The Effect of Polyethylene Glycol 8000 Additive on the Deposition Mechanism & Morphology of Zinc Deposits

By G. Trejo, R. Ortega & Y. Meas

The effect of polyethylene glycol (PEG) 8000 on the morphology and mechanism of zinc electrodeposition in a chloride acid bath was studied. A thermodynamic study of the species Zn(II)/Cl^-/H_2O was undertaken using a graphical method in order to identify the predominant zinc species in solution. The results of the thermodynamic study, together with those from a voltammetric study, show that PEG 8000 does not form complexes with zinc, and that its principal function is to act over the electrode surface. The presence of PEG 8000 in a solution causes the zinc electrodeposition mechanism to occur in two stages that involve the same chloride complex of zinc, $ZnCl_4^{-2}$, which is reduced to Zn^0. Scanning electron microscopy (SEM) of the deposit morphology showed that the presence of PEG 8000 generates compact deposits formed as hexagonal plates oriented perpendicular to the electrode surface. A lower corrosion rate was observed when the deposits were formed in the presence of the PEG 8000 additive.

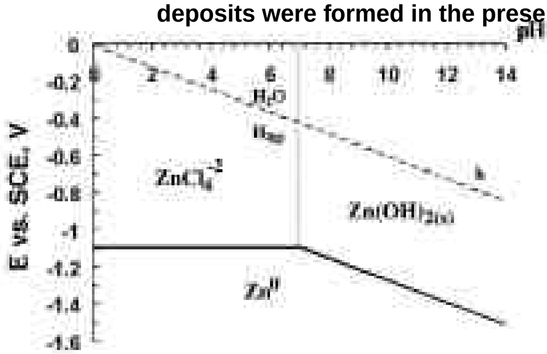

Fig. 1—Pourbaix-type diagram for the Zn(II)''/Zn^0 system at pZn' = 1.0, pCl' = -0.45. The H_2O/H_2 system is also shown.

The practical and industrial importance of zinc electrodeposits derives from their capacity to protect ferrous substrates from corrosion.[1-5] Zinc electrodeposits are strongly influenced by a range of factors that affect the deposition mechanism and depend on the composition of the electrolytic bath (concentration, complexing agents, additives). Nowadays, polyethoxylated compounds are widely used in the baths for metal electrodeposition. In spite of their proven utility, however, little is known about the behavior of these compounds during the electrodeposition process. One of the factors determining the final properties of the deposit is the molecular weight of the polyethoxylated additive. More homogeneous deposits are obtained when the molecular weight is between 1000 and 10000 g/mol.[6,7] Stoychev and Rashkov[8] established that the presence of polyethoxylated additive increases the overpotential during electrodeposition of copper in a sulfate bath. Similar results have been reported by Aragon, *et al*.[9] for the electrodeposition of tin.

Nuts & Bolts: What This Paper Means to You

For the moment, many plating processes depend on additives to make them work. Polyethylene glycol is one that is used in chloride zinc. Whether it works or not depends on molecular weight, and "8000" is just about right. In this work, the researchers, studying how PEG 8000 works, found that the additive orients the zinc crystals into certain alignments that help improve corrosion performance. The story is presented here.

The aim of the current work was to study the influence of polyethylene glycol (PEG) 8000 (molecular weight 8000 g/mol) on the morphology, corrosion resistance and electrodeposition mechanism of zinc in an acidic bath with a high chloride concentration.

Experimental Procedure

The effect of PEG 8000 on the electrodeposition of zinc was studied using an electrolytic bath with the following composition: 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3. The PEG 8000 concentrations studied were 0.0, 0.4, 0.8 and 1.2 g/L. All reactants were analytical grade. The solutions were prepared before every series of experiments using deionized water (resistivity 18 MΩ-cm). In all cases, the pH was adjusted to 5.0.

