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Zn electrodeposition in the presence of surfactants Part I. Voltammetric and structural studies

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Abstract

The zinc electrodeposition onto steel substrates in the presence of surfactants with different charged head groups, namely anionic sodium dodecylsulphate (SDS), cationic dodecyltrimethylammonium bromide (CTAB), and non-ionic octylphenolpoly(ethyleneglycolether)_n, n = 10 (Triton X-100) was studied by cyclic voltammetry. The effect of the switching potential and scanning rate on the deposition process was investigated. The structural characterisation and the chemical composition of the samples prepared potentiostaticaly, in the potential range where the voltammetric cathodic peaks appear, was performed by X-ray powder diffraction (XRD) and by energy-dispersive X-ray analysis (EDS), respectively. The experimental results show that the voltammetric behaviour, namely the deposition potential depends on the presence, nature and concentration of the tested surfactants. Zn deposition occurs at potential values more positive than the estimated equilibrium potential, peak C1, simultaneously with hydrogen formation. This fact is confirmed by XRD measurements. Zn bulk deposits prepared in the absence of surfactants and in the presence of SDS are more crystalline and with a higher grain size than the ones obtained in the presence of CTAB and Triton X-100. These facts may be justified by an increase on the overpotential deposition as the electrochemical study confirms.

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1. Introduction

It is well known that zinc electrodeposits on metals have special relevance due to their anticorrosive properties by the formation of passive layers on contact with air, and in aqueous solution. Moreover they are suitable metallic matrix to incorporate suspended inert particles [1]. These capacities are strongly related to the morphological and structural characteristics of the films, which depend on the electrodeposition conditions, namely, the presence of organic additives at the deposition bath and the current/potential profile applied.

The introduction of small amounts of adequate organic additives, in the electrodeposition bath, results in beneficial quality changes on the deposits, namely the homogeneity. Surfactants are commonly used in zinc electrodeposition to control the metallic crystal shape and size, in order to produce smooth and

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bright deposits [2–5]. Other additives such as polyacrylamine [6], thiourea [6] and benzylideneacetone [7] have been also used for zinc deposition. Common effects of the organic additives are changes in the preferred deposit orientation, morphology and an increase in the deposition overpotential.

The specific activity of the surfactants are generally understood in terms of adsorption at the cathode surface, during deposition, and depends on the concentration of the surfactant molecules. When the concentration approaches the critical micelle concentration (cmc) the formation of bilayers or multilayers at the electrode interface occurs [8].

The adsorption of surfactants aggregates onto electrodes can have large effects on the kinetics of the electron transfer and consequently on the electrodeposition process.

The effect on the electron transfer rates includes blocking of the active sites by the surfactants, and electrostatic interactions between electroactive species and adsorbed surfactants [9]. Due to those effects it is possible to modify the crystals growth mode and tailor the morphology and structure of the electrodeposits.

Our previous work on the electrodeposition of zinc onto steel in the presence of surfactants has shown that the charge of the

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surfactant headgroups has a marked effect on the films composition, structure and morphology [10,11].

Therefore, we have undertaken a voltammetric study of the zinc electrodeposition onto steel in acid aqueous solutions in the presence of cationic, anionic and non-ionic surfactants. Voltammetric measurements were used, as an exploratory technique, to evaluate the effect of the added surfactants on the zinc deposition mechanism. The use of this method for the electrodeposition studies was due to its potentialities, namely the possibility of both deposition and stripping being observed in one single experiment. Moreover the effect of blocking additives, due to its adsorption on the cathode surface, may be estimated from the current values measured in the presence and in the absence of the organic molecules [12]. The effect of the switching potential and the scanning rate, on the zinc deposition process, in the presence and absence of the surfactants, was analysed.

To complement this electrochemical study, a structural characterisation of the samples obtained potentiostatically in the potential range where the voltammetric cathodic peaks appear was performed by X-ray powder diffraction (XRD). The samples chemical composition was obtained by energy-dispersive X-ray analysis (EDS).

