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Application of self-assembly for replacing chromate in corrosion protection of zinc

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Abstract Due to the toxic and carcinogenic properties of hexavalent chromium ion, the corrosion protection with chromating technique needs replacement. Several environmentally friendly alternative metal pretreatments have already been proposed. One of these methods is the application of self-assembling molecules to form mono- or multilayers on the metal surfaces. These layers can prevent metal dissolution due to their dense and stable structure. The objective of our studies was to protect zinc surface against corrosion, with a thin phosphonate layer. Aqueous solutions of diphosphonic acid with different alkyl chain lengths were applied with different treatment times. The layer formation, stability, and corrosion protection of these films were monitored by electrochemical impedance spectroscopy and the effect of 1,5-diphosphono-pentane (DPP) on zinc was studied by polarization curves. The wetting properties were determined by static contact angle measurement. 1,5-Diphosphono-pentane forms a thin layer, with a pronounced protective ability in neutral aqueous solutions. The application of self-assembling molecules can be a promising method to replace the chromating technique on zinc surface.

Keywords Zinc · Diphosphonic acid · Protective layer · Corrosion

Introduction

One of the most important applications of zinc coatings is the cathodic protection of steel structures owing to the high corrosion resistance of zinc in atmospheric environment.

Nearly half of the zinc production is used for corrosion protection purpose. The oldest and the most commonly used technique even nowadays is the hot-dip galvanizing introduced in 1836 in France. To protect zinc coatings, chromate conversion layers are deposited from solutions containing either hexavalent or trivalent cations. Various degrees of corrosion protection are possible, which are dependent upon the composition of the chromate solutions and thickness of the layers [1]. Protection is due to the corrosion-inhibiting effect of hexavalent chromium contained in the film and the physical barrier presented by the film itself. Recent studies have shown that aqueous solutions of Cr^{6+} introduced directly into the organism of animals have caused an increased incidence of lung cancer [2]. The high toxicity of chromate leads to an increasing interest in using nontoxic alternatives.

Some authors have proposed soluble salts of rare earth metals, such as cerium, nickel, or bismuth to protect zinc and zinc coatings [3–6]. Molybdates [7], phosphonates, silicates, and some organic compounds have also been proposed. Other authors deal with the corrosion prevention involving chelation by organic substances which could form stable and hardly soluble organometallic compounds [8]. Long-chain aliphatic acids, such as phosphonic [9, 10], sulfonic, and hydroxamic acids [11], have been explored for their ability to produce self-assembling and induced assemblies on a variety of substrates. Some long-chain phosphonic acids such as octadecylphosphonic acid and hydroxydodecanphosphonic acid have been found to be effective for corrosion protection of zinc and aluminum [12, 13].

The aim of this paper is to investigate the protective effect of α,ω -diphosphono-alkane (DPA) [$\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2$, $n=5, 7, 8$, and 12] derivatives on the corrosion behavior of zinc. The surface treatment was achieved by immersion in DPA solutions (pH=7) for different immersion times at room temperature. The effect of formed DPA layers on zinc corrosion was studied in Na_2SO_4 (pH=7) supporting electrolyte using electrochemical techniques such as electrochemical impedance spectroscopy and polarization curves. The protective layer formation was monitored in

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situ in the treating DPA solution with electrochemical impedance measurements. Static contact angle measurements were carried out to determine the wetting properties of the treated zinc surface. The treated samples in some cases were characterized morphologically by scanning electron microscopy (SEM) and they were analyzed chemically by energy disperse spectrometry (EDS) measurements.

Materials and methods

The series of α,ω -diphosphono-alkane [$\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2$, $n=5, 7, 8$, and 12] derivatives was synthesized in our laboratory using the Michaelis–Arbusov method [14]. The purity of the diphosphonic acids were verified by melting point, by element analysis, and by thin layer chromatography (Kieselgel, gips-free, eluent: benzene-methanol-acetic acid—5/1/3—developer: rhodanide solution). The synthesized substances were double recrystallized. Table 1 summarizes the melting points measured and the literature data of diphosphonic acids.

The treatment of zinc was achieved by dipping into DPA solutions for variable immersion times. After that, the samples were washed with distilled water and dried in argon flow to remove the excess of phosphonates from the surface. The electrodes were immersed into a neutral 10^{-1} M Na_2SO_4 electrolyte for 24 h to study the corrosion properties of the formed layer. The electrolyte was prepared in distilled water from Na_2SO_4 (Fluka). The working electrode used for experiments was zinc with 99.99% (Goodfellow) embedded into epoxy resin, with a surface area of 0.785 cm^2 (some pre-experiments were carried out previously with an industrial zinc with 97% purity). Wet grinding on silicon carbide abrasive papers (220–1,200 grit) was used for surface preparation to ensure a reproducible and known surface condition. The electrodes were rinsed with distilled water, ultrasonicated for 10 min in distilled water, and dried in argon gas flow.

