

INHIBITION MECHANISM OF CARBON STEEL IN NEUTRAL SOLUTIONS BY *N*-PHOSPHONO-METHYL- GLYCINE

A. SHABAN, E. KÁLMÁN and I. BICZÓ*

Department of Solution Chemistry and Corrosion Research, Central Research Institute for Chemistry,
Hungarian Academy of Sciences, H-1525 Budapest, Pf17, Hungary

*Technical University of Budapest

Abstract—Corrosion inhibition of carbon steel in neutral aqueous solutions by *N*-phosphono-methyl-glycine (NPMG) is based mainly on the formation of an inhibiting film that protects the base metal. In order to understand the structure and composition, the layers formed on carbon steel were sputtered by an argon beam to obtain a depth profile using Auger electron spectroscopy (AES). The influence of changes in the water composition using model solutions (with and without calcium) in contact with carbon steel on the formation and growth rate of the film was studied. In addition, the effect of several factors such as time of contact and the addition of some cations, such as Ca^{2+} and Zn^{2+} , on the formation and composition of the inhibiting films was investigated. In addition to surface analysis, weight loss method was used to optimize and characterize the inhibitor efficiency and the effect of synergism.

INTRODUCTION

CORROSION kinetics can be influenced by inhibitors. There are many types of chemicals that have corrosion inhibitive properties. One of these types are screening inhibitors where a film is formed in order to protect (isolate) the metal.

Phosphonates are one class of this inhibitor type. They could be introduced alone or in combination with other metallic corrosion inhibitors, such as zinc ions. Research in this area has been stimulated by the need to develop inhibitor formulations that are free from chromates, nitrates and inorganic phosphorus compounds. Phosphonates contain phosphorus carbon (P-C) bonds in contrast to the phosphorus-oxygen bonds in inorganic phosphates.

The P-C bonds are much more resistant to conversion into orthophosphate than are the P-O bonds in inorganic phosphates. Phosphonates when blended with certain cations and polymers in corrosion inhibitor mixtures further reduced the critical inhibitor concentration needed for inhibition, due to the synergistic effect of the components.

Synergism is one of the most important effects in inhibition processes and serves as a basis for all modern corrosion inhibitor formulations.¹

Once a compound is set to have inhibition properties, the other question arises on how does the inhibitor act? In other words, what is the inhibition mechanism? Different methods were utilized to study this branch of research. Surface analysis or film analysis techniques are recently widely used. Up to the early seventies, the characterization of the protective films formed by corrosion inhibitors on iron surface was very cumbersome. Mostly, these techniques required the removal of the protective film by a variety of methods, prior to examining the film by electron

diffraction.² Radiochemical techniques were also used to confirm the presence of radioactive isotopes of carbon.³

Then, in 1978, the advantages of studying protective films directly by AES were illustrated by producing Auger depth profile studies of films formed on iron.^{2,4} Since the last decade, the Auger depth profile techniques have been used extensively to investigate surface films formed under different water and metal surface conditions.⁵⁻⁷

EXPERIMENTAL METHOD

In order to study the dependence of the inhibition characteristics of *N*-phosphono-methyl glycine (NPMG) on some variables such as the contacting media, contact time and the solution composition, solutions of 0.5 M NaClO₄ and model water (see Table 1) were used to differentiate between two media. Contact times of 4h, 24 h and 5 days were used to study the effect of time on film growth.

Addition of some cations, such as zinc in the form of ZnSO₄ or calcium in the form of CaSO₄ illustrated the synergistic effect of changing solution composition.

Weight-loss method

This method was used to optimize the concentration of NPMG needed for inhibition of carbon steel. It was also used to illustrate the synergistic effect of calcium and zinc cations. Throughout this method, only sodium perchlorate was used as a contact solution.