The present work illustrates how the presence, nature and concentration of surfactant, like cationic CTAB, anionic SDS and non-ionic Triton X-100, influences the deposition process and consequently the structural characteristics and composition of the electrodeposits.

Attempts to correlate electrochemical deposition conditions and deposit structure were done. Morphological studies of the films as well as the nucleation and growth mechanisms will be described in a subsequent paper.

2. Experimental

The electrochemical experiments were carried out in a threeelectrode glass cell with a stainless steel disc (AISI 316, diameter of 12 mm) as working electrode, a platinum mesh as counter electrode and a commercial satured calomel electrode (SCE) as reference electrode. All potentials are reported with respect to this reference. Before the experiments, the stainless steel discs were polished with silicon carbide, sonicated for 5 min and rinsed thoroughly with Millipore Milli-Q ultrapure water (18 M Ω). Cyclic voltammetric studies were done at room temperature with an EG and G PAR model 263 potentiostat connected to a Philips PM 8271 recorder.

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, cetyl trimethyl ammonium bromide (CTAB, Aldrich), sodium dodecyl sulphate (SDS, Sigma) and octylphenolpoly (ethyleneglycolether)_n, n = 10 (Triton X-100, Fluka) were added to this base solution, without further purification. The surfactant concentrations were selected taking into account the critical micelle concentration values [13,14]. All chemicals were analytical grade. For all solutions the pH value was 4. Before each experiment, the substrate surface was cleaned and the solution deareted with N₂ for 15 min. The electrodeposited films were prepared potentiostatically in stirring solution, at room temperature under a slight N_2 flux. After, the samples were thoroughly rinsed in Millipore water, dried in nitrogen stream and immediately transfer to a desiccator.

Electrodeposits X-ray diffraction analysis was carried out using a Philips X-ray diffractometer (model PW 1710) with Cu K α radiation ($\lambda = 0.15604$ nm), working at 30 mA and 40 kV. The diffractograms were obtained in the 2θ range of 20–80° using a 0.02° step and acquisition time of 2 s/step.

A JEOL scanning electron microscope (model JSM-6301F) coupled with an energy-dispersive spectroscopic (Noran/ Voyager) were used to analyse the elemental composition of the electrodeposited samples. The energy of the primary electrons beam was 15 keV.

3. Results and discussion

3.1. Voltammetric studies

3.1.1. Studies on Zn^{2+} solutions

A typical cyclic voltammogram of steel, recorded in $0.06 \text{ mol dm}^{-3} \text{ Zn}^{2+}$ solution, between the open circuit potential (-0.4 V) and -1.4 V versus SCE, is shown in Fig. 1(a). 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 versus SCE. A voltammogram obtained in the absence of Zn²⁺ ions is also presented.

The comparison of the voltammograms obtained in the presence and absence of Zn^{2+} ions suggests that shoulder (C1) is due to hydrogen evolution since this reaction occurs significantly at these potentials when the Zn^{2+} ions are absent. Others authors have found a similar result [15–17].

In order to study in more detail the shoulder C1, a scan was performed between -0.3 and -1.12 V (Fig. 1(b)). As it can be seen, the current increases at -0.85 V reaching a maximum near -1.05 V, following the attainment of a plateau. On the positive sweep no anodic peak is observed, indicating that the reduction process is irreversible.

Similar data were obtained by Kim et al. for the zinc deposition at iron electrodes, and explained in terms of Zn underpotential deposition [18], although no anodic peak was observed, as it is expected for underpotential metallic deposition [19].

In what concerns peak C2, centred at -1.26 V, it corresponds to the zinc bulk deposition. In this potential region the hydrogen evolution also occurs as it is detected by direct observation, and described by the reaction [20]:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Upon the sweep reversal, two current crossovers appear indicating the formation of stable growth centres, at the substrate surface [21].

The anodic stripping peak (A) centred at -1.0 V, is attributed to the oxidation of metallic zinc to Zn^{2+} . This potential value is in good agreement with the results referred in the literature [22].