Electrochemical impedance measurements were carried out using Zahner Im5d Impedance Spectrum Analyzer. A standard three-electrode cell was used for the measurements. The counter electrode was a half-cylindrical platinum net. The electrode potential was measured against a saturated calomel electrode (SCE). The impedance spectra were recorded in the frequency range between 100 kHz and 10 mHz. A sinusoidal wave with 10 mV amplitude was used to perturb the system. The evaluation of the imped-

Table 1 Melting points of diphosphonic acids measured and the literature data

Substance	Melting point (°C)	
	Measured	Literature data [14]
1,5-Diphosphono-pentane	155–156.5	155
1,7-Diphosphono-heptane	145–146	153.5–155
1,8-Diphosphono-octane	180–182	187–189
1,12-Diphosphono-dodecane	183.3–184.6	–

ance spectra was made using the EQUIVCRT software written by Boukamp [15]. Polarization curves were obtained with the polarization rate of 10 mV min^{-1} using IR compensation during the measurements. Cathodic and anodic polarization curves were obtained separately starting from E_{corr} after a 30-min preliminary hold time.

The samples in some cases were characterized morphologically by Hitachi S570 scanning electron microscope and they were analyzed chemically by Röntec EDR 288 energy disperse spectrometer.

To determine the wettability of the phosphonate-treated samples, static contact angles were determined with drop shape analysis method. Zinc electrodes (99.99%) were first mechanically polished with abrasive papers (220–1,200 grit), rinsed with distilled water, ultrasonicated for 10 min in distilled water, and finally dried in argon gas flow. The cleaned samples were immersed into a neutral 10^{-3} M 1,5-diphosphono-pentane (DPP) solutions for different treatment times (1, 2, 4, 8, 24, and 48 h). Surface tension of solutions in various concentrations has been determined using Pt ring, with known dimensions to characterize the aggregation behavior of 1,5-diphosphono-pentane. Usually, the ring is used to determine the absolute value of the surface tension of a liquid. The measurements were carried out using DST9005 Dynamic Surface Tensiometer with a withdrawal speed of 5 mm/min.

Results and discussions





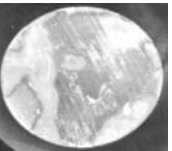
Zinc surface treatment with alkyl-diphosphonic acids

The surface treatments of zinc electrodes were performed by simple immersion into different 10^{-3} M (pH=7) α,ω -diphosphono-alkane (DPA) solutions for the same treatment time, 24 h. Table 2 contains the images and visual observations of polished and DPA-treated samples.

In the case of 1,12-diphosphono-dodecane (DPD) and 1,8-diphosphono-octane (DPO), corrosion was taking place during the treatment. Formation of protective layers could not be observed under these conditions. Protective layer formation after long time immersion was obtained using the molecules with shorter chain length. Thick precipitated layer formation was observed using 1,7-diphosphono-heptane (DPH). No visible changes can be seen on the electrode surface after treatment with 1,5-diphosphono-pentane. The morphology of zinc treated with 1,5-diphosphono-pentane (Fig. 1b) and 1,7-diphosphono-heptane has also been investigated by SEM.

In the case of sample treated with DPP, the EDS measurement (Fig. 1e) shows a small amount phosphorous on the zinc surface, which suggests that a thin layer has been formed. The morphology of zinc treated with DPH is shown in Fig. 1c and d. As can be seen, thick precipitated layer is evident and is distributed on all surfaces (the cracks in the film structure could be the effect of the vacuum applied during SEM measurements—see Fig. 1d). The EDS analysis (Fig. 1f) showed the presence of phosphorous and oxygen on the surface layer. It is probably a mixed

Table 2 Images of zinc samples treated with diphosphonic acids in comparison with polished surface

Treatment with DPA	Surface of electrodes	Visual observations
Polished surface (1,200-grid emery paper)		—
1,5-Diphosphono- Pentane (DPP)		Thin layer—no visible changes
1,7-Diphosphono- heptane (DPH)		Thick homogeneous, precipitated layer
1,8-Diphosphono- octane (DPO)		Corrosion products
1,12-Diphosphono- dodecane (DPD)		Corrosion products

layer consisting of zinc oxide/hydroxide and phosphonate. Results from electrochemical pre-experiments underlined that this layer has a corrosion protective effect only for a short time.

From the pre-experiments, 1,5-diphosphono-pentane has proved to be the best layer-forming compound. The 1,5-diphosphono-pentane layer formation properties and the corrosion protective effect of the formed layer have been studied in details.

