

Wettability Effect on the Corrosion Kinetics of Iron Anodes in Sulfuric Acid Solutions

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ABSTRACT

The interdependence of electrode wetting and electrode corrosion rate was studied for the iron anode in aqueous sulfuric acid solutions. The effects of acid solution concentration and surface-active agents on the corrosion rate and passive-active transition current oscillation amplitude were measured. The results show that both are dependent on the electrode wetting. The electrode wettability is shown to change as a function of time which results in convective liquid displacement around the electrode and on variable corrosion rates.

Organic surfactants are widely used as polishing agents in electroplating, as corrosion inhibitors, and in polarography. The investigation of surfactants on solid surfaces is thus important for understanding the interaction mechanisms between the electrolyte and the corroding metal surface. Initially, one has to consider that surfactants may well strengthen or weaken the passivating layer of metals (1). One of the main points of discussion here is the nature and structure of the protective film formed in aqueous environments at the electrode-electrolyte interface (2, 3). Films of reaction intermediates and/or inhibitors are formed. These layers act as so-called interphasic inhibitors (4) retarding mainly the mass-transfer controlled cathodic corrosion reaction.

A second point to be considered is the effect of surfactant on the dissolution rate of electrodes in the active state (5). Many surfactants are low molecular weight substances which affect the wetting and spreading behavior of liquids without noticeably changing either the liquid viscosity or other solute diffusion coefficients. The use of surfactants allows an assessment of the relative contributions of the diffusion-limited reactions and of capillary phenomena, as affecting the iron electrode dissolution.

Since surfactants modify the solid-liquid interface, we have decided to examine the interdependence of electrode wetting, passive-active transition potential, and electrode dissolution rate. This was done by measuring electrode corrosion rate, passive-active transition current oscillation amplitude, and electrode-electrolyte contact angles for iron electrodes in contact with aqueous sulfuric acid solutions of different concentrations. The electrode corrosion rate was also measured in the presence of various detergents in 1M H₂SO₄ solutions.

Experimental

Corrosion current measurements.—Voltammograms and corrosion rate experiments were performed in an air tight, two-compartment glass cell shown schematically in Fig. 1. The counterelectrode compartment was separated from the main compartment by a glass frit. A cylindrical platinum gauze 10 × 5 cm² was used as the counterelectrode. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials are referred to SCE. The reference electrode was placed close to the working electrode. The working electrodes were pieces of 0.15 mm diam iron wire (99.99% pure from Carlo Erba), washed with methanol and bi-distilled water prior to use. The (fully immersed) electrode height was 0.1 cm, placed 1 cm below the liquid level. In these experiments, there was not any iron-air interface. Ultrapure argon (grade U) from White Martins was bubbled through the cell at all times except during the corrosion rate measurement and voltammogram recording. Sulfuric acid was from Merck. The following surface-active substances were used: CTAB (ce-

tyltrimethylammonium bromide, Hopkin & Williams); TTAB (tetradecyltrimethylammonium bromide, Sigma); BDHACl (benzyltrimethyl n-hexadecyl ammonium chloride, BDH); SOS (sodium octyl-sulfate, courtesy of Dr. I. Robb from Unilever Research, Port Sunlight); SDS (sodium dodecylsulfate, Aldrich). The polyacrylamide sample was CFN-10, a high MW, nonionic product from Crosfield. All measurements were conducted at 25°C. The solutions were bubbled with ultrapure argon for 30 min prior to use. Air-formed oxide films on iron wires were removed by cathodic polarization at -0.50 vs. SCE for 30 min under argon. After cleaning, a passive film was formed, by means of a potential step from -0.50V to +400 mV vs. SCE. The corrosion rates were recorded at -150 mV vs. SCE, obtained by means of a potential step from 400 mV vs. SCE; the potentiostat used in this work has been described previously (6). The electrode current was recorded by a Hewlett-Packard 7100 BM strip chart recorder and a Hewlett-Packard 7004 X-Y recorder. Cathodic scans were obtained for various concentrations of H₂SO₄ solutions, to which surfactants were added. These curves were obtained with a sweep rate of -2 mV/s starting at ca. 400 mV vs. SCE.