The electrochemical study was carried out in a conventional three-electrode cell. The working electrode was an AISI 1018 steel disc of geometrical area 0.037 cm^2 (.006 $in.^2$). A saturated calomel electrode (SCE) was employed as the reference electrode and a platinum wire was used as the counterelectrode. Prior to each experiment, the working electrode was polished to a mirror finish using 0.05 µm alumina. All experiments were performed under a nitrogen atmosphere. The temperature was imposed and maintained constant at 25°C (77°F) using a constant temperature circulator. The experiments were controlled using a potentiostat/galvanostat controlled by a personal computer running data acquisition software. The surface morphology of the deposits was studied using scanning electron microscopy (SEM).

Results

Thermodynamic Study

A thermodynamic study of the predominant zinc species in solution under a given set of working conditions was carried out using the graphical method proposed by Rojas, *et al*.[10,11] and thermodynamic formation constants reported in the literature.[12] Figure 1 shows a Pourbaix-type diagram (E = f(pH)) for the system Zn(II)''/Zn^0 in chloride media.

Zn(II)'' indicates the generalized second order species[10] of zinc: pZn' = 1.0 and pCl' = -0.45. The solid line represents the equilibrium of the redox pair Zn(II)''/Zn^0. The vertical dashed lines correspond to the boundary between predominant zones of Zn(II)'' species. It is observed that in the pH interval from 0.0 to 7.04 the zinc reduction process involves the redox pair $ZnCl_4^{-2}/Zn^0$, as is shown in the following equation:

$$ZnCl_4^{-2} + 2e^- \rightarrow Zn^0 + 4Cl^- \qquad (1)$$

The conditional potential associated with this reaction ($E'ZnCl_4^{-2}/Zn^0$) can be evaluated using Equation 2, obtained from the Pourbaix-type diagram, which is valid in the pH interval from 0.0 to 7.04, noted earlier.

$$\mathbf{E}'ZnCl_4^{-2}/Zn^0 = -1.01 + 0.12\ pCl' - 0.03pZn' \qquad (2)$$

For the experimental conditions used in this study, $E'ZnCl_4^{-2}/Zn^0$ has a value of –1.094 V(SCE) .

Voltammetric Study

In order to determine the effect of PEG 8000 on the zinc reduction process, a voltammetric study was carried out in the potential range from +0.8 to –1.6 V(SCE), with and without PEG 8000 in solution.

Voltammetry Without PEG 8000

Figure 2 shows a typical voltammogram obtained from a base solution without PEG 8000. During the cathodic scan a reduction peak (I_c) [E_{pc} = –1.2 V(SCE)] is observed, which is associated with the reduction of Zn(II) to Zn^0. In the anodic scan, an oxidation peak is observed (I_a). Previous studies[13] have demonstrated that the reduction process associated with the peak I_c is controlled by mass transfer. The voltammogram also shows that an inversion of the scan in the anodic direction (*i.e.*, a cross-over between the two scans is observed). This behavior is characteristic of processes in which a new phase is formed. The potential at which the cross-over occurs is referred to as the cross-over potential (E_{CO}).

The behavior of E_{CO} was studied using the potential switching technique, as reported in the literature[14,15] fixing the switching potential (E_λ) at the foot of the reduction peak. Figure 3 shows a typical voltammogram obtained under these conditions. It is important to mention that E_{CO} occurs at a non-zero current, probably because of the absorption of the species over the electrode surface. A similar behavior was observed by González, *et al.*[16] during the electrodeposition of silver.

When E_λ is successively inverted in the potential range from –0.9 to –1.08 V(SCE), E_{CO} has a constant value of –1.097 V(SCE). Fletcher, *et al.*[15] have proposed that when E_{CO} is independent of E_λ, the process of nucleus formation is controlled by charge transfer. Moreover, under these conditions E_{CO} can be assumed to be the conditional potential for the metal/ion system involved. The value of E_{CO} obtained using this assumption is very close to the value that was calculated in the thermodynamic study for the $ZnCl_4^{-2}/Zn^0$ system. These results suggest that the reduction process in the absence of PEG 8000 occurs via the reaction proposed in the thermodynamic study (Equation 1).