Aggregation behavior of alkyl-diphosphonic acids in solution phase

DPA molecules consist of two polar parts (phosphono groups) and an apolar part as a spacer, which is an alkyl chain with different length. At high diphosphonic acid concentrations, gel-type aggregation of molecules was observed in the solution. To characterize the aggregation behavior of diphosphonates, surface tension of solutions as a function of concentration was determined. Solutions of 1,5-diphosphono-pentane with different concentrations

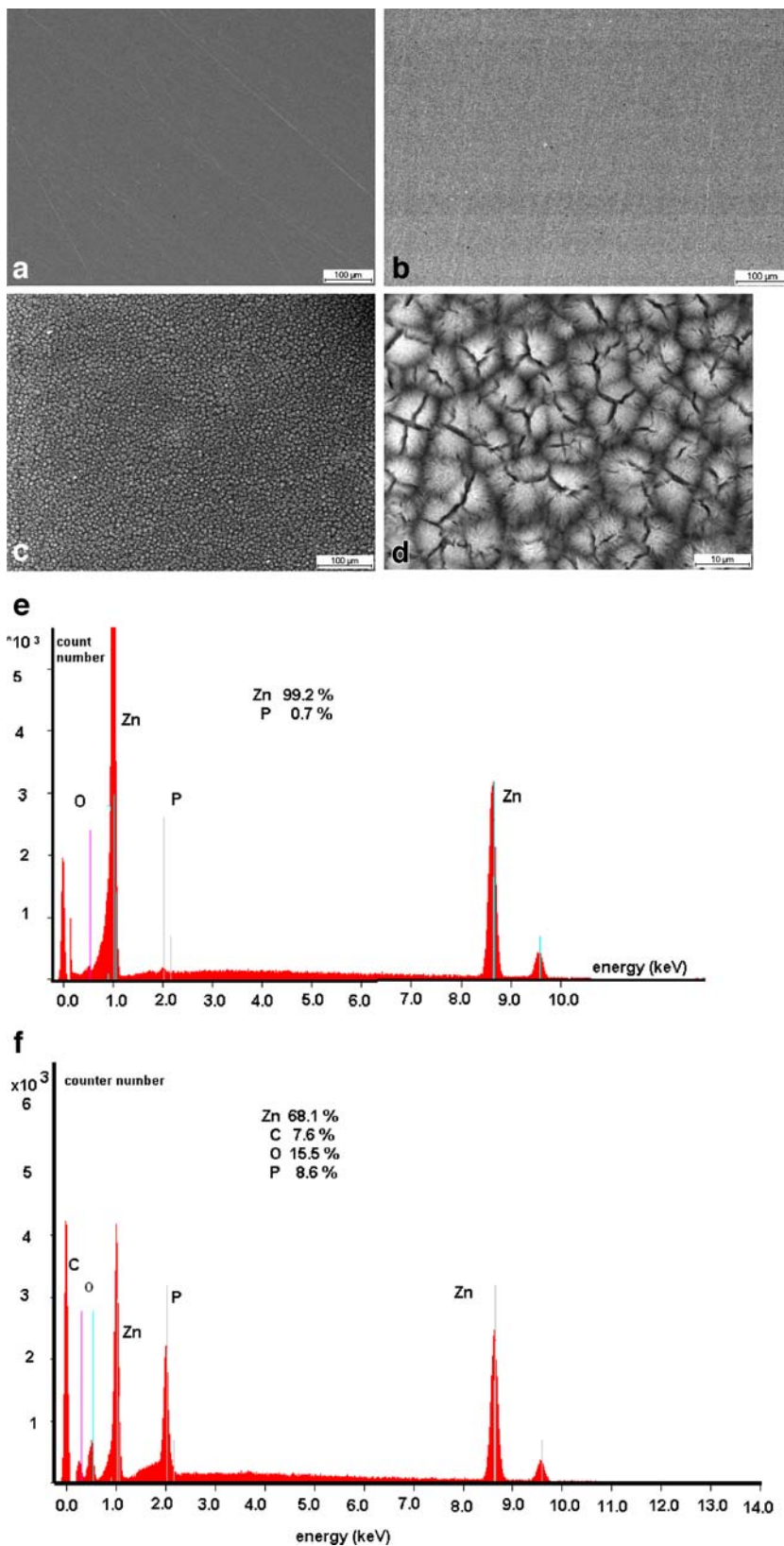
were prepared and the surface tension was measured with DST9005 Dynamic Surface Tensiometer.

Figure 2a shows the change of surface tension of 1,5-diphosphono-pentane solution by the concentration. The figure shows similar behavior as classical amphiphilic surfactants (Fig. 2b). At wide concentration range ($c < 10^{-2}$ M), only slight change in surface tension is detected. The surface tension of solutions in this concentration range is high ($\gamma = 70\text{--}72$ mN/m), which is actually the same as the literature value of pure water ($\gamma = 72.8$ mN/m). At higher concentrations, the surface tension is decreased due to the fact that the molecules arrange into micelles (aggregates). The so-called critical micelle concentration was not reached up to 1 M concentration. Thus, adsorption as individual molecules to the metal surface at 10^{-3} M concentration can be supposed.

