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Potentiostatic and AFM Morphological Studies of Zn Electrodeposition in the Presence of Surfactants

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Zinc electrodeposition onto a steel substrate in the presence of surfactants with different charged head groups, namely, anionic sodium dodecylsulfate (SDS), cationic dodecyltrimethylammonium bromide (CTAB), and nonionic octylphenolpoly(ethyleneglycolether)_n, n = 10 (Triton X-100), was studied by both chronoamperometric and atomic force microscopy (AFM) techniques. AFM analysis shows that Zn electrodeposition, in the absence of surfactants, begins in the underpotential deposited (UPD) region with the formation of different-sized circular aggregates with a random distribution, which indicates that progressive nucleation takes place. In the presence of SDS, CTAB, and Triton X-100 no change of the electrodeposit morphology is observed as a function of the surfactant presence. The Zn UPD deposition region, where the hydrogen evolution that goes together with the zinc deposition, the analysis of the current–time transients indicates that the Zn electrodeposition occurs by instantaneous nucleation and three-dimensional growth controlled by diffusion in the surfactant-free solution and in the presence of SDS. When the CTAB and Triton X-100 were added to the bath, change from instantaneous to progressive nucleation arises as a consequence of the simultaneous adsorption of the surfactant that inhibits the nucleation sites. The kinetic parameters values obtained from the Heerman and Tarallo model are in accordance with the dimensionless analysis of the transients. AFM confirms the effect of surfactants on the zinc bulk deposition.

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Surfactants are commonly used in the zinc electrodeposition to control the metallic crystal shape and size in order to produce smooth and bright deposits.¹⁻⁴ A variety of studies on zinc electrodeposition onto different substrates, in the presence of a range of surfactants, can be found in the literature.⁴⁻⁶

In order to analyze the role played by the surfactants, study of the early stages of the deposition process is very important, because they determine the morphology and physicochemical properties of the electrodeposits.

Different mechanisms are considered to explain the interaction of the surfactants with electrode surface: electrostatic adsorption, chemisorption bonding, electronic polarization of π electrons, and hydrophobic/hydrophilic interactions.⁷ When the interaction between ionic surfactants and the electrode surface is electrostatic it is expected that the potential controls the electrode coverage.⁸ The adsorption of the surfactants at the electrode surface has an effect on the growth site density and the adion concentration on the surface, as well as the adion surface diffusion activation energy and the diffusion coefficient.⁹

It is well accepted that the association of different techniques, namely, chronoamperometry and atomic force microscopy (AFM), is very useful for the understanding of the mechanism and kinetics of the early stages of metal deposition.^{5,6,10-15} The transient's analysis provides reliable information on the nucleation and growth mechanisms and kinetics, which can be complemented by AFM imaging. The interpretation of the current-time transients for metal deposition is developed by using different established theoretical models.¹⁶⁻²² Hyde and Compton reviewed the subject in 2003.²³ More recently the contribution of secondary redox processes occurring simultaneously with metallic nucleation and growth and its effects on the shape of the transients has been discussed.^{24,25}

In a previous paper we reported a voltammetric and structural study on the zinc electrodeposition onto a steel substrate in the presence of different surfactants: anionic sodium dodecylsulfate (SDS), cationic dodecyltrimethylammonium bromide (CTAB), and nonionic octylphenolpoly(ethyleneglycolether)_n, n = 10 (Triton X-100). The results show that the zinc deposition occurs at potential values

more positive than the estimated equilibrium and thermodynamic potentials, and the deposition at overpotential region depends on the presence and concentration of the tested surfactants.²⁶

The aim of this paper is to further explore the systematic comprehension of the deposition mechanism and kinetics and, in particular, the role of the surfactants. To reach this goal a study of the initial stages of the zinc electrodeposition was undertaken using both chronoamperometric and AFM techniques.

Experimental

The electrochemical experiments were carried out in a threeelectrode glass cell with a stainless steel disk (AISI 316, diameter of 12 mm) as working electrode, a platinum mesh as counter electrode, and a commercial saturated calomel electrode (SCE) as reference. All potentials are reported with respect to this reference. Before each experiment, the stainless steel disks were washed with detergent, etched in HNO₃, and finally polished to a mirror finish using silica powder and ultrasonically cleaned with Millipore Milli-Q ultrapure water (18 M Ω) during 10 min. The electrochemical cell was connected to a Voltalab 32 Radiometer apparatus connected to an IMT 102 interface, controlled by a personal computer through the VoltaMaster 2 software.