Fig. 1. (a) Cyclic voltammograms obtained for stainless steel electrode in $0.06 \text{ mol } \text{dm}^{-3} \text{ ZnSO}_4 + 1.2 \text{ mol } \text{dm}^{-3} \text{ MgSO}_4$ (full line) and $1.2 \text{ mol } \text{dm}^{-3} \text{ MgSO}_4$ (dotted line). (b) Cyclic voltammogram obtained for stainless steel electrode in $0.06 \text{ mol } \text{dm}^{-3} \text{ ZnSO}_4 + 1.2 \text{ mol } \text{dm}^{-3} \text{ MgSO}_4$ in the potential range of -0.4 and -1.2 V. Scanning rate 10 mV s^{-1} . The arrows indicate directions of scan voltages.

Beyond peak A the current approaches to zero, indicating that the majority of the deposited zinc has been removed from the substrate surface.

The influence of the potential scan rate (v) on the Zn deposition is shown in Fig. 2. The data reveals that an increase in sweep rate shifts the peak potentials to more negative values and increases the peak current. Plots of logarithm of peak current density (i_p) versus logarithm of the sweep rate, give slope values near 0.5 for the two cathodic peaks. The relation between the cathodic peak current and the square root of scan rate $(v^{1/2})$ is presented on the inset in Fig. 2. The variation is linear but the lines do not pass through the origin. The linearity is expected for a reduction processes that occurs under mass transfer control. However the intercept higher than zero indicates that an additional process other than diffusion occurs [23].

Fig. 3 shows the voltammograms obtained at different switching potential (E_{λ}) . It can be seen that the crossover potential (E_c) remains constant when E_{λ} is successively switched from -1.35 to -1.25 V. A similar result was obtained by Diaz-Arista et al. for Zn electrodeposition on Pt [7]. According to Fletcher et al. this result indicates that the Zn nucleation is charge limited under the studied conditions [21]. Since in this circumstances



Fig. 2. Linear voltammograms for stainless steel electrode in 0.06 mol dm^{-3} ZnSO₄ + 1.2 mol dm⁻³ MgSO₄, at various sweep rates: 5 mV s⁻¹ (1), 10 mV s⁻¹ (2), 20 mV s⁻¹ (3), 50 mV s⁻¹ (4) and 100 mV s⁻¹ (5). Inset: variation of peak current density with sweep rate for peak C1 (a) and peak C2 (b).



Fig. 3. Cyclic voltammograms for stainless steel electrode in 0.06 mol dm^{-3} ZnSO₄ + 1.2 mol dm⁻³ MgSO₄, showing the effect of the scan negative limits: -1.25, -1.30 and -1.35 V. Scanning rate 10 mV s^{-1} .



Fig. 4. Cyclic voltammograms obtained for stainless steel electrode in $0.06 \text{ mol dm}^{-3} \text{ ZnSO}_4 + 1.2 \text{ mol dm}^{-3} \text{ MgSO}_4$ containing 10 mmol dm⁻³ SDS (a), 0.1 mmol dm⁻³ CTAB (b) and 0.06 mmol dm⁻³ Triton X-100 (c). The dotted lines refer to the voltammograms obtained in the same solution in the absence of surfactant. Scanning rate 10 mV s⁻¹.

the crossover potential is equal to the metal/metal-ion reversible potential, it can be assumed that the equilibrium potential for Zn/Zn^{2+} is -1.14 V versus SCE. This value is more negative than that calculated from Nernst equation (-1.05 V versus SCE), due to crystallisation overpotential related to the steel substrate.

As expected, changes on the E_{λ} to less negative values led to a decrease of the anodic peak size, accompanied by a negative shift of the peak potential, due to an easier dissolution of the deposit.

