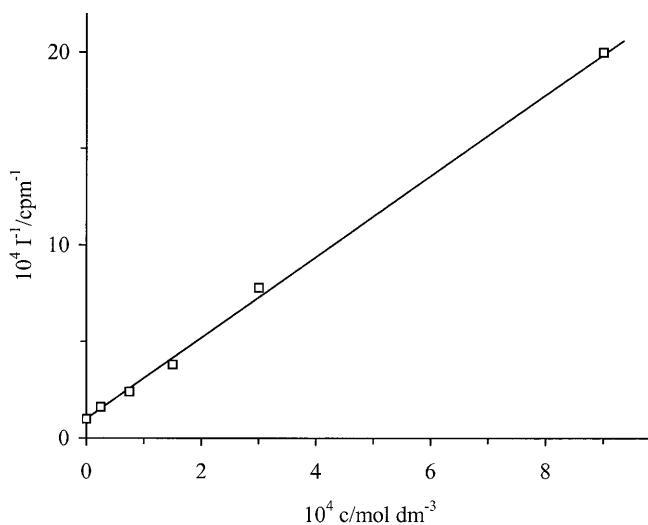

Fig. 2 $1/I$ versus DPG concentration representation of the data reported in Fig. 1

Fig. 5. (Despite the significant scattering of the data they can be described by a linear relationship at least to a first rough approximation.) The adsorption isotherm on a relative scale calculated by Eq. (7) is presented in Fig. 6. Finally, the displacement of sulfate species by DPG and HEDP is compared in Fig. 7. It may be seem from this figure that the adsorbability of the two inhibitors is almost the same.

Similarly to phosphate it was of interest to study the adsorption of chromate ions. The results obtained are represented in Figs. 8, 9, and 10. The effect of CrO$_4^{2-}$ ions and phosphate ions on the adsorption of labeled sulfate species is compared in Fig. 11. It may be seen from this figure that the adsorbability of chromate is lower than that of phosphate. The experimental results, which are based upon the different
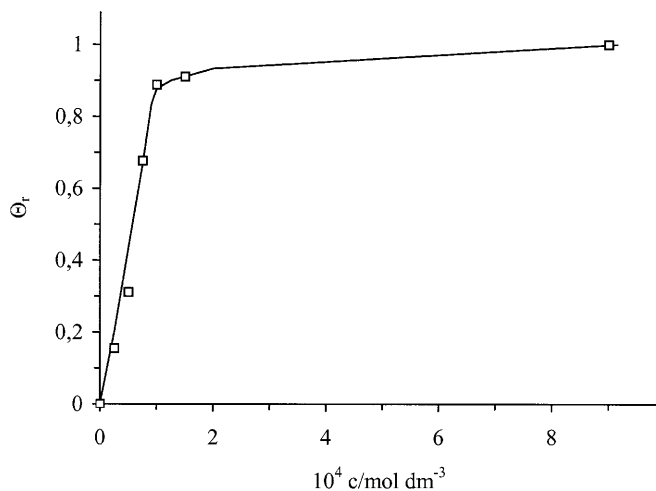
Fig. 3 Adsorption isotherm of DPG in arbitrary θ units calculated by Eq. (7)
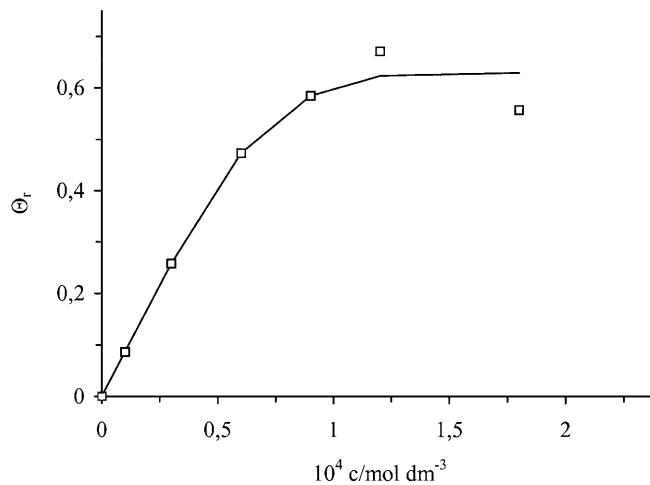