The electrolyte solution containing 0.06 mol dm⁻³ ZnSO₄·7H₂O and 1.2 mol dm⁻³ MgSO₄·6H₂O was prepared from Millipore Milli-Q water using Merck analytical grade reagents. Separately, 1.0 mmol dm⁻³ cetyl trimethyl ammonium bromide (CTAB, Aldrich), 10 mmol dm⁻³ sodium dodecyl sulfate (SDS, Sigma), and 0.06 mmol dm⁻³ octylphenolpoly(ethyleneglycolether)_n, n = 10 (Triton X-100, Fluka) were added to this solution. All chemicals were analytical grade. The surfactants were used without further purification. For all solutions the pH value was 4. Before each experiment, the solution was deaerated with N₂ for 15 min.

AFM images were recorded in tapping mode in a Nanoscope IIIa multimode microscope (Digital Instruments, Veeco). Measurements were performed in air using etched silicon cantilevers (RTESP, Veeco) with a resonance frequency of ca. 300 kHz.

A JEOL scanning electron microscope (model JSM-6301F) was used to characterize the surface morphology of the zinc electrodeposits. The energy of the primary electron beam was 15 keV.

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Figure 1. Cyclic voltammograms for a steel electrode in 0.06 mol dm⁻³ ZnSO₄ + 1.2 mol dm⁻³ MgSO₄ (full line) and 1.2 mol dm⁻³ MgSO₄ (dotted line). Scan rate 10 mV s⁻¹. XRD patterns of electrodeposited samples prepared at -1.12 and -1.27 V for $t_{dep} = 90$ and 60 min, respectively, in surfactant-free solution.

Results and Discussion

In a previous paper we presented a voltammetric study of the Zn deposition on steel in the presence and absence of various surfactants.²⁶ This study allowed the definition of the deposition potential region for the different studied systems.

Figure 1 shows a cyclic voltammogram for zinc deposition on a steel substrate from the surfactant-free solution and the corresponding X-ray diffractograms of the deposit, prepared at -1.12 and -1.27 V during 90 and 60 min, respectively. The voltammogram main features are the sharp cathodic peak C2 and the corresponding anodic stripping peak A. A shoulder C1, without anodic counterpart is observed between -0.8 and -1.2 V vs SCE. By means of X-ray diffraction analysis it was possible to identify the solid phases formed on peaks C1 and C2. For all the studied systems, the samples prepared potentiostatically, in the region of peak C2, were constituted by zinc.

In what concerns the potential interval, where peak C1 appears, the studies were not totally conclusive. Taking into account that we are dealing with an underpotential deposition (UPD) region it is important to get a better understanding of the processes occurring on that region. For this purpose, potentiostatic studies and AFM analysis were performed.

Ex situ AFM morphological studies.— AFM was used in order to look closely into the surface morphology of the zinc deposits on the steel substrate, in the presence and absence of various surfactant molecules, in the early stages of the deposition process.

AFM examination of the pretreated steel surface was performed before the deposition process with the purpose of determining the substrate surface roughness and morphology. The obtained images indicate that the steel presents a smooth enough surface (root-mean-square roughness on a 10 \times 10 μm^2 scan area was 7.9 nm), appropriated for the analysis of the very initial formation of the zinc electrodeposits by AFM.²⁷

The samples observed by AFM were prepared potentiostatically in the UPD (C1) and overpotential deposited (OPD) (C2) regions.

Underpotential deposition.— Figure 2 presents AFM images obtained, at $2 \times 2 \mu m^2$ scanned area, from the deposits prepared for 6 s, at the peak C1 potential region, more precisely, at -1.00, -1.05, -1.10, and -1.12 V vs SCE, in the absence of surfactants.

As it can be seen, the coverage of the steel surface, as well as the shape and size of the clusters, strongly depends on the applied potential. At the lowest value, -1.00 V, the presence of isolated, small zinc circular clusters, with different size, dispersed at the substrate surface is observed. Cross-sectional profiles of the surface, along a line, show that the cluster width is always greater than its height, indicating a tendency toward two-dimensional (2D) growth.