The effect of 1,5-diphosphono-pentane on zinc

The effect of DPP has been investigated based on polarization curves. The polarization curves of zinc in 10^{-1} M Na_2SO_4 (pH=7) and in 10^{-3} M (pH=7) 1,5-

Fig. 1 SEM image of **a** zinc surface polished with emery paper of 4,000 grit, **b** zinc surface treated with 1,5-diphosphono-pentane, **c,d** zinc surface treated with 1,7-diphosphono-heptane (different magnification), **e** the EDS spectrum of the 1,5-diphosphono-pentane and **f** 1,7-diphosphono-heptane treated sample



diphosphono-pentane (DPP) solution can be seen in Fig. 3. IR compensation was applied during the measurements. Table 3 shows the values of corrosion potential (E_{corr}) and

corrosion current densities (i_{corr}), calculated by using Tafel extrapolation method, of the corresponding curves from Fig. 3.

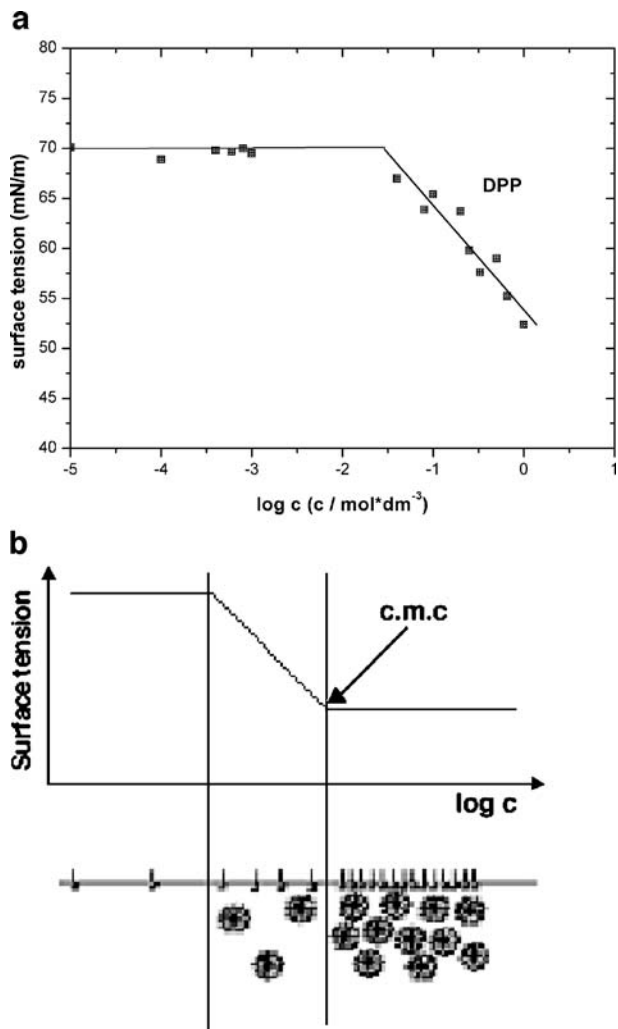


Fig. 2 Concentration dependence of surface tension of 1,5-diphosphono-pentane (DPP) measured by tensiometry (a), theoretical graph of surface tension vs log of the surfactant concentration of amphiphiles (b)

Zinc dissolution mechanism in neutral solutions occurs with the formation of divalent zinc ions [16–18]. The zinc is covered in neutral salt solutions with a porous oxide/hydroxide layer, which is formed during the short preliminary hold time at the free corrosion potential [16–19]. The zinc dissolution occurs mainly through the chemical dissolution of ZnO but it is stimulating by the SO_4^{2-} ions as well. The SO_4^{2-} ions adsorb on the metal surface and have an acceleration influence on the active dissolution, while the oxide formation is tending to inhibit the dissolution process [17].

The major cathodic reaction in the pH range of 4–11 is the reduction of dissolved oxygen [18–20]. The corrosion of zinc in these solutions is controlled by diffusion of oxygen to the metal surface [16, 17]. It is mentioned in the literature that in the vicinity of the corrosion potential, the oxygen reduction occurs through a more or less porous

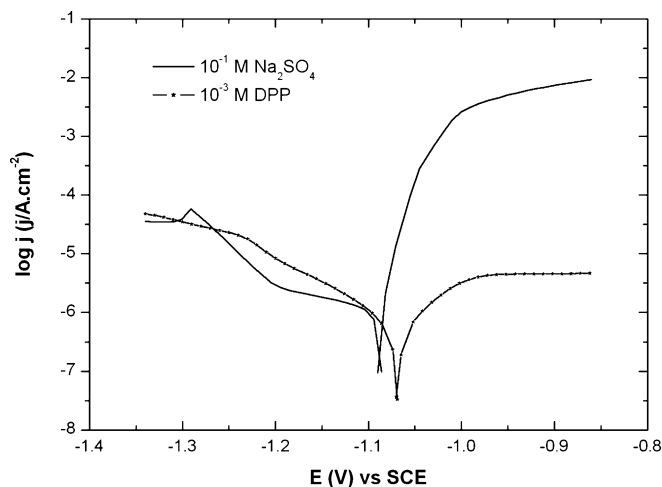


Fig. 3 Polarization curves of untreated zinc in neutral solution of 10^{-1} M Na_2SO_4 and zinc in neutral 10^{-3} M 1,5-diphosphono-pentane (DPP) solution

layer. Around -1.3 V a reduction peak appears which is typical to the ZnO film reduction [19].