Voltammetry With PEG 8000

The concentrations of PEG 8000 studied were 0.4, 0.8 and 1.2 g/L. Figure 4 shows a typical voltammogram obtained from a solution containing PEG 8000. Two peaks are observed to form during the cathodic scan. With peak A—peak potential E_{PA} = –1.13 V(SCE)—the current density increases with increasing PEG concentration. At more cathodic potentials, a second reduction peak is observed—peak B, E_{PB} = -1.23 V(SCE). This peak is dependent on the PEG 8000 concentration. With inversion of the potential scan in the anodic direction, a cross-over characteristic of processes involving the formation of a new phase is observed. Moreover, in the potential range studied, only the oxidation peak (peak C) is observed during the anodic scan. Additional experiments inverting the direction of the potential scan in the anodic direction to different values of E_λ ($E_{PB} \leq E_\lambda \leq E_{PA}$) show that the current density of peak C depends on both reduction peaks (A and B).

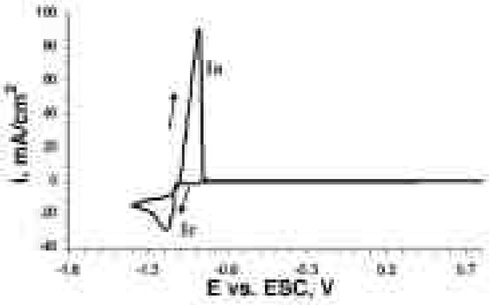

Fig. 2—Typical voltammogram obtained from a solution of 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3 over an AISI 1018 steel electrode, pH = 5.0, v = 30 mV/s.

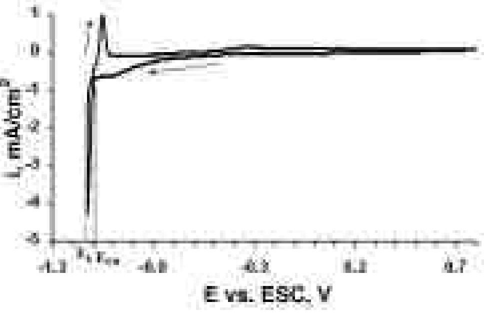

Fig. 3—Typical voltammogram showing the presence of the cross-over potential (E_{co}) and the switching potential (E_λ), from a solution of 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3 over an AISI 1018 steel electrode, pH = 5.0, v = 30 mV/s.

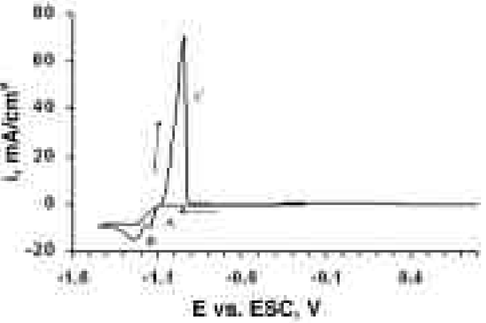

Fig. 4—Typical voltammogram obtained from a solution of 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3 + 0.8 g/L PEG 8000, over an AISI 1018 steel electrode, pH = 5.0, v = 30 mV/s.

It is important to mention that in the presence of PEG 8000, peak A appears at more anodic potentials than the peak I_c observed in the absence of PEG 8000, whereas peak B appears at more cathodic potentials.

The E_{CO} values obtained using the potential switching technique at different concentrations of PEG 8000 have a mean value of -1.097 V(SCE), which is independent of E_λ. This value is identical to that obtained in the absence of PEG 8000, -1.097 V(SCE), and quite similar to the conditional potential calculated in the thermodynamic study for the $ZnCl_4^{-2}/Zn^0$ system ($E'ZnCl_4^{-2}/Zn^0$ = -1.094 V(SCE)). These results indicate that the reduction process for peaks A and B involves the soluble species $ZnCl_4^{-2}$, and from this, it can be concluded that the compound PEG 8000 does not form complexes with Zn^{+2}.