With increasing potential, more clusters appear and they merge into larger ones. At the highest potential value (-1.12 V) a more complex morphology is found. The analysis of this sample by scanning electron microscopy (SEM; Fig. 3) in parallel with the observation of the corresponding three-dimensional (3D) AFM images (data not shown), enables a flat deposit zone and different-sized vertical structures to be observed. Small, circular clusters and crystallites with an almost hexagonal shape form the flat zone. The last ones probably correspond to zinc crystallites with a (00.2) crystallographic orientation and are aligned parallel to the substrate. This is an expected result considering the previous structural characterization.²⁶ The 3D images suggest that the "vertical" struc-

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tures exhibit polyhedral shapes, namely, pyramidal. Because we are dealing with ex situ analysis, it is impossible to know exactly which growth mechanism was involved in the formation of the hexagonal and pyramidal agglomerates.

These results obtained near the equilibrium potential indicates that the zinc deposition could follow the Stranski-Krastanov growth, which predicts the nucleation and growth of the 3D clusters on the



Figure 3. SEM image of Zn electrodeposit on steel substrate prepared in surfactant-free solution at -1.12 V during 6 s.

top of the 2D phase. This result is similar to the observations made by Kibler et al. for rhodium electrodeposits from in situ scanning tunneling microscopy investigations.²⁸

Based on the previous discussion it can be concluded that the nucleation and growth of Zn deposits occurs at potential values less negative than both the equilibrium and thermodynamic potential, -1.14 V and -1.05 V vs SCE, respectively, as it has been proposed previously.²⁶ In the potential region, where peak C1 appears, 2D nucleation occurs for the less negative values and a 2D–3D nucleation transition is observed for more negative potentials. The 2D growth in the early stages of Zn deposition can be understood in terms of a relation between the Zn deposit close-packed arrangement and the planes of the steel substrate. This is in accordance with the literature which reports that in the initial stages of electrodeposition, the Burgers orientation relationship always holds between zinc crystals and the ferrite substrate.

A similar study has been performed in the presence of surfactants. AFM images obtained for the deposits prepared at -1.120 V (peak C1), for 6 s, in the presence of SDS, CTAB, and Triton X-100, show that the deposit morphology is very similar to the one obtained in the absence of surfactant molecules (see Fig. 4). A flat deposit and a random distribution of different sized vertical aggregates were observed, which indicates that progressive nucleation takes place. These results demonstrate that the presence of the surfactant molecules does not have a great effect on the zinc deposition in this potential region.

Overpotential deposition.— The AFM images obtained from deposits prepared at -1.27 V (peak C2) during 3 s are shown in Fig. 5. All samples present a similar and peculiar morphology, characterized by randomly arranged long, curved ridges. No isolated nuclei can be detected. The analysis of Fig. 5 shows that the vertical growth is promoted against the lateral growth. For the deposit prepared in the absence of surfactant molecules, the morphology can be assigned to the formation and adsorption of hydrogen bubbles, on the steel substrate and growing deposit, which inhibit and/or condition the zinc nucleation due to physical interaction between hydro-



Figure 4. (Color online) 2D AFM amplitude image $(1 \times 1 \ \mu m^2)$ for a flat zone of the Zn electrodeposit prepared in surfactant-free solution at -1.12 V, during 6 s.

gen bubbles and the steel substrate as well as the zinc growing deposit.^{14,31} According to Grujicic and Pesic, in the case of the nickel electrodeposition the hydrogen evolution is responsible for the aggregation of small clusters into larger ones due to physical interaction between hydrogen bubbles and the nickel clusters.¹⁵

For the surfactant-containing systems, adsorption of the surfactant molecules occurs, in addition to the previous effect, as suggested by the earlier voltammetric studies.²⁶ A detailed analysis of these images shows exclusion areas on the substrate surface and that the coverage by the deposit crystallites depends on the type of surfactant in the solution. Although electrostatic interactions between the CTAB and the electrode surface are expected, leading to a block-

Table I. Root-mean-square roughness (Rq) for the electrodepose	s -
its prepared at -1.27 V, obtained from a $10 \times 10 \ \mu m^2$ area.	

	Sample	Surfactant- free	SDS	CTAB	Triton X-100
-	Rq (nm)	128	137	123	105

age of the active sites, the deposit morphology is similar to the ones obtained in the presence of SDS and in the surfactant-free solution.