Contact angle measurements.—Contact angle measurements were done in an airtight Plexiglas box, as shown in Fig. 2, under a positive argon pressure (20 mm of water). Inside this compartment there was a cylindrical cell (1) with a diameter of ~5 cm and 10 cm height which contained deaerated H₂SO₄ solutions as shown in Fig. 2. A coiled platinum wire was used as a counterelectrode, and a saturated calomel electrode (SCE) was the reference electrode. The air-formed oxide film was removed by an initial electrochemical reduction at -0.50V vs. SCE for 10 min. After the oxide removal the electrode was removed from this solution and rinsed intensively with deaerated twice-

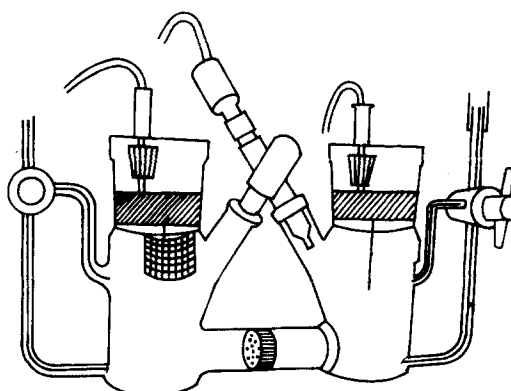


Fig. 1. Air tight two-compartment glass cell with a diameter of ~5 cm and 15 cm height used for voltammograms and corrosion rate experiments.

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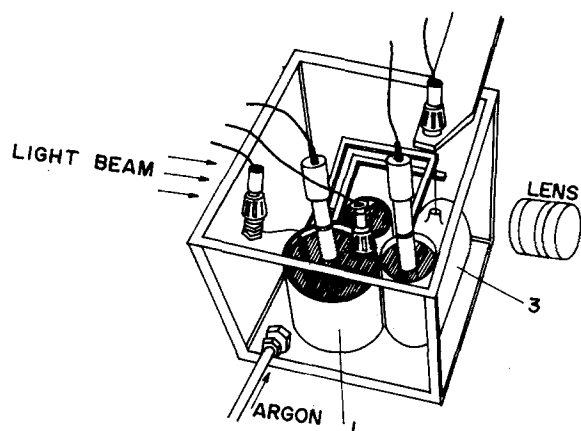


Fig. 2. Airtight Plexiglas box containing a cylindrical cell (1) with a diameter of ~ 5 cm and 10 cm height used for removal of oxide formed under air; a reservoir (2) for collecting the rinsing solution; and an U-shaped cell (3) for contact angle measurements.

distilled water. After electrode rinsing and optical observation of its surface, the electrode was dried inside the box in an argon atmosphere for 30 min. Microscopic observations at the electrode-liquid interface were also performed using an Olympus 52-TR-BR stereoscope with a maximum magnification of 160X.

The electrode-electrolyte contact angles were measured in cell (3) as shown in Fig. 2. This cell has been previously described (6). It consists of a U-shaped Pyrex glass cell. At one end there is platinum gauze 10×5 cm² shaped into a cylindrical surface acting as a counterelectrode; a saturated calomel electrode (SCE) acts as the reference electrode. At the other end of the U-shaped cell a meniscus is formed and adjusted by moving the liquid at the first end. All experiments were performed with solution deaerated with U-argon for at least 30 min, and at a temperature of 20°C.

The contact angle at the iron tip as a function of electrode voltage is obtained via measurements of the liquid interface image projected on a wall, 5m away from the apparatus. The projection system is adjusted so that it gives a magnification of 100X, resulting in a precision in the measurement of meniscus displacements of around $\pm 10^{-4}$ cm.