A study of the overpotential ($\eta = Ep_{A,B} - E_{CO}$, ($Ep_{A,B}$ corresponding to the potential of peak A or B) at a range of PEG concentrations was carried out, the results of which are shown in Table 1. When the PEG concentration is 0.4 g/L, peak A is poorly defined, although an increase is observed in η compared with the value obtained in the absence of PEG. This change is associated with the formation of peak B.

At a PEG 8000 concentration of 0.8 g/L, peak A is well defined and its overpotential is less than that calculated in the absence of

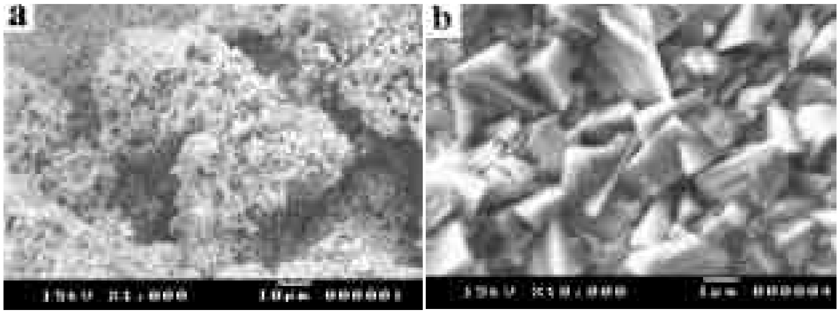

Fig. 5—SEM micrographs obtained from zinc electrodeposits on AISI 1018 steel from a solution containing 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3, at different potentials: (a) –1.075V vs SCE; (b) –1.2V vs SCE.

Table 1—Dependence of Nucleation Overpotential, η, Over AISI 1018 Steel Electrode on Concentration of PEG 8000

PEG 8000 g/L	E_{CO} V vs. SCE	E_A V vs. SCE	$\eta_A(E_A-E_{CO})$	E_B V vs. SCE	$\eta_B(E_B-E_{CO})$
0.4	-1.099	--------	--------	-1.245	-0.146
0.8	-1.097	-1.144	-0.047	-1.268	-0.171
1.2	-1.097	-1.138	-0.041	-1.234	-0.137

Without additive: E_p = -1.185; E_{CO} = -1.097; η_{wA} = -0.088

the additive, whereas the overpotential calculated for peak B is greater. A similar result was observed at 1.2 g/L PEG 8000.

These results show that the presence of PEG 8000 in solution modifies the mechanism of zinc deposition, from a reduction mechanism that involves only one stage to a mechanism that involves two stages (peaks A and B), associated with the reduction of the species $ZnCl_4^{-2}$. The overpotential is different for each stage, however, indicating the possible existence of active growth sites with different characteristics. In this way, PEG not only adsorbs over the electrode surface, but also modifies the mechanism of zinc deposition.

The way in which PEG 8000 acts is complex and involves other processes in addition to its partial adsorption over the electrode surface. Stoychev, *et al.*[17] have shown that polyethoxylated compounds can attract anions such as Cl^- that are adsorbed on the substrate surface, leaving free growth-active sites. This process would explain the behavior observed for peak A. In addition, polyethoxylated compounds have surfactant properties that cause the blocking of active sites, which lead to more energy being required for the discharge of the chlorine complex of zinc. This process explains the behavior of peak B and is responsible for the massive deposit of zinc.

Scanning Electron Microscopy (SEM)

SEM was used to analyze the morphology of the deposits obtained under different conditions. The deposits were grown under potentiostatic conditions until a charge of 5 C was obtained, stopping the potential scan in different zones of the voltammogram.