3.1.2. Studies on Zn^{2+} solutions containing surfactant molecules

Fig. 4 contrasts the voltammograms obtained in similar conditions in the absence and presence of 10 mmol dm⁻³ SDS (a), 0.1 mmol dm^{-3} CTAB (b) and $0.06 \text{ mmol dm}^{-3}$ Triton X-100 (c). The presence of the surfactant molecules causes significant changes on the shape of the voltammograms and also on the current intensity values. These results indicate that the presence and chemical nature of the surfactant affects both the Zn deposition and stripping processes. The two current crossovers in the cathodic region are evident, for all the systems, indicating that nucleation and growth of Zn centres occur, for the tested conditions. Moreover, the cathodic peak C1 is similar to the one obtained in absence of surfactant molecules, suggesting that, for this potential range, the presence of surfactant has no effect on the reduction process.

A more detailed inspection of the data reveals that in the presence of SDS (Fig. 4(a)) the cathodic voltammetric profile is analogous to the one obtained in the absence of surfactant, presenting peaks C1 at -1.05 V and C2 at -1.25 V. On the anodic sweep, a smaller oxidation peak (A) is observed at about -1.0 V versus SCE. This result pointed out that the rate of zinc dissolution is inhibited by the presence of this surfactant. This is in accordance with the results obtained by Fuchs-Godec and Doleček show that the SDS acts as an inhibitor for the copper dissolution [24].

When CTAB and Triton X-100 are present in the solution, smaller currents for the peaks C2 and A are recorded, being the decrease slightly more pronounced for the system containing Triton X-100. This can be explained by an inhibition effect on the Zn deposition, by blocking the active sites available for the deposition, due to the surfactant adsorption on the electrode surface. This inhibition depends on the type and size of the organic molecules and, on the specific interaction between the surfactant and the substrate.

It is expected that electrostatic interactions occur between the CTAB, a surfactant with positive head charge group, and the electrode surface, leading to a blockage of the active sites. On the other hand, Triton X-100 being a large non-ionic molecule can minimize the rate of mass transfer. The presence of hydroxyl groups would strengthen the adsorbability on the metal surface. Moreover hydrocarbon tails mesh with each other to form a film, which repels the aqueous solution, establishing a diffusion barrier to the solution flow, towards the electrode surface [25]. Besides that, Triton X-100 adsorption depends on the applied potential as the voltammograms indicate. Similar assumptions were proposed for the copper deposition in the presence of polyethyleneglycol (PEG) [26–28].

Table 1 presents the voltammetric charge densities estimated for peaks C1, C2 and A for all the studied systems, by integrating, over the appropriate potential range.

For all the studied systems, peak C1 presents a charge density value around 15 mC cm⁻², similar to the one obtained in the absence of surfactants. This value is much higher than the calculated one (523 μ C cm⁻²) for the deposition of a hexagonal close packed zinc monolayer, indicating that it results from the zinc deposition simultaneously with hydrogen formation. The

 Table 1

 Voltammetric peak charge densities for the studied systems

$q_{\rm p}~({\rm mC~cm^{-2}})$	Surfactant			
	None	SDS	CTAB	Triton X-100
C1	-14	-15	-16	-16
C2	-101	-98	-72	-57
A	80	46	40	34



Fig. 5. Linear voltammograms for stainless steel electrode in $0.06 \text{ mol } \text{dm}^{-3}$ ZnSO₄ + 1.2 mol dm⁻³ MgSO₄ (—), containing 10 mmol dm⁻³ SDS (···), 0.1 mmol dm⁻³ CTAB (---) and 0.06 mmol dm⁻³ Triton X-100 (-·-).

charge high values are in accordance with those obtained by Casanova et al. [15] for the zinc deposition on steel in the potential region where peak C1 appears. They have concluded that this peak is not only due to an underpotential deposition (UPD) process. And, the UPD peak would be masked by the current due to hydrogen evolution on steel.

In what concerns peak C2, the maximum charge value was found for the surfactant free solution. For the surfactant containing systems it decreases in the following order SDS, CTAB and Triton X-100. This result could be associated with the decrease on the amount of deposited zinc when the surfactants are present in the solution.