Carbon steel coupons were acid cleaned, degreased by acetone and washed with distilled water prior to being weighed to obtain the initial weight of the coupon. Duplicate coupons then were immersed in an 800 ml beaker containing 500 ml of 0.5 M NaClO₄ and different concentrations of NPMG with adjusted pH in the range of 7.0 ± 0.3. Contact time was about 24 h for all runs at room temperature. Rotating blades were used to keep species in the solution moving. At the end of the measurement, the coupons were cleaned, brushed, washed with HCl acid and placed in an ultrasonic vibrator to remove the corrosion products, then washed with distilled water and acetone, then allowed to dry prior to weighing again to get the final weight. The inhibitor efficiency (IE) was calculated from the following equation:

$$IE\% = \frac{W_0 - W_i}{W_0} \times 100$$

where W_0 = corrosion rate without inhibitor, and W_i = corrosion rate with inhibitor. The corrosion rate was measured in mm y⁻¹ according to ASTM standard D-2688.

Different concentration combinations of NPMG and Ca²⁺ or Zn²⁺ were used to investigate synergism. The gravimetric method was used to study and optimize the concentration of the inhibitor and cation blend.

Auger depth profile technique

Auger depth profiles were performed using a Perkin-Elmer SAM 545/A scanning Auger microprobe instrument. The ion gun and the analyser probe were mounted onto an ultra-high vacuum system which uses oil diffusion and turbo pumps. The base pressure of this system was always in the range of 1 × 10⁻⁹ Torr.

An argon ion gun was used for the sputtering of the films. Argon gas was introduced into the system by back-filling the chamber. During sputtering the argon gas pressure in the vacuum chamber was between 10⁻⁴ and 10⁻⁵ Torr. During sputtering, a derivative spectrum was recorded. By a computer program, the

TABLE 1. MODEL WATER COMPOSITION

Component	Concentration (g l ⁻¹)
NaHCO ₃	1.5
MgSO ₄ · 2H ₂ O	1.364
CaCl ₂ · 2H ₂ O	1.258
CaSO ₄ · 2H ₂ O	0.885

peak-to-peak height of the elements was determined and used as an intensity indicator. The peaks for each run were normalized and the resulting atomic percentage was then plotted vs sputtering time.

EXPERIMENTAL RESULTS AND DISCUSSION

Weight-loss tests

Different concentrations of NPMG were used in order to find the critical concentration level at which corrosion inhibition is achieved at best efficiency. A concentration of around 40 ppm of NPMG appeared to be most efficient and produced the lowest corrosion rate. Synergism with Zn cations reduced the corrosion rate of carbon steel and reduced the concentration of NPMG needed for optimum protection. A concentration ratio of 1:1 between zinc cations and NPMG was optimal. NPMG concentrations between 10 and 60 ppm tend to reduce the corrosion rate, while at higher concentration the efficiency decreases. The synergistic effect in both cases of Zn and Ca was best at concentration ratios of about 1:1.

These results indicate that protection or passivation of carbon steel is possible with the existence of some cations, such as zinc or calcium, dissolved in the contact solution. Zinc and calcium cations tend to form a complex compound with NPMG in the form of NPMG–Zn and NPMG–Ca. The presence of calcium cations in the solution leads to the formation of an NPMG–Ca complex which results in an increase in the adsorption of NPMG on the metal surface. Calcium ions are not directly responsible for passivation of carbon steel but are responsible for the formation of an insoluble NPMG–Ca complex on the metal surface. Zinc and calcium cations play different roles for the corrosion inhibition by forming weakly soluble complex compounds with NPMG. Because the deposition of the NPMG–Zn or NPMG–Ca complex depends upon the saturation index of the complex which is a function of the concentration of NPMG and zinc or calcium ions, thus variations of NPMG and Zn^{2+} or Ca^{2+} may lead to different films on the metal.

Auger depth profiles

The corrosion inhibition of NPMG in this case was evaluated in two solutions, $NaClO_4$ and a model water, and for different contacting times. The presence of dissolved ions was also studied. AES profiles were performed to obtain information on the composition of the protective films.