In the case of 1,5-diphosphono-pentane, the corrosion potential shifts to the anodic direction (from -1.088 to -1.062 V). The current shows a decrease with three orders of magnitude in the anodic region. Metal dissolution is blocked indicating that the surface is protected with the formed diphosphonate layer. The formed layers decrease the oxygen reduction rate at low cathodic overpotentials. The typical peak observed in the cathodic range of the polarization curve in the case of the untreated sample could not be observed which might be the effect of the formed phosphonate layer. In the following, the effect of phosphonate adsorption on the polarization curves of zinc electrode has been investigated. For comparison, an industrial chromated sample was used. Figure 4 shows the polarization curves of untreated, chromated, and DPP-treated zinc (in neutral 10^{-3} M DPP solution—different adsorption times, 1 and 4 h).

Table 4 summarizes the corrosion potentials (E_{corr}) and the corrosion current densities (i_{corr}) calculated from Tafel extrapolation of the polarization curves from Fig. 4.

The corrosion potential shifts to the anodic direction in the case of treated samples. A significant decrease of current was obtained in the anodic region. Metal dissolution is blocked indicating that the surface is protected with the formed diphosphonate layer. At a critical potential

Table 3 Values of corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), and Tafel slopes calculated from the polarization curves from Fig. 3

Solution	E_{corr} (mV)	i_{corr} ($\mu A cm^{-2}$)	b_a (mV/decade)	b_c (mV/decade)
10^{-1} M Na_2SO_4	-1088	1.027	16	-263
10^{-3} M DPP	-1062	0.544	65	-107

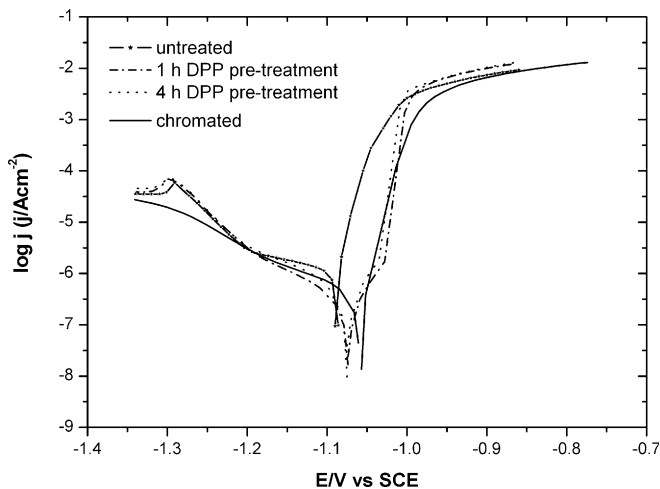


Fig. 4 Polarization curves of chromated zinc, zinc without and with 1,5-diphosphono-pentane pretreatment (1 and 4 h) in aerated neutral 10^{-1} M Na_2SO_4 solution

value, the current increase can be observed in the case of DPP-treated samples, which is due to the breakthrough of the protective phosphonate layer. The treatment time does not have a significant effect on the anodic behavior of the treated samples. Comparing the cathodic currents at lower polarization potential decrease of current can be observed which is the effect of the formed phosphonate layer. At more negative potential values, the current densities are comparable with the values measured in the case of untreated zinc.

The formed layer by chromate has an effect on both branches of the polarization curves. The anodic current density decreases blocking the metal dissolution process. In the cathodic branch, the peak present in the case of untreated sample around -1.3 V does not appear indicating that the formed chromate layer has a blocking effect on the zinc oxide reduction.

Surface treatment of zinc by 1,5-diphosphono-pentane

The layer formation was monitored with electrochemical impedance measurements in situ in the treating DPP solution without supporting electrolyte. Immersing the zinc electrode into the neutral 10^{-3} M DPP solution for 1 day, electrochemical impedance spectra were recorded step by step. Neutral solutions were used for surface treatment because it is known from the literature that the phosphonic

Table 4 Values of corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) from Tafel extrapolation of the polarization curves from Fig. 4

Solution	E_{corr} (mV vs SCE)	i_{corr} ($\mu\text{A cm}^{-2}$)
10^{-1} M Na_2SO_4	-1088	1.027
10^{-3} M DPP (1 h)	-1071	0.165
10^{-3} M DPP (4 h)	-1072	0.088
Chromating bath	-1059	0.128