SEM Without PEG 8000

Figure 5a shows the morphology of a deposit obtained from a solution without PEG. The deposit was obtained at E = –1.075 V(SCE). The selected potential is more anodic than the potential of peak I_c in the corresponding voltammogram. Under these conditions, hydrogen evolution and the formation of a white precipitate over the cathode surface are observed. The formation of the white precipitate is associated with the local increase in pH caused by the production of hydroxyl ions during the reduction of water molecules.[18,19] The SEM analysis shows that the deposits have a porous structure that corresponds to the formation of zinc hydroxide adsorbed on the electrode surface, as was observed in the study using potential switching technique (see Fig. 3).

When the deposits were grown at E = –1.2 V(SCE) (Fig. 5b), corresponding to the maximum current density in the voltammogram, the SEM shows crystals of irregular size. Surface chemical microanalysis using EDX indicated that these crystals consist of pure zinc.

SEM With PEG 8000

Figure 6a shows the deposits obtained at E = –1.075 V(SCE) from a solution containing 0.8 g/L PEG 8000. The morphology is similar to that seen in the absence of PEG at the same potential, although the deposits are more compact. The deposits grown at more cathodic potentials show a different morphology that depends on the deposition conditions. The deposits were grown at the potentials at which peaks A and B formed during the corresponding cathodic potential scan.

When the concentration of PEG 8000 was 0.8 g/L, the deposits obtained at E = –1.13 V(SCE) (peak A) are made up of a few crystals in the form of groups of needles in nodules (Fig. 6b). Oriented crystal growth commences at this potential. When the deposition was carried out at E = –1.24 V(SCE) (peak B), corresponding to the massive deposition of zinc, hexagonal crystals oriented perpendicular to the substrate surface are observed (Fig. 6c).

PEG 8000, therefore, induces oriented growth of the crystals. The deposits that form in the presence of PEG 8000 are gray and compact. A similar behavior was observed at any PEG 8000 concentration within the range under study.

Corrosion Resistance

In order to determine the influence of PEG 8000 on the corrosion resistance of the zinc coatings, corrosion tests were carried out using electrochemical polarization. The deposits used for these tests

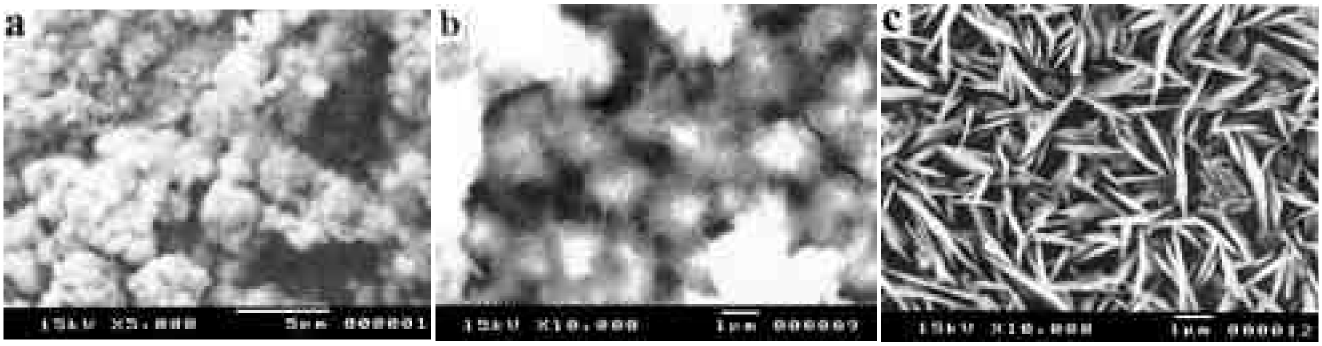

Fig. 6—SEM micrographs obtained from zinc electrodeposits on AISI 1018 steel from a solution containing 82 g/L $ZnCl_2$ + 208 g/L KCl + 25 g/L H_3BO_3 + 0.8 g/L PEG 8000, pH = 5.0, at different potentials: (a) –1.075V vs SCE, (b) –1.1V vs SCE, (c) –1.22V vs SCE.