Iron and oxygen profiles

Figure 1 shows a profile of the major elements present in the base metal of carbon steel. The primary use of the iron and oxygen in the Auger depth profiles was the determination of the film thickness. All of the iron and oxygen depth profiles were very similar in shape but differed in intensities. The ratio of oxygen to iron changes drastically, as the base metal is approached oxygen decreases and iron increases to a constant value.

In Figs 2–7, the shape of the iron and oxygen depth profiles show atomic ratios through the oxide film that might indicate the formation of heterogeneous oxides such as $\gamma\text{-Fe}_2\text{O}_3$ and/or Fe_3O_4 .

The initial iron signal intensity in the depth profiles ranged between 8 and 20% on the atomic percentage scale. As the protective films were penetrated by argon ions, the iron profile showed a gradual increase until it became the major component (about 80%), at the interface and into the bulk metal. The gradual increase in iron

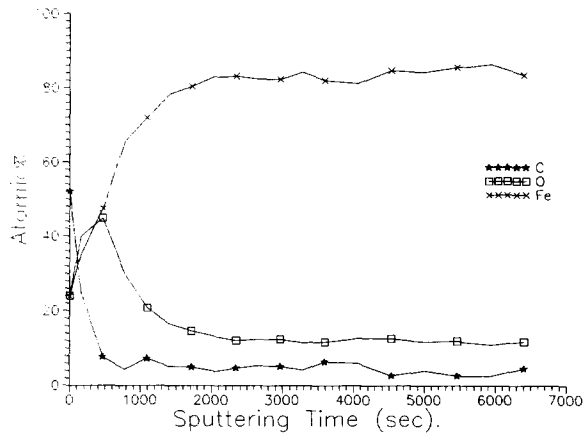


FIG. 1. Auger depth profile of untreated carbon steel coupon.

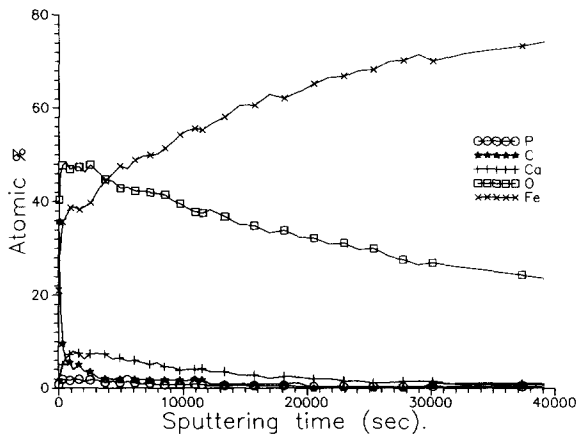


FIG. 2. Auger depth profile of untreated carbon steel coupon in model water solution containing 40 ppm of NPMG. Contact time is 5 h.

signal intensity might be as a result of a gradual increase in iron concentration and/or preferential sputtering. Oxygen is a major component throughout the layer. The oxygen signal was high at the surface and then gradually decreased to a constant value at the interface.

Carbon profiles

The presence of carbon on the outer surface of the layer was attributed to impurities and contamination because the carbon signal was of an elemental type. The carbon, bonded signal, was present in all layers with initial intensities of 10–50% on the atomic scale (Figs 2–7). As the layer was penetrated, the carbon signal reduced to 1–4 at %. Through the layer the carbon signal detected was a bonded type which is attributed to the presence of calcium carbonate or other carbonate salts. The

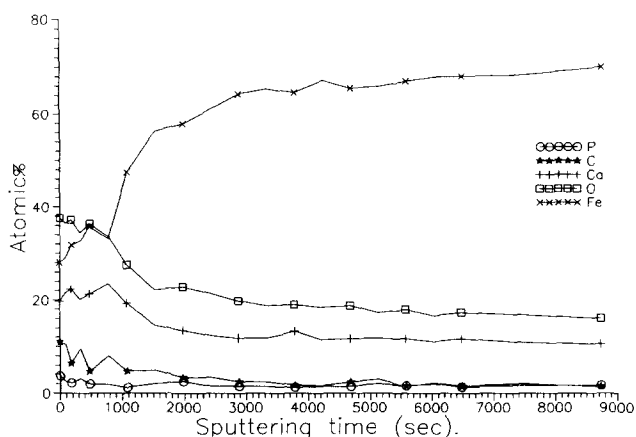


Fig. 3. Auger depth profile of untreated carbon steel coupon in model water solution containing 40 ppm NPMG and contact time of 5 days.