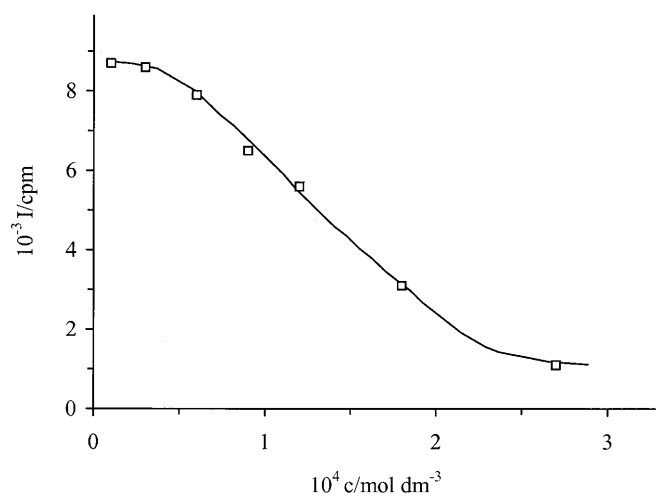**Fig. 6** Adsorption isotherm of HEDP in arbitrary θ units calculated by Eq. (7)

Fig. 4 The displacement of adsorbed labeled sulfate species by 1-hydroxyethane-1,1-diphosphonic acid (*HEDP*) 2×10^{-4} mol dm^{-3} labeled H_2SO_4 in 0.5 mol dm^{-3} $NaClO_4$; pH 2.5 (2 mg Fe_2O_3/cm^2)
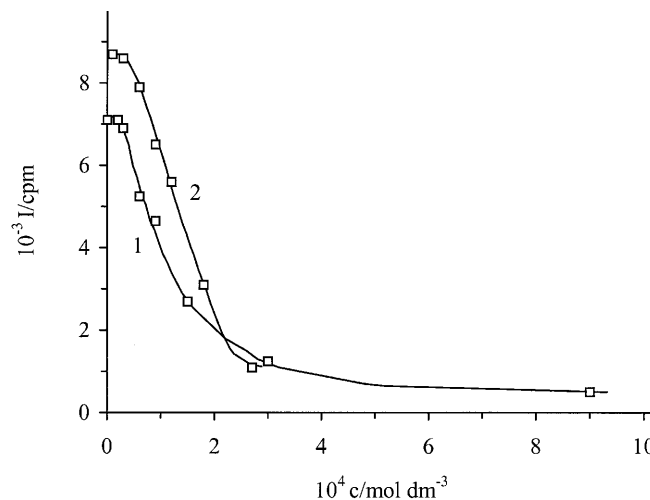
Fig. 7 Comparison of the effect of DPG (*1*) and HEDP (*2*) on sulfate adsorption (data in Figs. 1, 4)

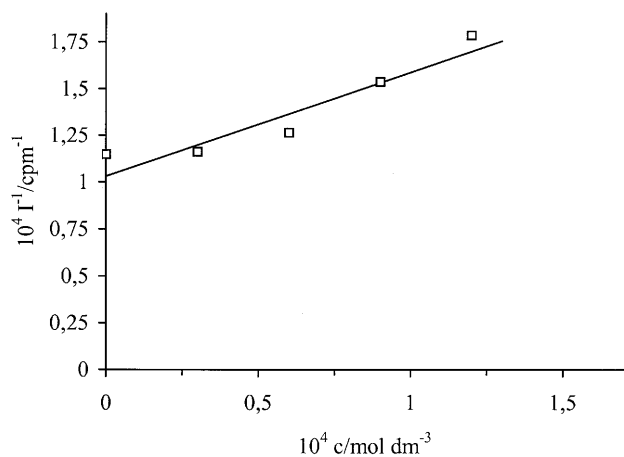adsorbability of the corrosion inhibitors, are in good agreement with previous corrosion studies [10], where the inhibition effects of these corrosion inhibitors were studied extensively.

Conclusions

The experimental data presented here confirm the idea that the study of the sorption phenomena taking place on metal oxides may contribute to a better understanding of corrosion phenomena.