Results and Preliminary Discussion

Surfactant effect on current-potential curves.—Iron electrode voltammograms were obtained in aqueous 1M H₂SO₄, to which surfactants were added, in order to investigate the passive-active transition voltage region. Cationic surfactants have a drastic effect on these voltammograms, as shown in Fig. 3. In the case of 0.5% TTAB (Fig. 3a), oscillations are suppressed; on the other hand, the effect of 0.25% CTAB is to decrease oscillation amplitude (Fig. 3b). In the presence of this surfactant, oscillations separate two active regions, instead of separating active from passive potential regions (compare to Fig. 3c). Iron electrodes, in the presence of both surfactants, are still active at potentials well above 280 mV, which is the active-passive transition potential in aqueous, 1M H₂SO₄.

As the active-to-passive electrode transition is due to the formation of an iron oxide layer at the electrode surface, we conclude that cationic detergents destroy this coating or, at least, require higher potentials for their formation. Anionic and nonionic detergents have little effect, on the electrode voltammograms.

Surfactant effect on the iron electrode anodic currents at constant voltages.—Iron electrodes were cathodically deoxidized and polarized at -150 mV vs. SCE. The current was measured as a function of time: it decreases slowly, as described in Fig. 4a. When the same procedure is followed but detergents are added to 1M H₂SO₄ solution, a different behavior is observed (Fig. 4a, b): (i) initial anodic currents are lower (3–4 mA, as compared to 11 mA), in the presence of various detergents, and show little dependence on the detergent type used; (ii) anodic currents tend to increase,

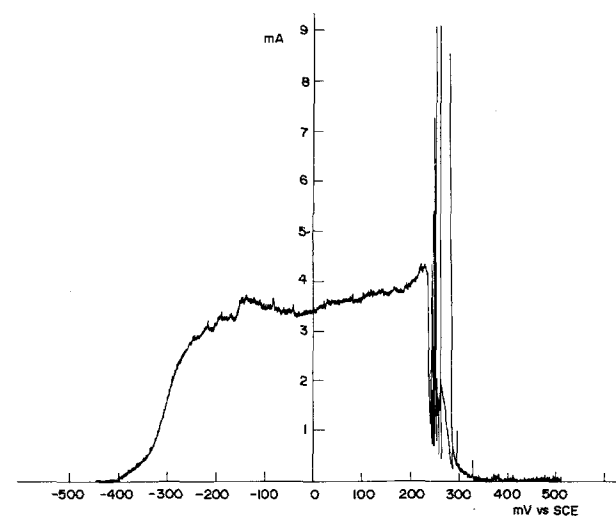
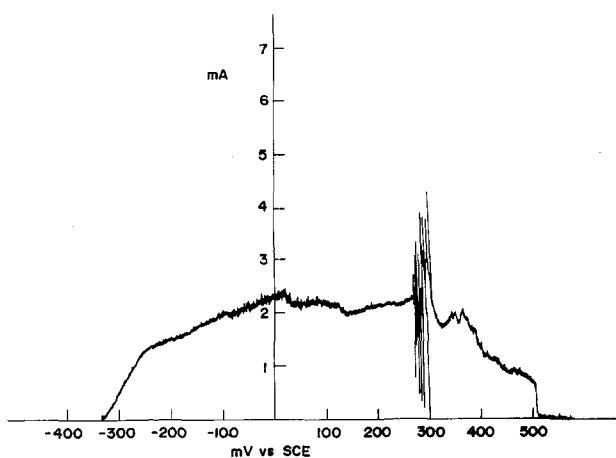
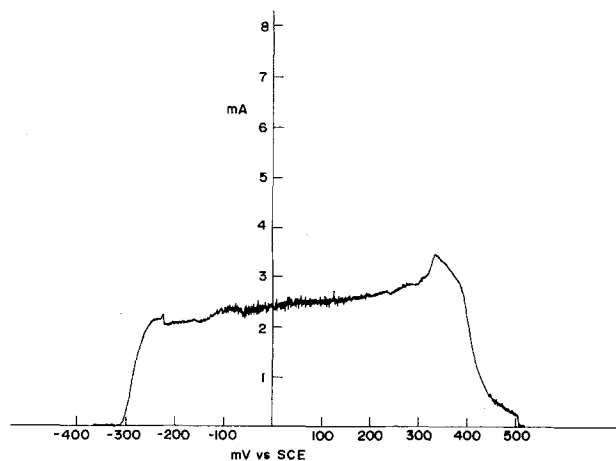