When Triton X-100 is added to the bath, a less compact, ridged morphology is observed. This effect is more obvious for high concentrations of the nonionic surfactant. This should be related with an easier adsorption of the Triton X-100, at the steel surface and/or at the growing deposit, in this potential region.²⁶

This result is confirmed by the data shown in Table I where the electrodeposit root-mean-square roughness (*Rq*), obtained for a $10 \times 10 \ \mu\text{m}^2$ area, is compared.

The AFM morphological study performed at the C2 peak region indicates that the presence of the surfactant molecules affects the deposition process in the OPD region.

Potentiostatic studies.— Potentiostatic studies were used to elucidate the nucleation mechanism of zinc onto a steel substrate in the UDP and OPD regions, in the presence and the absence of surfactant molecules.

Underpotential deposition.— In order to obtain kinetic information on the UPD region, potential-step measurements were done in the interval where the voltammetric peak C1 appears. Figure 6a shows a set of current-time transients obtained from surfactant-free solutions, when the potential is stepped from the open-circuit potential to -1.00, -1.05, -1.10, or -1.12 V vs SCE. In the inset, current transients obtained in the absence of Zn²⁺ ions under similar experimental conditions are presented. In this case no current peaks are observed, as expected. Furthermore, the current densities increase



Figure 5. (Color online) 3D AFM images of electrodeposits prepared onto a steel substrate, in the absence and in the presence of the studied surfactant molecules, at -1.27 V.



Figure 6. (Color online) (a) Potentiostatic current transients for the electrodeposition of zinc onto a steel substrate, obtained from 0.06 mol dm⁻³ ZnSO₄ and 1.2 mol dm⁻³ MgSO₄ at different potentials in the UPD region. The inset presents potentiostatic current transients obtained at the same potentials in 1.2 mol dm⁻³ MgSO₄ solution. (b) Theoretical and experimental dimensionless plots (i/i_m) vs t/t_m for Zn deposition onto steel substrate.

with applied potential. This result suggests the occurrence of a redox process, namely, hydrogen evolution, as the previous voltammetric study has shown.²⁶

For the Zn^{2+} -containing solution, each transient presents a welldefined current maximum followed by a current decay that stabilizes on a steady-state current plateau. With increasing deposition potential the maximum current and the steady-state current plateau increase.

The behavior of the current maximum, particularly the shift to shorter times and higher current densities with increasing potential, suggests the existence of nucleation and growth processes in the UPD region.³² This conclusion is supported by the AFM morphological study, which shows that in this potential region 2D zinc clusters are formed.

A direct comparison of the experimental current transient in a dimensionless form, i/i_m vs t/t_m , with the theoretical curves given by the well-known model developed by Bewick, Fleischmann, and Thirsk for potentiostatic growth of a two-dimensional circular island, ³³ has been performed.

This comparison is presented in Fig. 6b which shows that the theoretical curves for 2D nucleation do not fit the experimental results. One possible reason for this behavior could be related to other parallel processes occurring simultaneously that are beyond the theoretical model used.

Abyaneh and Fleischmann proposed a description of the currenttime transient due to 2D nucleation and growth together with hydrogen evolution, on the top and at the edge of the growing centers.^{34,35} An attempt to qualitatively compare our experimental transients with Abyaneh and Fleischmann's predicted transient, presented in Fig. 1 of Ref. 34, shows that the agreement is good for the falling part but at short times a deviation is apparent. The reason for this may well be that initially other processes may take place on the substrate surface, namely, hydrogen adsorption and/or evolution.

Figure 7 shows a set of current-time transients obtained from Zn^{2+} solutions containing the surfactant molecules (a) SDS, (b) CTAB, and (c) Triton X-100, at different potentials, within the zinc UPD region. For all the systems the transient shapes are similar to the ones obtained from surfactant-free solutions. As it can be seen, the maximum current density is lower and t_m longer for the systems containing CTAB or Triton X-100 than for the SDS system. A comparison between the experimental current transient in a dimensionless form, with the Bewick, Fleischmann, and Thirsk theoretical model, was performed. As expected, the transients do not show a good fit to the shape predicted.

Table II shows the charge density values under the peak for all the systems at the different applied potentials. Examination of these results showed that the charge density increases with the applied potential. For potentials higher than -1.00 V the values are bigger than those estimated for the deposition of one hexagonal close-packed zinc monolayer: $523 \ \mu C \ cm^{-2}$. This result compares well with the AFM analysis, particularly the results obtained at -1.12 V (Fig. 4), for which a multilayer growth is observed.