In the presence of CTAB and Triton X-100, the result should be a direct consequence of the surface substrate coverage, by the surfactant molecules, which is responsible for the displacement of the reduction potential to more negative values and the decrease on the cathodic current as Fig. 5 shows. This cathodic polarization effect has been reported for other organic compounds in metallic electrodeposition [29].

In what concerns peak A, a charge trend similar to peak C2 is observed. A decrease of 43, 50 and 58% was estimated for the systems containing SDS, CTAB and Triton X-100, respectively.

The ratio between the anodic and cathodic density charge, stripping efficiency, is smaller than 1 for all the systems. For the surfactant free system, this lower stripping efficiency can be due to the cathodic charge consumed by proton reduction and/or to an incomplete oxidation of the Zn electrodeposited. Lower values were obtained in the presence of the surfactants, which can be related to modifications occurred in the structure/morphology of the Zn electrodeposited films.

Fig. 6 is a collection of cyclic voltammograms obtained in the presence of the surfactants, which illustrates the effect of the negative potential limit on the zinc deposition.

The data show that for all the systems, the crossover potential does not depend on the potential limit and presents the values -1.13 V (SDS), and -1.16 V for the systems containing CTAB and Triton X-100. For the later systems the crossover potential is more negative than the obtained in the absence of surfactants. This can be explained assuming that, in the interface region, the Zn²⁺ concentration is lower in the presence of these surfactants, as well as higher activation energy for the Zn²⁺ reduction.

Voltammograms obtained at various sweep rates, for the Zn deposition in the presence of the surfactants showed that the cathodic peak current increases with increasing sweep rate, for all the systems. Logarithmic plots of i_p versus ν gave slopes approaching 0.5, for the peaks C1 and C2.

Linear plots of the cathodic peak current densities (i_p) as function of $\nu^{1/2}$, for peak C1 and peak C2 were obtained as expected for a reduction process that occurs under mass transfer control.

For the peak C1 this dependence, is not in accordance with the published results that show that the zinc reduction in the presence of additives and, in the underpotential region, is adsorption controlled (i_p linear with ν) [30]. Our results could be explained assuming that peak C1, is not only due to the zinc deposition, but simultaneously hydrogen formation occurs. Similar slopes for the three surfactants were obtained. The values agree well with the one obtained in the surfactant free solution.

In contrast for peak C2, the slopes depend on the nature of the surfactant, with positive intercepts in the absence of additives and for the SDS containing solutions. For the other two additives the intercept approaches zero.

Although the hydrogen evolution competes with the zinc deposition in this potential region in the absence and presence of surfactants, a comparison between the apparent Zn^{2+} diffusion coefficients was done. The apparent diffusion coefficients calculated for the Zn^{2+} species, for the different solutions, are



Fig. 6. Cyclic voltammograms for stainless steel electrode in $0.06 \text{ mol dm}^{-3} \text{ ZnSO}_4 + 1.2 \text{ mol dm}^{-3} \text{ MgSO}_4$ containing 10 mmol dm⁻³ SDS (a), 0.1 mmol dm⁻³ CTAB (b) and 0.06 mmol dm⁻³ Triton X-100 (c), recorded with different negative limits of the voltage scan: -1.25, -1.30 and -1.35 V. Scanning rate 10 mV s⁻¹.

Table 2

Apparent diffusion coefficients for the Zn²⁺ species, in the different studied solutions, and respective correlation coefficients for the i_p vs. $\nu^{1/2}$ plots

Surfactant	$10^{6} \mathrm{D/cm^{2} s^{-1}}$	R^2
None	8.53	0.99973
SDS	8.68	0.99883
CTAB	2.28	0.99941
Triton X-100	0.56	0.99808

presented in Table 2. The values obtained in the absence and in the presence of SDS are of the same order of the one reported by Turnham, 6.9×10^{-6} cm² s⁻¹, for Zn²⁺ species in 0.1 M KNO₃ [31]. However, lower values were determined in the presence of CTAB and Triton X-100, which can be explained by viscosity changes on the solution as well as by the possible formation of zinc complexes [32].