Fig. 3. Voltammograms of Fe in 1M H₂SO₄ aqueous solutions at 25°C; scanning initiated at 500 mV vs. SCE with a sweep rate of 2.0 mV/s; (a, top) 0.5% TTAB; (b, center) 0.25% CTAB; (c, bottom) no detergent added.

in the first minutes of reaction; (iii) anodic current vs. time curves depend on the detergent concentration. Figure 5 shows a plot of the dissolution current for various concentrations of CTAB; and (iv) a maximum is observed in electrode current vs. detergent concentration plots, at fixed reaction times as shown in Fig. 6, drawn from data in Fig. 4 for $t = 2$ min.

These results (i–iv) clearly indicate that the active iron anode current is affected by detergents in a complex way. Decreased current at zero time is due to surfactants adsorbing at the electrode: this should decrease the metal exposed area, thus decreasing the reaction rate. As the reaction proceeds, its rate depends on the rate of reactant and

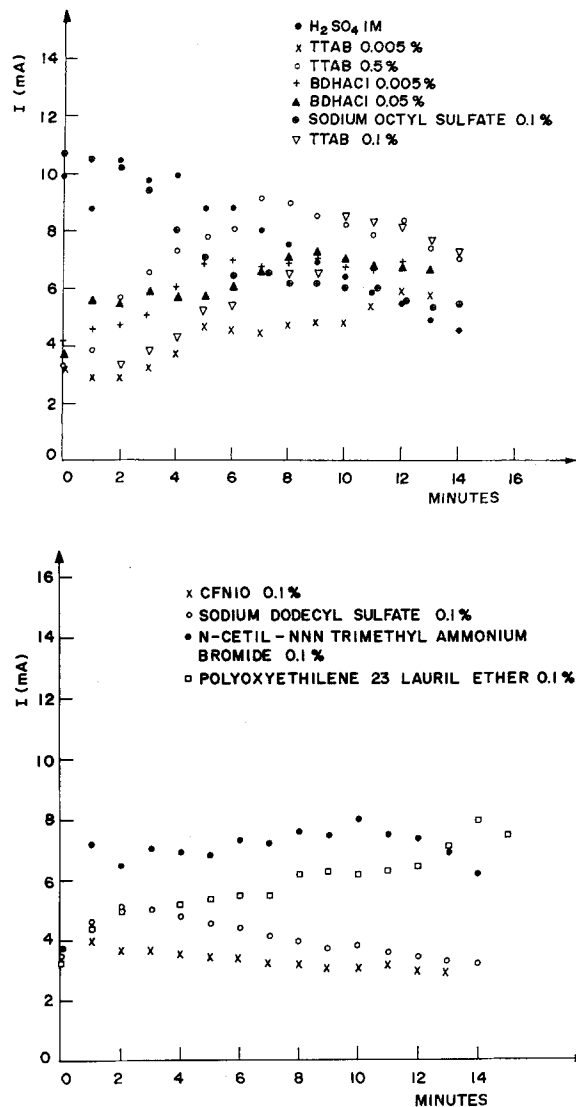


Fig. 4. Electrodissoolution current for iron electrode polarized at 150 mV vs. SCE in 1M H_2SO_4 aqueous solutions and for various surfactants.

products movement, to and from the electrode-electrolyte interfacial region. We shall come back to this point, after examining some other results.

Surfactant effect on current spike amplitude.—Detergents also affect the current spike amplitude at the active-passive transition voltage. The variation of the first current oscillation peak height as a function of surfactant concentration for TTAB is plotted in Fig. 7a and for CTAB in Fig. 7b. Peak amplitude is a measure of reaction extent and, indirectly, of metal-electrolyte contact area. Therefore, we assume that possible factors decreasing peak height are: incomplete metal coating removal, depletion of reagent (sulfuric acid) in the metal-electrolyte interface, effectiveness of the newly formed oxide layer as a barrier at low thicknesses.