Overpotential deposition.— A family of current-time transients obtained from surfactant-free solutions, at different potentials within the zinc bulk deposition region, is depicted in Fig. 8a. The transients present the typical response of a nucleation and growth process, i.e.,



Figure 7. Potentiostatic current transients obtained from 0.06 mol dm⁻³ ZnSO₄ and 1.2 mol dm⁻³ MgSO₄ solution containing (a) SDS, (b) CTAB, and (c) Triton X-100 at different potentials in the UPD region.

a rising current, due to the nucleation and growth of the nuclei followed by a falling portion due to linear diffusion to a planar electrode. $^{16}\,$

Table II. Transient charge densities for the studied systems.					
	$-q/mC \text{ cm}^{-2}$				
-E/V vs SCE	Surfactant- free	SDS	CTAB	Triton X-100	
1.00	0.669	0.562	0.261	0.359	
1.05	1.185	1.541	0.958	0.878	
1.10	1.987	2.025	1.209	1.579	
1.12	2.242	2.280	1.707	1.885	

Current transients were recorded, also, in the base electrolyte, i.e., in the absence of Zn^{2+} ions, under similar experimental conditions (inset). No current peaks are observed, as expected. Furthermore, the current densities increase with applied potential and are of the same order of those measured, in the presence of Zn^{2+} ions, at times longer than that corresponding to the current maximum. It appears that the falling currents, recorded in the base electrolyte, are related with other faradaic processes, namely, proton reduction and hydrogen evolution. This result suggests that the proton reduction reaction and hydrogen bubble formation take place simultaneously



Figure 8. (Color online) (a) Potentiostatic current transients for the electrodeposition of zinc onto a steel substrate, obtained from 0.06 mol dm⁻³ ZnSO₄ and 1.2 mol dm⁻³ MgSO₄ at different potentials in the bulk deposition region. The inset presents potentiostatic current transients obtained at the same potentials in 1.2 mol dm⁻³ MgSO₄ solution. (b) Theoretical and experimental dimensionless plots $(i/i_m)^2$ vs t/t_m for Zn deposition onto steel substrate.



Figure 9. Potentiostatic current transients obtained from 0.06 mol dm⁻³ ZnSO₄ and 1.2 mol dm⁻³ MgSO₄ solution containing (a) SDS, (b) CTAB, and (c) Triton X-100 at different potentials in the bulk deposition region.

with the zinc nucleation. However the well-defined maximum on the current-time transients clearly indicates that zinc nucleation is the preferential process.

This assumption is in accordance with the recent publications of Palomar-Pardavé et al.²⁴ and Milchev and Zapryanova²⁵ which have discussed the influence of secondary redox processes taking place prior to and simultaneous with the nuclei formation and their contribution to the total current.

It would be expected that the growth of the zinc films onto the steel substrate, in the investigated conditions (metallic ion concentration and potential range), occur by nucleation and 3D growth controlled by diffusion.¹⁶ The transients presented in Fig. 8a appear, at first sight, to resemble the predicted theoretical curves. In fact, the current at the maximum increases in magnitude as the potential is stepped to more negative values and inversely, as t_m decreases. A



Figure 10. (Color online) Theoretical and experimental dimensionless plots $(i/i_m)^2$ vs t/t_m for Zn deposition onto a steel substrate in the presence of surfactants (a) SDS, (b) CTAB, and (c) and Triton X-100 (data from Fig. 9).

closer inspection shows that at longer times, after the maximum, the current for the different growth potentials does not decay to a single limiting current according to the Cottrell equation, in disagreement with the model proposed by Scharifker and Hills (SH model).¹⁴ The reason for this may well be that the SH model is not adequate to describe the experimental transient after the maximum.

Assuming that the hydrogen evolution contribution is minor initially,^{6,36} the fitting of the experimental transients to the dimensionless theoretical curves derived by Scharifker and Hills for 3D growth, instantaneous and progressive nucleations were attempted.¹⁶



Figure 11. (Color online) Comparison between the experimental transient obtained during deposition of zinc at -1.27 V and the theoretical ones (solid line) obtained from the nonlinear fitting (Eq. 2) for the systems studied.