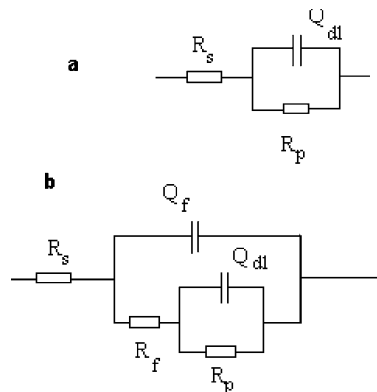


Fig. 5 Equivalent circuits applied in fitting: R_s —solution resistance, Q_{dl} —constant phase element of double layer, R_p —charge transfer resistance, R_f —layer resistance, and Q_f —constant phase element of surface layer

acids, in general, have inhibition effect on different metals in neutral and slightly alkaline solution [21]. The measured impedance spectra were evaluated by fitting to an electrical equivalent circuit (Fig. 5), and the change of calculated polarization resistance values in time are plotted in Fig. 6.

At the beginning, the change of polarization resistance is increasing continuously in time, that after 5 h, it reaches a maximum value (~ 58 $\text{k}\Omega \text{ cm}^{-2}$); there was no further significant change in R_p (Fig. 6). From this result, we can suggest that the layer formation is completed after 5 h of immersion.

Corrosion protective effect of phosphonate layers

The corrosion behavior of treated zinc was investigated by electrochemical impedance measurements in a neutral solution of 10^{-1} M Na_2SO_4 . The surface treatment of zinc was achieved by dipping the electrodes into a neutral 10^{-3} M DPP solution for different immersion times at room

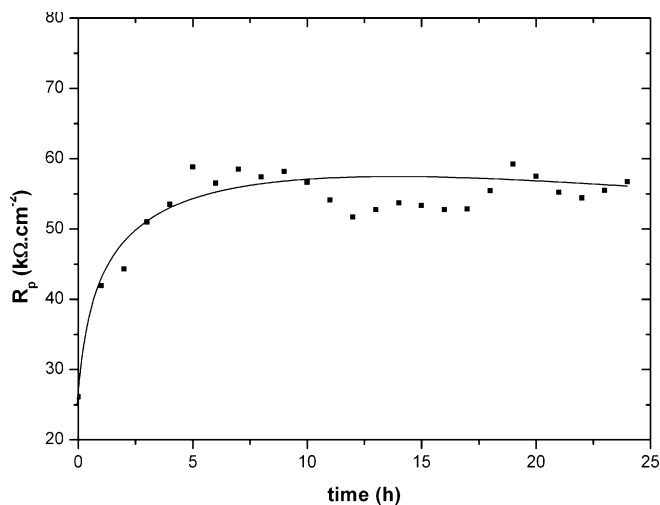


Fig. 6 Change of polarization resistance of zinc in neutral 10^{-3} M 1,5-diphosphono-pentane solution during 1 day of immersion