Effect of sulfuric acid concentration on iron dissolution rates.—The effects observed in the presence of detergents indicate that interfacial tensions or stresses (considering that one of the phases is a solid) play an important role, in current oscillations and dissolution rates. Since metal/electrolyte/metal (oxide) coating interfacial tensions should also be affected by acid concentration, we have examined this effect on the time-dependent dissolution current amplitude at +150 mV vs. SCE. The initial contact area (electrode-electrolyte) was $4.7 \times 10^{-3} \text{ cm}^2$. The results are shown in Fig. 8. Current amplitude (at fixed time $t = 0$) vs. concentration curves display a maximum. Figure 9 shows that iron corrosion rates are greatest at intermediate acid concentrations.

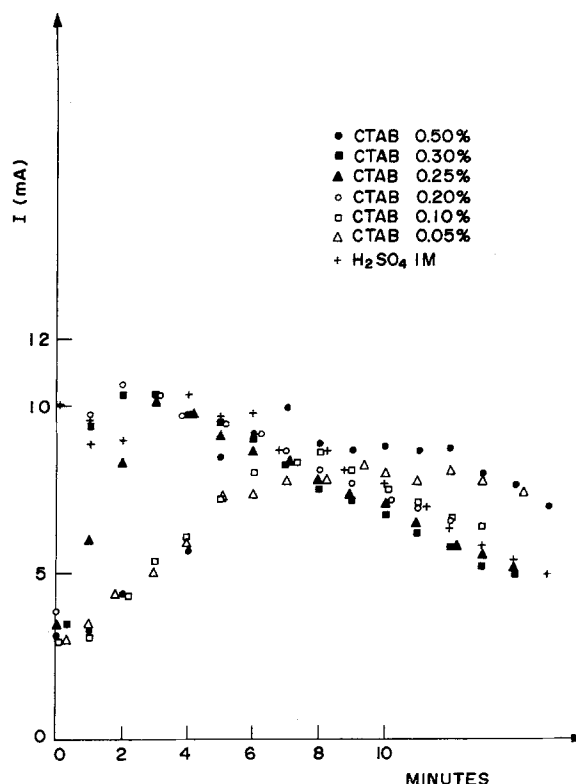


Fig. 5. Electrodissoolution current for iron electrodes polarized at 150 mV vs. SCE in 1M H_2SO_4 aqueous solutions for various concentrations of CTAB.

Effect of sulfuric acid concentration on the current oscillation amplitude.—Voltammograms were obtained for various H_2SO_4 aqueous solution concentrations. Figure 10 shows a plot of amplitudes of the most anodic current spike obtained in the voltammograms vs. H_2SO_4 solutions concentrations. Current amplitude dependence on concentration shows the same functional relations obtained for the corrosion current.

Effect of sulfuric acid concentration on electrode wetting.—Iron electrode wettability was evaluated by measuring contact angles between electrode and electrolyte as a function of time for various H_2SO_4 solution concentrations. Initially, the oxide formed under air was removed by polarizing the electrodes at -600 mV vs. SCE , in a separate cell. The removal of the oxide formed under air is important for obtaining the contact angle between bare iron metal and the solution. As the reaction goes on, the electrode surface is being constantly renewed.

The results are shown in Fig. 11a-e for 0.1, 0.3, 0.5, 1, and 2M H_2SO_4 solutions, respectively. The measurements are

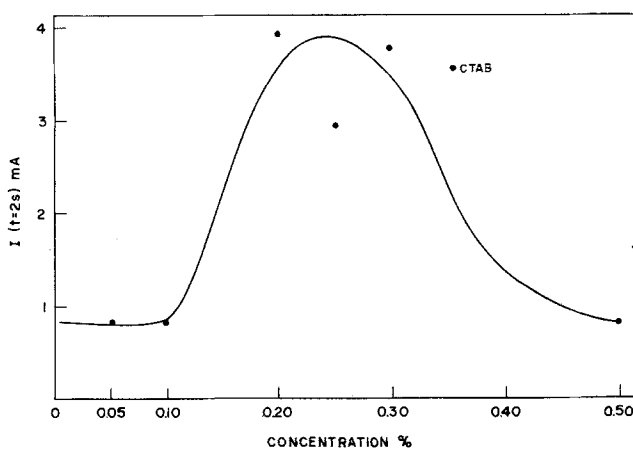


Fig. 6. Electrodissoolution current for iron polarized at +150 mV vs. SCE, 2 min after the reaction onset.