Dimensionless plots of $(i/i_m)^2$ vs t/t_m for the experimental transients shown in Fig. 8a are presented in Fig. 8b, with the corresponding theoretical curves. The rising parts of the transients follow the theoretical curve for instantaneous nucleation, up to the current maximum, in good agreement with the results obtained by others.^{4,5} In what concerns the falling parts, the data lie between the two theoretical curves, approaching the instantaneous one for the most negative growth potential. For the less negative potentials, the nucleation process varies with time from an instantaneous to a progressive one.

Figure 9 shows current-time transient families obtained from Zn^{2+} solutions containing the surfactant molecules: (a) SDS, (b) CTAB, and (c) Triton X-100.

The transients are similar to the ones recorded in the absence of surfactant molecules, consistent with nucleation and 3D controlled by diffusion.¹⁶ In the same way, at long times, the current for the different growth potentials do not decay to a single current. The maximum current is lower than in surfactant-free solution and decreases in the following order: SDS, CTAB, and Triton X-100. The inverse variation is observed for the time of the maximum current density. These results are expected, taking into account the previous voltammetric studies,²⁶ and are interpreted by the decrease of the nucleation and growth rates due to the presence of the surfactant molecules at the electrode surface, mostly CTAB and Triton X-100.

Trejo et al. obtained similar results for the electrodeposition of zinc onto Pt in the presence of several ethoxylated additives of different molecular weights.⁴

Figure 10 compares data from the experimental transients for the different systems with the dimensionless plots for instantaneous and progressive nucleation, where the differences in the nucleation mechanism are clearly seen.

The data fits well the instantaneous nucleation in the case of the SDS-containing system, for the whole transient, whereas in the presence of CTAB the transients follow the plot for progressive nucleation. With regard to Triton X-100, the data lie between the two calculated curves for the entire transient. This change in the nucleation mechanism may occur due to CTAB and Triton X-100 adsorption which prevents the Zn^{2+} species from approaching the steel electrode surface and consequently, a competition for sites takes place. These results point out the dominant role played by the presence of the surfactant molecules in the zinc nucleation mechanism. Similar effects have been reported for Zn electrodeposition in the presence of other surfactants.⁴⁻⁶

Although the SH model usually used in the form of dimensionless curves provides a satisfactory diagnostic for the "progressive/ instantaneous" character of the process, in practice it is difficult to extract the nucleation rate constant (A) and the number density of active sites (*No*), because the two parameters appear as a product in the equation that relates the current density and time, and the estimation of the electrocrystallization parameters is based only on a single point, the maximum current.²³

More recently, Heerman and Tarallo (HT) proposed a new model that assumes that the expansion of the diffusion layer should be a function not only of time, but also of the nucleation rate constant.²⁰ It is commonly accepted that the experimental transients can be described and the kinetics parameters extracted using this theoretical model for diffusion-controlled crystal nucleation and 3D growth.^{5,6,20,21,37}

The analytical expression for the current transient derived by the HT model is given by

$$i(t) = zFDc(\pi Dt)^{-(1/2)} \left(\frac{\Phi}{\Theta}\right) [1 - \exp(-\pi k N_0 Dt\Theta)]$$
[1]

where

$$k = \left(\frac{8\pi cM}{\rho}\right)^{1/2}$$
$$= 1 - \frac{1 - \exp(-At)}{At}$$

and

$$\Phi = \Phi[(At)^{1/2}]$$

related to Dawson's integral, is given by

Θ

$$\Phi = 1 - \frac{\exp(-At)}{(At)^{1/2}} \int_0^{(At)^{1/2}} \exp(\lambda^2) d\lambda$$

where A is the nucleation rate constant, N_0 is the number density of active sites on the surface of the substrate, D is the diffusion coefficient, c is the concentration of the metal ions in solution, and M and ρ are the molecular weight and density of the metal, respectively.