The so-called indirect radiotracer technique, using labeled sulfate ions as indicator species, proved to be useful to follow the adsorption of inhibitor molecules as the displacement of adsorbed labeled sulfate species (emitting β radiation) by inhibitors takes place. The relative adsorption strength of various inhibitors (both
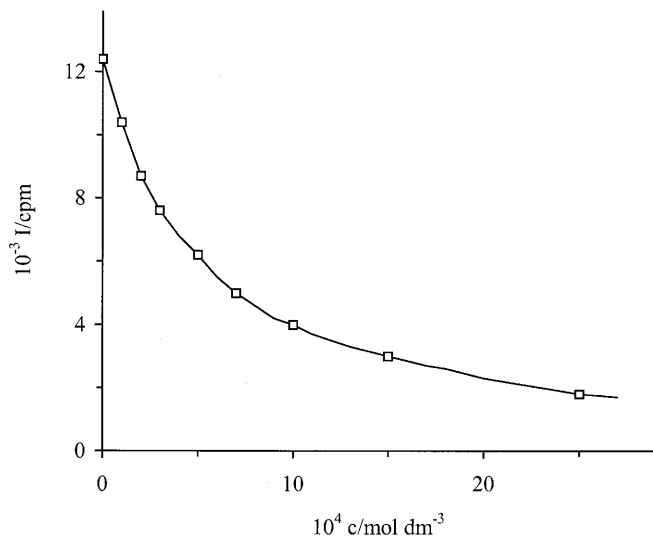

Fig. 5 $1/I$ versus HEDP concentration representation of the data reported in Fig. 4

Fig. 8 The displacement of adsorbed sulfate species by chromate ions (3 mg Fe_2O_3/cm^2). Other data as in Fig. 1

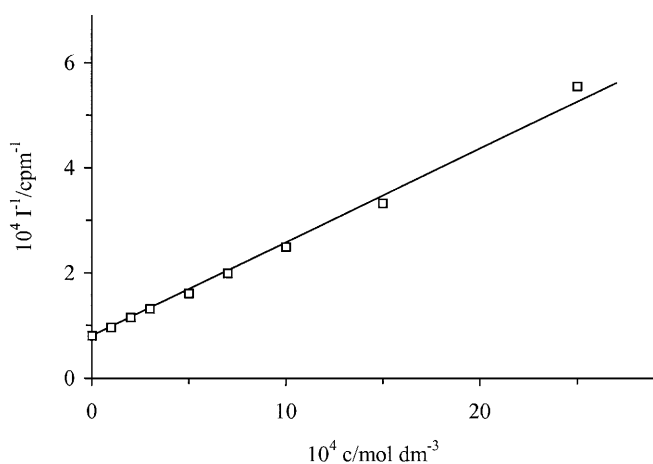**Fig. 10** Adsorption isotherm of chromate species in arbitrary θ units calculated by Eq. (7)

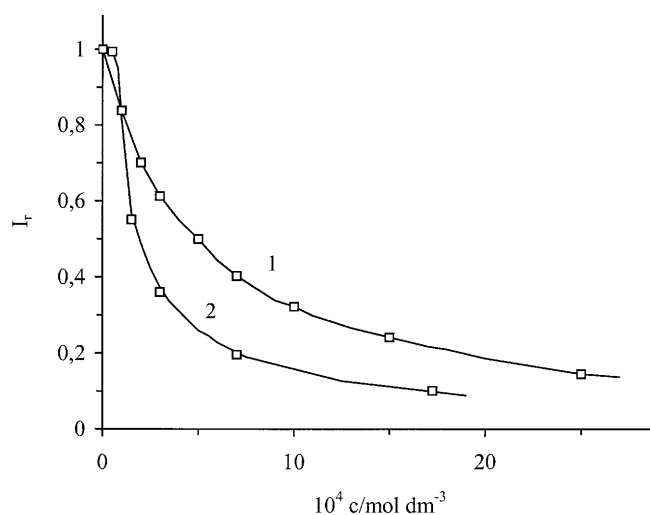**Fig. 9** $1/I$ versus chromate concentration representation of the data reported in Fig. 8

Fig. 11 Comparison of the effect of chromate (*1*) and phosphate (*2*) on the adsorption of labeled sulfate. (Radiation intensities are given on a relative scale: initial value = 1.)

inorganic and organic ones) can be estimated through their efficiency in the displacement of sulfate ions. It was found that at fixed concentrations the extent of the displacement of adsorbed sulfate species by organic phosphonic acids was higher than that by phosphoric acid and that the two phoshono compounds (DGP and HEDP) have different displacement ability. On the other hand, the effect exerted by phosphoric acid is more pronounced than that found in the presence of CrO_4^{2-}.

There is a parallelism between the corrosion inhibitor efficiencies and the adsorbabilities, found through the displacement effect, of the species studied. Accordingly this technique offers a quick screening method for the study of corrosion inhibitor efficiencies.

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