Fig. 7 shows the surfactant concentration effect on the zinc deposition. It is clear that, changes on the SDS concentration has no effect on the voltammetric profile which contrasts with what happens for the CTAB and Triton X-100 containing solutions. The concentration effect is more obvious for the potential region where peak C2 appears, due to changes on the adsorbed surfactant structure at more negative potentials.

The inhibition effect on the zinc deposition, caused by the surfactant concentration increase, is due to a blockage of the electrode surface. In fact the higher number of surfactant molecules in the vicinity of the electrode hinders the access of Zn^{2+} species. In addition, higher surfactant concentration affects the structure of the adsorbed layer and consequently the diffusion of Zn^{2+} species, through this surfactant compact adsorbed layer, is much slower. Changes on the electrical properties of the surfactant layers at the substrate surface can also occur which originate modifications on the deposition process [33].

All these effects lead to a decrease on the voltammetric current. The degree of surface coverage for the surfactants were evaluated from Eq. (1):

$$\theta = \frac{i - i_{\rm S}}{i} \tag{1}$$

where i and i_S are the current densities without and with surfactants, respectively, measured at a constant potential value [12].

Table 3

Degree of surface coverage obtained at E = -1.30 V vs. SCE for the surfactants studied at different concentrations

Surfactant	<i>c</i> (mM)	θ
0.00	1	0.05
5D8	10	0.09
	0.1	0.48
СТАВ	1	0.83
T 1 100	0.06	0.57
Triton X-100	0.30	0.79
	0100	0179

The coverage values obtained at E = -1.30 V versus SCE are presented in Table 3. As it was expected the lowest coverage degree was obtained for the SDS.

Based in these findings, linear sweep experiments were performed at low sweep rates (1 mV s⁻¹), for the CTAB and Triton X-100 containing solutions in order to fit θ values to standard isotherms. The best fit was obtained by assuming the Langmuir isotherm according to Eq. (2):

$$\frac{c}{\theta} = c + \frac{1}{K} \tag{2}$$

where *K* is the equilibrium constant of the adsorption reaction and *c* is the surfactant concentration in the bulk solution [34]. The two plots c/θ versus *c*, presented in Fig. 8, are linear and have slopes close to the unity as required by Eq. (2).

The adsorption equilibrium constant was evaluated and values of 1.5×10^4 and 1.6×10^5 were obtained for CTAB and Triton X-100, respectively, showing that Triton X-100 is more easily adsorbed than CTAB.

3.2. X-ray diffraction study

A structural study of the solid phase formed in the potential regions of peaks C1 and C2, was performed. The deposits were grown during 1:45 and 1 h, respectively, for peaks C1 and C2. Although bulk deposits were obtained and analysed, the information is useful to understand the deposition process.

Fig. 9 shows the diffractograms obtained for samples prepared in the presence and absence of surfactant molecules, in



Fig. 7. Cyclic voltammograms for stainless steel electrode in $0.06 \text{ mol dm}^{-3} \text{ ZnSO}_4 + 1.2 \text{ mol dm}^{-3} \text{ MgSO}_4$ containing different concentrations of SDS (a), CTAB (b) and Triton X-100 (c). Scanning rate 10 mV s^{-1} .



Fig. 8. c/θ vs. c plots for (a) CTAB and (b) Triton X-100 containing solutions.

the potential region where peak C1 appears, more precisely at -1.12 V. The diffraction lines observed for the deposits obtained in the surfactant free solution and in the presence of SDS (Fig. 9(a) and (b)) correspond to the zinc hexagonal structure [35]. Surprisingly, in the case of the electrodeposits prepared from the solutions containing the cationic and non-ionic surfactant, this diffraction pattern is not observed. The XRD measurements have proven that the films consist of Zn₄SO₄(OH)₆, ZnO and ZnSO₄ [36]. This result has been confirms by EDS analysis.