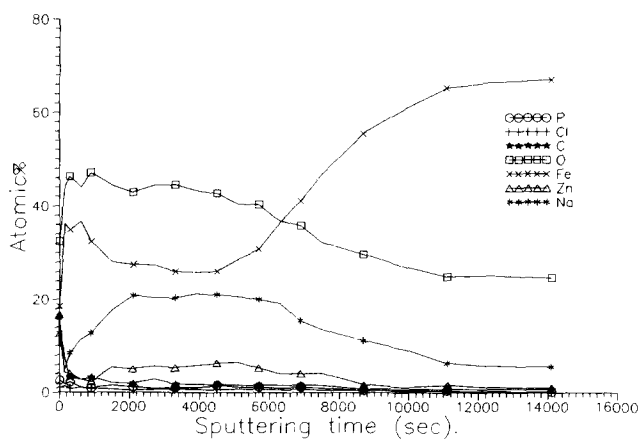


Fig. 4. Auger depth profile of untreated carbon steel coupon in NaClO_4 solution containing 20 ppm of NPMG and 20 ppm of Zn^{2+} and contact time of 5 h.

behaviour of the carbon signal changed from quite intense at the interface and then rapidly dropped to a trace value throughout the film.

Calcium profiles

Calcium intensities were monitored only in samples where model water was used as contact solution. Figures 2, 3 and 6 show that the initial calcium intensities on the outer film surface ranged from 0.5 to 20 on the atomic scale. The lower value was in the case of 5-h contact time (Fig. 2), while the higher value was for the 5-day period (Fig. 3). The calcium signal persisted into the film until the metal–film interface was approached. By comparison, the calcium signal shows similar behaviour to that of the carbon signal which suggests an association between the two in forming CaCO_3 or any other compounds.

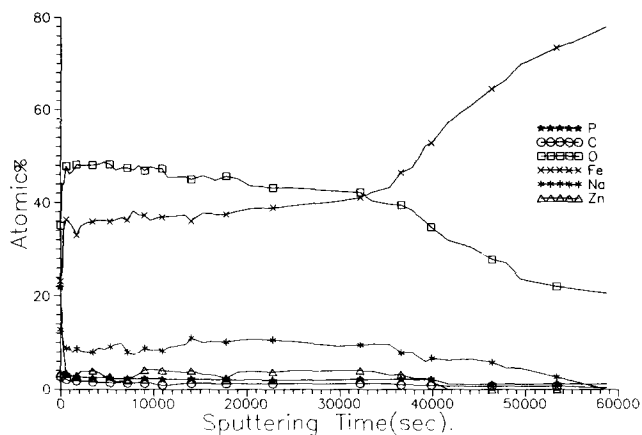


Fig. 5. Auger depth profile of untreated carbon steel coupon in NaClO_4 solution containing 20 ppm NPMG and 20 ppm Zn^{2+} and contact time of 24 h.