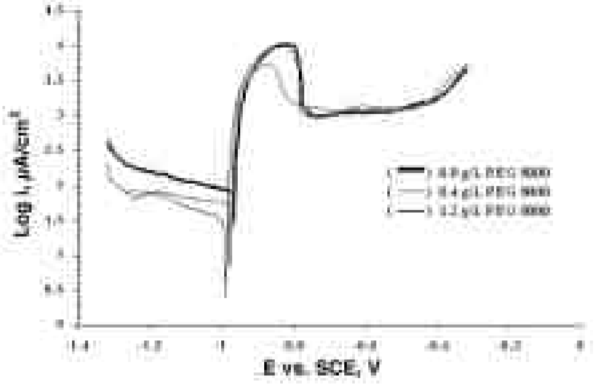

Fig. 7—Tafel polarization curves for zinc electrodeposited onto AISI 1018 steel at different concentrations of the additive PEG 8000.

were prepared in the presence of different concentrations of PEG 8000 by subjecting the solution to potentiostatic conditions (E = –1.28 V(SCE)) until a thickness of 12 µm was obtained. AISI 1018 steel of geometrical area 1 cm^2 (0.16 in^2) was used as the substrate.

The corrosion resistance was evaluated in a corrosive environment using a solution of 3.5 wt% NaCl, through which ultra-pure oxygen was bubbled for 1 hr prior to each experiment. The corrosion rate was determined according to ASTM G5, the standard method for electrochemical evaluation of corrosion. The potential scan (v = 0.166 mV/s) was begun at a potential 300 mV more cathodic than the corrosion potential (E_{corr}), and scanned in the anodic direction until an anodic current of 5 mA was observed.

Figure 7 shows the typical behavior of the resulting Tafel curves. An anodic peak is observed in the potential interval from –1.0 to –0.8 V(SCE). This peak is associated with the formation of a passive zinc oxide film. At more anodic potentials, between –0.8 and –0.42 V(SCE), a passive region is observed because of the passivating effect of the oxide film. Dissolution of the steel was subsequently observed at E = –0.42 V(SCE).

Table 2 shows the results of the evaluation of the corrosion parameters of the coatings. The corrosion rate decreased when the deposits were formed from solutions with higher concentrations of PEG 8000. The difference observed in the corrosion rate could be related to the structure of the deposits.

Conclusions

The mechanism of zinc reduction under working conditions, both in the absence and presence of PEG 8000, occurs via the redox pair $ZnCl_4^{-2}/Zn^0$, because the polyethoxylated compounds do not form complexes with zinc under these particular working conditions.

The compound PEG 8000 acts primarily on the electrode surface, modifying the energetic conditions of the active sites. PEG shows dual behavior—on the one hand, liberating active sites through the attraction of Cl^-, while on the other hand, blocking active sites through preferential adsorption. These processes induce the formation of active sites with different energies, and lead to the formation of zinc in a two-stage process that involves the complexed species $ZnCl_4^{-2}$.

The additive PEG 8000 also induces oriented growth in the zinc crystals. This behavior seems to be favored when the PEG 8000 concentration is greater than or equal to 0.8 g/L. Under these conditions, the corrosion resistance of the zinc deposits increases.

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Table 2—Corrosion Parameters in 3.5 wt% NaCl Solution for Zinc Electrodeposits onto AISI 1018 Steel*

PEG 8000 g/L	Thickness µm	E_{corr} V vs. SCE	i_{corr} µA/cm^2	Corrosion Rate mil/yr
0.0	10.0	0.95	70.79	1.06
0.4	10.0	0.97	50.11	0.75
0.8	10.0	0.99	28.12	0.42
1.2	10.0	0.99	27.05	0.40

*Obtained at different concentrations of the additive PEG 8000.

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