Commercial software based on the Levenberg-Marquardt algorithm was used to obtain the parameters, A, No, and D according to Eq. 1 for the current density due to 3D growth diffusion control (i_{3D}) . The agreement between the experimental transients and the nonlinear fit is very satisfying. In order to increase the correlation values, the contribution of the double-layer charging current (i_{dl}) has been considered for the total current density

$$i_{\text{total}} = i_{\text{dl}} + i_{3\text{D}}$$
^[2]

Based on the literature, the descending current observed at the initial stages of the transients corresponds to the double-layer charging effect. Hölzle et al. showed that such a charging effect could be correlated quantitatively to the adsorption-desorption process of ions on the electrode surface.³⁸ The estimation of the double-layer charging effect was based on a Langmuir-type adsorption-desorption equilibrium and is given by

$$i_{\rm dl} = k_{\rm ads} \exp(-k_{\rm des}t)$$
[3]

where $k_{ads} = k_{des}Q_{ads}$.

Figure 11 shows a comparison of the experimental current density transients obtained for all the systems at -1.27 V vs SCE with the theoretically generated curve from the nonlinear fitting of the experimental data to Eq. 2. These results clearly show that the applied model successfully describes the experimental current transients.

The variation of the kinetic parameters *A* and *No*, obtained from the fitting, with the applied potential is presented in Fig. 12. In general, both *A* and *No* values increase for more negative deposition potentials. It is also observed that the highest *A* value was obtained in the absence of surfactants. For the surfactant-containing systems the following order is verified: SDS, CTAB, and Triton X-100. An inverse behavior is encountered for the *No* parameter. These results



Figure 12. Variation of kinetic parameters *A* and *No* with the applied potential. The vertical bars represent the standard deviation.

indicate that for the surfactant-free system an instantaneous nucleation mechanism (large A and small No) occurs, while for CTAB and Triton X-100 a progressive nucleation (small A and large No) takes place.³⁹ This is in accordance with the dimensionless plot analysis.

With regard to the nucleation rate, the values obtained for the systems containing CTAB and Triton X-100, in comparison to the others, indicate a blocking effect of the surfactants and/or a decrease of the ion rate transferred across the electric double layer. A similar interpretation of the influence of different additives on the Zn nucleation and growth has been given by other authors.^{4,5} These results are in accordance with the AFM analysis (Fig. 5), where the effect of the surfactants, namely, CTAB and Triton X-100, in the bulk zinc deposition at -1.27 V is clearly observed.

The values of the Zn^{2+} ion diffusion coefficient, *D*, estimated from the nonlinear fitting (Table III) show the expected variation caused by the presence of the surfactants, and they are in good agreement with earlier reports.³¹ They are lower, however, than those previously calculated from voltammetric data.²⁶ These differ-

Table III. Diffusion coefficients for the Zn^{2+} species estimated from the nonlinear fitting.

		$D imes 10^6/\mathrm{cm}^{-2}~\mathrm{s}^{-1}$		
-E/V vs SCE	Surfactant- free	SDS	CTAB	Triton X-100
1.25	3.36	1.87	1.97	2.00
1.27	4.02	2.29	2.54	2.33
1.29	4.50	3.95	2.49	2.36

ences are not physically meaningful and may be due to the use of distinct electrochemical techniques to get this parameter.

Conclusions

Zinc electrodeposition onto a steel substrate using both electrochemical and AFM techniques has been studied.

AFM analysis shows that Zn electrodeposition, in the absence of surfactants, begins in the UPD region with the formation of nanometric circular clusters homogeneously distributed on the steel surface. This result indicates a strong interaction between the steel substrate and the growing deposit. In the presence of SDS, CTAB, and Triton X-100 no meaningful changes of the electrodeposit morphology are observed in this potential region.

In all cases free areas on the steel surface coexist with small aggregates and the impingement of growing aggregates, indicating that progressive nucleation takes place. The Zn UPD is confirmed by the chronoamperometric measurements performed in this potential region.

With regard to the bulk deposition region, where the hydrogen evolution goes together with the zinc deposition, the analysis of the current-time transients indicates that the Zn electrodeposition occurs by instantaneous nucleation and 3D growth controlled by diffusion in the surfactant-free solution and in the presence of SDS. When the CTAB and Triton X-100 were added to the bath, change from instantaneous to progressive nucleation arises as a consequence of the simultaneous adsorption of the surfactant that inhibits the nucleation sites. The kinetic parameter values obtained from the HT model are in accordance with the dimensionless analysis of the transients. AFM confirms the effect of surfactants on the zinc bulk deposition.

In summary, this work shows that the application of different techniques to the study of zinc deposition has been rewarded by a considerable improvement in our understanding of the early stages of deposition, in particular, allowing us to confirm Zn UPD onto a steel substrate.

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