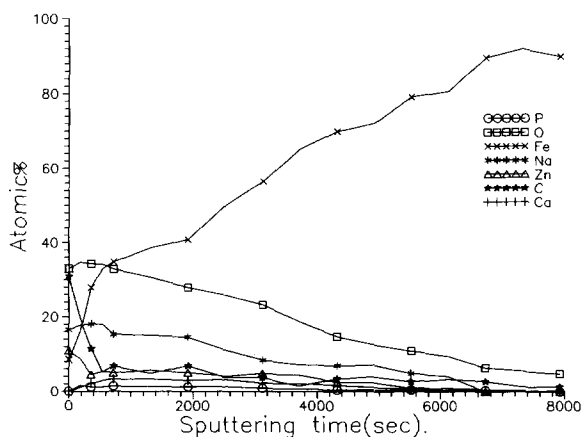


Fig. 6. Auger depth profile of untreated carbon steel coupons in model water solution containing 20 ppm NPMG and 20 ppm Zn^{2+} and contact time of 5 h.

Zinc profiles

In cases where zinc was added to the contact solution, the zinc intensities were significant throughout the outer film (Figs 4–7).

The zinc signal decreased into the film but persisted at low value until the interface. The presence of zinc at high intensities on the outer film could be an indication of the formation of $\text{Zn}(\text{OH})_2$, ZnCO_3 or zinc phosphonates. When zinc was added to model water, a decrease in the calcium signal was noticed due to gradual replacement of calcium by zinc in the film by ion exchange.

Sodium profiles

Sodium signals were very difficult to distinguish from the zinc signal due to overlapping. In Fig. 7, sodium intensity was present throughout the film but

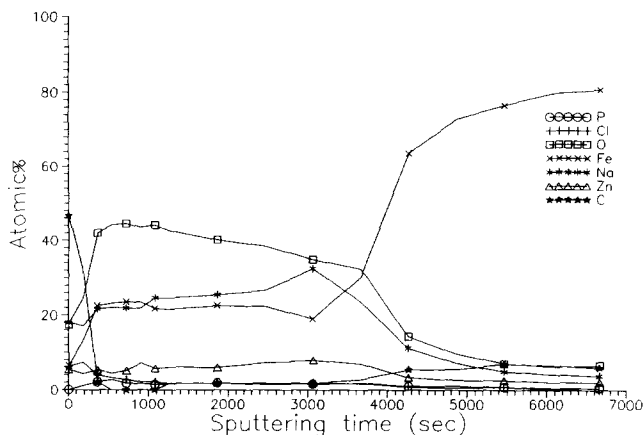


Fig. 7. Auger depth profile of untreated carbon steel coupons in NaClO_4 solution containing 20 ppm Zn^{2+} and contact time of 5 h.

diminished at the interface. Since sodium is not of importance for the structure of the film, it could be regarded a minor element.

Contact-time effect on film

Variations of contact time provided some useful information on the growth rate of the film. By comparing Figs 4 and 5, the increase of contact time from 5 to 24 h increased the film thickness considerably. In time zinc penetrated through the film and persisted until reaching the interface. In other comparisons, the intensity of iron in the film increased by time which is an indication of the formation of more corrosion products. Figure 3 shows that the film formation is a self-limiting process. This process is hindered by an optimum thickness of the film.

Solution composition effect on film

The change in solution composition could demonstrate the influence of chemical parameters on the formation and composition of the film. By comparing Figs 6 and 7, the model water solution produced thinner film but the interface between the metal and the film was sharper in the case of NaClO_4 . Zinc and calcium diffused into the outer film and form complex products that further stabilize the film.

CONCLUSION

Corrosion inhibitors such as NPMG form more complex corrosion inhibiting films under calcium containing water than in NaClO_4 solutions. Dissolved oxygen was mainly responsible for passivity in inhibited neutral solutions by virtue of its heterogeneous reaction with iron to form a film of oxides which hinders the formation of further corrosion products. The intense oxygen and iron signals throughout the layer confirms the formation of iron oxides as the primary mechanism of corrosion inhibition of screening inhibitors. Calcium and zinc cations form a passivating complex with NPMG which protects the metal surface. Variations of NPMG and Ca^{2+} or Zn^{2+} cause the formation of different films on the metal surface. Zn^{2+} cations addition produced better inhibition efficiency due to a more insoluble

complex. Zn and Ca complexes also play a role in plugging the pores of the protecting film hence further isolating the metal.

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