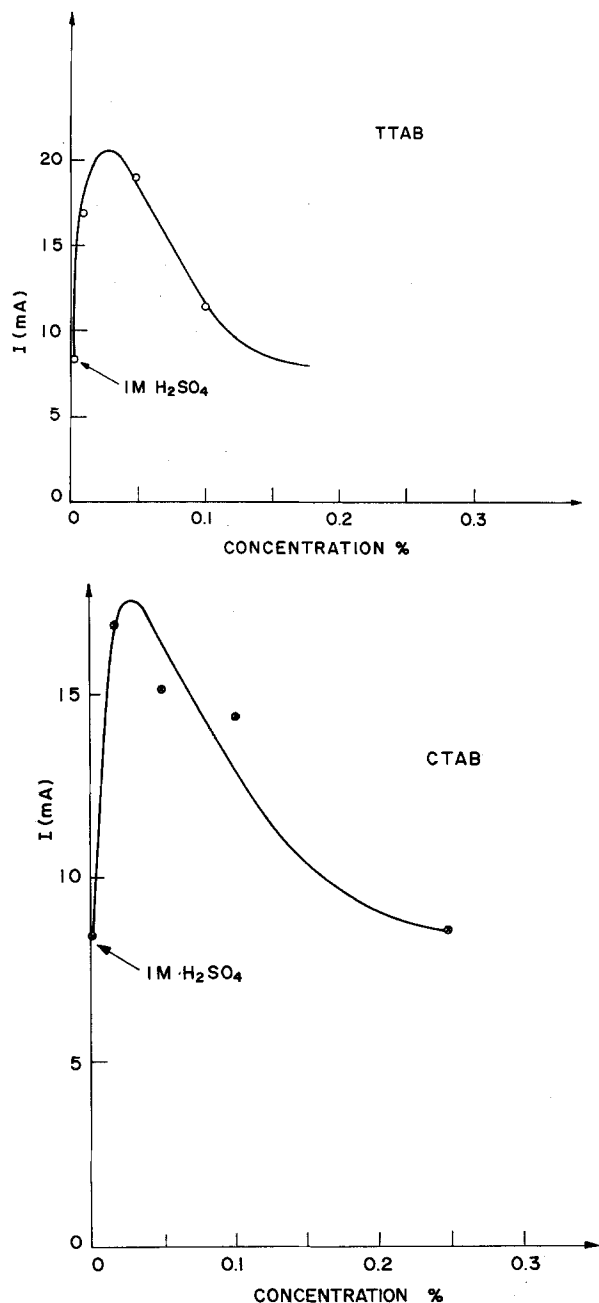


Fig. 7. First current oscillation peak height as a function of surfactant concentration in 1M H_2SO_4 aqueous solution, obtained in a cathodic scan starting at +500 mV vs. SCE with a scanning rate of 2 mV/s; (a, top) TTAB, (b, bottom) CTAB.

very reproducible except for very high acid concentrations (2M). At the onset of the experiment ($t = 0$) we obtain the contact angle for the bare metal and the electrolyte solutions. As the reaction goes on, it modifies the region around the electrode by the presence of the reaction products and consequently the contact angle changes. The contact angle curve was monitored up to 10 min after the process initiation. The maximum variation of wettability with time is for 0.5M H_2SO_4 solution.

Discussion

Previous work from this group pointed to the correlations between electrode activity and electrode coverage with Teflon (7), and to electrical and capillary phenomena in the iron/aqueous sulfuric acid anode (6); in this paper, we show that there is an interdependence between electrode corrosion rate and electrode wetting.