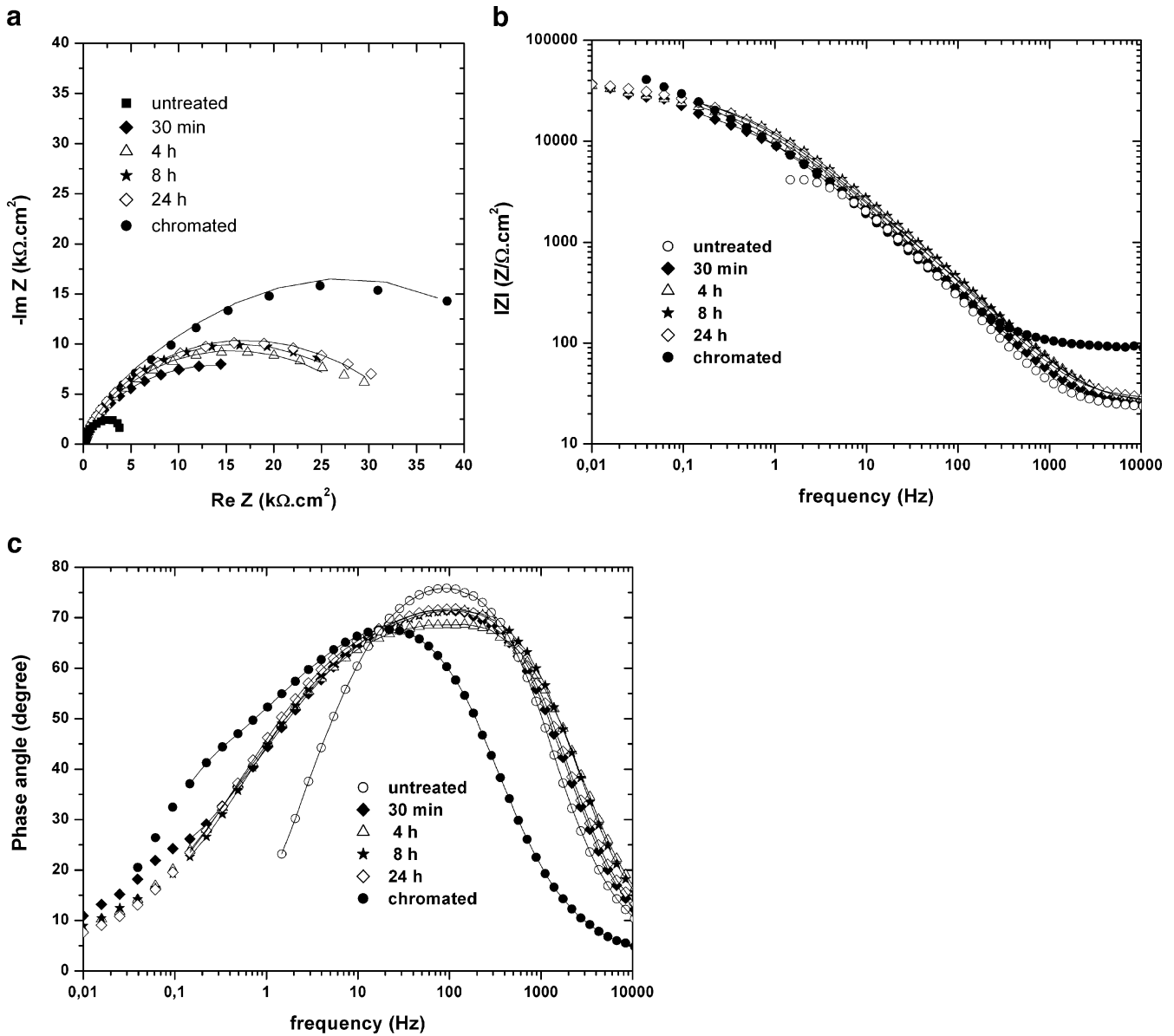


Fig. 7 Nyquist (a) and Bode (b,c) plots of the untreated, treated (surface treatment was made in neutral 10^{-3} M DPP solution for various treatment times—30 min, 4, 8, 24 h), and the chromated zinc measured after 30 min in neutral 10^{-1} M Na_2SO_4 aqueous solution

temperatures. The treated samples were washed with distilled water to remove the excess of DPP molecules from the surface, and dried in argon flow. For comparison, an industrial chromated sample was used. Surface treatment with DPP modified substantially the metal behavior in the corrosive medium. Figure 7 shows the Nyquist (a) and Bode plots (b, c) of the untreated, phosphonate-treated, and the chromated zinc measured after 30 min in a neutral 10^{-1} M Na_2SO_4 solution. The fitted curves are plotted with solid lines in all cases. The experimental spectra were evaluated using the equivalent electrical circuits in Fig. 5, where the R_s is the solution resistance, R_f (layer resistance) and Q_f (constant phase element of surface layer) are related to the surface layer, R_p is the charge transfer resistance of metal dissolution, and Q_{dl} is the constant phase element of double layer.

The pretreated samples were analyzed on the basis of equivalent circuit shown in Fig. 5b, while the untreated sample was analyzed with the equivalent electrical circuit

Table 5 The polarization resistance values, the calculated capacitance values, and the protection efficiencies of the untreated, treated, and chromated zinc (after 30 min in neutral 10^{-1} M Na_2SO_4)

Surface treatment	R_p ($\text{k}\Omega \cdot \text{cm}^2$)	C ($\text{F} \cdot \text{cm}^{-2}$)	η (%)
Untreated	5	5.14×10^{-6}	—
30 min DPP	35	3.68×10^{-6}	85
4 h DPP	36	2.81×10^{-6}	87
8 h DPP	41	2.91×10^{-6}	87
24 h DPP	40	3.24×10^{-6}	87
Chromated	51	4.25×10^{-6}	90

Table 6 The polarization resistance values and calculated values of protection efficiencies (after 4 and 24 h in neutral 10^{-1} M Na_2SO_4) of the untreated and treated zinc

Surface treatment time	Immersion in 10^{-1} M Na_2SO_4			
	After 4 h		After 24 h	
	Rp ($\text{k}\Omega \text{ cm}^2$)	η (%)	Rp ($\text{k}\Omega \text{ cm}^2$)	η (%)
Untreated	8	–	15	–
30 min DPP	30	75	30	50
4 h DPP	40	81	45	67
8 h DPP	40	81	36	58
24 h DPP	40	81	38	60

shown in Fig. 5a. The first model is generally used in the case where the surface layer properties do not appear in the impedance spectra. The second model is used for the film-covered surface. The given equivalent electrical circuits have already been used for conversion layers [22], for filmed electrodes [16], and metals covered with organic-phosphonate film [23].

Table 5 shows the polarization resistance, capacitance values calculated from the impedance measurements at 1,000 Hz frequency, and calculated values of protection efficiency.

A significant corrosion protection effect was found to be independent of the applied surface treatment times ($\eta=85$ – 87%). The surface treatment time influences the corrosion protection effect only in small compass. A good protective layer formation has been reached after a short time treatment, and the DPP molecules adsorb fast on the zinc surface. The protective effect of classical chromated sample ($\eta=90\%$) has been approached but has not been reached. The decrease of the capacitance values shows that the phosphonate is adsorbed on the zinc surface. These results are in good agreement with the increase of the Rp values.