These results are somewhat unexpected since the voltammetric profiles (Fig. 4), in the potential region where peak C1 appears, are similar for all the studied systems. It should be noted, that zinc deposition is a complex process due to the simultaneous reactions that could occur, namely hydrogen evolution. Taking into account that at this potential region, the production of hydrogen gas was observed, changes in the local pH values take place and consequently the formation of Zn(OH)₂ and/or ZnO is possible. Moreover the possibility of zinc hydroxysulphate (Zn₄SO₄(OH)₆) formation cannot be discarded. Considering that more negative E_c values were found for the systems containing CTAB and Triton X-100, the reduction of these phases to zinc would be more difficult, what could explain its presence in these conditions.



Fig. 9. XRD patterns of electrodeposited samples prepared at -1.12 V during 1:45 h, in absence (a) and presence of surfactant: SDS (b), CTAB (c) and Triton X-100 (d). Diffraction lines due to the substrate (*), Zn₄SO₄(OH)₆ (\bigstar), ZnO (\bigcirc) and ZnSO₄ (\diamondsuit). The bars indicate the zinc tabled diffraction lines [35].

On the other hand in the surfactant free solution and in presence of SDS, the formation of zinc occurs at potentials more positive than the equilibrium potential. This could be due to a strong deposit–substrate interaction, which promotes the initial zinc growth and slows down the hydrogen evolution reaction in these conditions.

Fig. 10 shows the diffractograms obtained for samples prepared in the presence and absence of surfactant molecules in the C2 potential region, more precisely -1.27 V. As expected, for all the samples, the zinc is the main phase present.

A more detailed analysis of the film diffractograms shows that the intensity of the highest diffraction line increases in the sequence Triton X-100, CTAB, SDS and surfactant free solution. This variation can be due to an increase of the film thickness and/or crystallinity, which is associated with the zinc ion concentration at the substrate interface and with the surface coverage by the surfactant. It is interesting to note that these results are correlated with the charge of the cathodic peak C2 present in Table 1.

Changes in the crystal orientation obtained for the electrodeposits obtained in the absence and in the presence of the organic molecules were observed. As stated before, the changes in crystallographic orientation are due to modifications on the metal's surface energy by the adsorption of the organic molecules [19]. Each surfactant develops specific interactions with the differ-



Fig. 10. XRD patterns of electrodeposited samples prepared at -1.27 V during 1 h, in absence (a) and presence of surfactant: SDS (b), CTAB (c) and Triton X-100 (d). Diffraction lines due to the substrate (*). The bars indicate the zinc tabled diffraction lines [35].

ent crystal planes that induce different growth mechanisms [11].

Diffractions lines, with a very weak intensity, attributed to $Zn_4SO_4(OH)_6$, ZnO and ZnSO₄ were also observed. It is interesting to note that these phases are more visible for the samples prepared with the solutions containing CTAB and Triton X-100. Similar situation was already observed for the potential region where peak C1 appears.

4. Conclusions

The conclusions from this work can be summarized as follows:

- The voltammetric behaviour of the zinc deposition onto steel in aqueous solution depends on the presence, nature and concentration of the tested surfactants SDS, CTAB and Triton X-100.
- (2) Zn deposition occurs at potential values more positive than the estimated equilibrium potential, peak C1, simultaneously with hydrogen formation. This fact is confirmed by XRD measurements.
- (3) An increase in the deposition potential with respect to the surfactant free bath is observed for the CTAB and Tri-

ton X-100 containing solutions. This increase goes along with a decrease on the anionic peak charge, reflecting the decrease on the amount of Zn deposited. These findings were explained by the surfactant adsorption on the electrode surface.

(4) Zn bulk deposits prepared in the absence of surfactants and in the presence of SDS are more crystalline and with a higher grain size than the ones obtained in the presence of CTAB and Triton X-100. These facts may be justified by an increase of the overpotential deposition as the electrochemical study performed confirms.

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