The long-term corrosion behavior of the protective phosphonate layers has also been investigated. The polarization resistance of the untreated zinc is increasing in time, which is due to the blocking effect of the formed corrosion products on metal surface. Comparing the polarization resistance values (Table 5) to the long time treatment polarization resistance values (Table 6), a slight decrease can be observed in a neutral 10^{-1} M Na_2SO_4 solution.

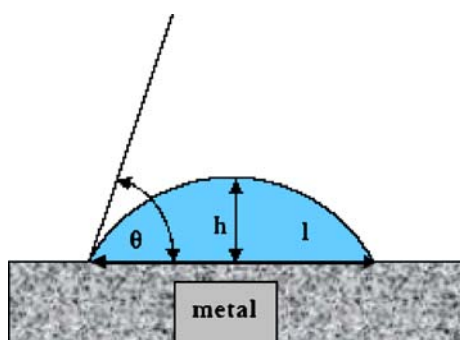


Fig. 8 Static contact angle measurement

Table 7 The static contact angle values of untreated and DPP-treated samples

Time (h)	θ (degree)
0	59
1	60
2	42
4	44
8	50
24	55
48	64

No visible corrosion product could be observed on the surface even after 24 h of immersion in corrosive solution. A long-term corrosion protection could be achieved with DPP surface treatment.

Wetting properties of phosphonate layers

Wetting properties of DPP-treated zinc surface have been studied with sessile drop experiments. Contact angle (CA) provides useful information about the advancement of adsorption process. Some authors have investigated the wetting properties of zinc [24]. It has been found that among the native corrosion products (with different chemical composition formed on zinc surface), the most hydrophobic is the ZnO layer ($\text{CA}=88^\circ$). The measurement route was the following: first $10 \mu\text{l}$ Milli-Q water drops has been placed on the untreated (mechanically polished) and DPP-modified zinc surface. After the spreading on the surface, drop images were captured by digital camera and the CAs were determined from drop size parameters. Figure 8 shows the contact angle (θ) for a drop of water placed on a metal substrate.

Supposed for the drop shape an ideal segment of a circle static contact angles were calculated according to the following equation:

$$\theta = \arcsin \frac{hl}{\frac{l^2}{4} + h^2},$$

where l is the length of drop base and h is the height of drop.

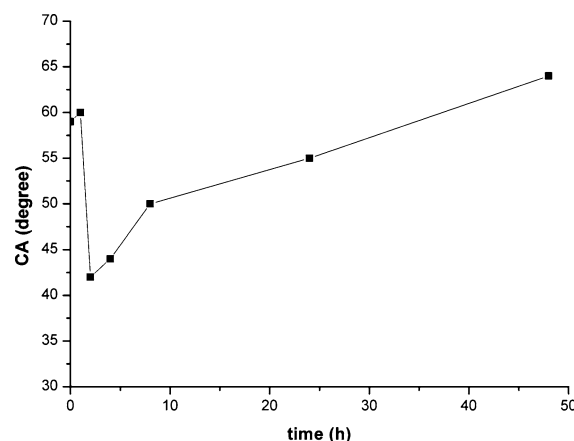


Fig. 9 The change of static contact angle by the treatment time

Table 7 summarizes the calculated static (advancing) contact angle values (given with an error of $\pm 3^\circ$) of untreated and 1,5-diphosphono-pentane-covered zinc.

Wettability of the modified zinc changed compared to the native zinc after 2 h DPP treatment (decrease of contact angle can be observed—Fig. 9) which is obviously an effect of phosphonate adsorption. The contact angle value increases with long time treatment. This effect is based upon the change of zinc surface due to the continuous oxide layer formation.

Conclusions

Surface treatment of zinc with aqueous solutions of alkyl-diphosphonic acid derivatives [$\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2$, $n = 5, 7, 8$, and 12] has been investigated to protect metal against corrosion. Protective layer formation is taking place using the molecules with shorter chain length ($n=5$ and 7). Corrosion of zinc was observed during surface treatment in aqueous solutions of 1,8-diphosphono-octane and 1,12-diphosphono-dodecane.

Thick precipitated layer was formed using 1,7-diphosphono-heptane, which has only slight protection against zinc corrosion. Thin layer formation could be accomplished by surface treatment with 1,5-diphosphono-pentane solution, with a pronounced protective ability in neutral 10^{-1} M Na_2SO_4 solution. The contact angles of the samples have been compared before and after treatment. Based on the experimental data, it can be concluded that 1,5-diphosphono-pentane interacts with the metal surface. The DPP showed better protective effect compared to the longer chain-length molecules. This may be due to a structural effect and kinetic of adsorption processes.

Surface treatment with 1,5-diphosphono-pentane solution could be applied to replace the chromating process on zinc and galvanized steel.

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