We believe that these correlations may be understood, if we acknowledge that electrode reactions are interfacial reactions whose rate depends primarily on the extent of electrode metal-electrolyte contact. Reagent access is en-

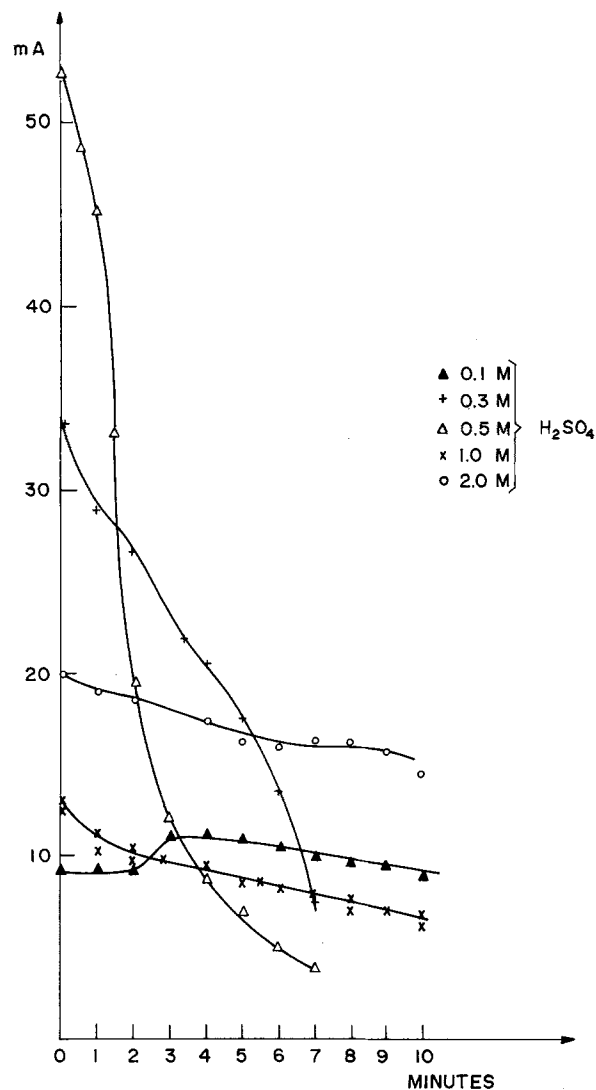


Fig. 8. Electrodeposition current for iron polarized at +150 mV vs. SCE in various sulfuric acid concentrations, as a function of time.

hanced by fast reaction product removal from the interface as this prevents the access of fresh reagent. Reagent and product mass transfer to and from the interface are increased if any kind of convective liquid displacement sets on around the electrode, which can be created by interfacial tension gradients $\Delta\gamma$ according to the Marangoni effect: this effect is the carrying of bulk material through motions energized by surface tension gradients (8). We plotted in Fig. 11 the variation of the surface ten-

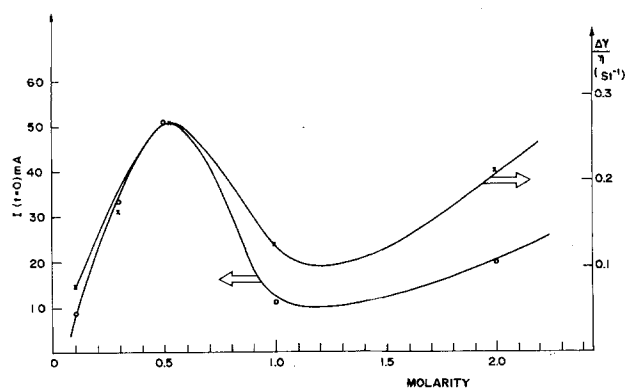


Fig. 9. Electrodeposition current for iron polarized at +150 mV vs. SCE in various sulfuric acid concentrations, obtained from Fig. 8 for $t = 0$ (reaction onset). $\Delta\gamma/\eta$ is plotted as a function of sulfuric acid concentrations where $\Delta\gamma = \cos \theta_1 - \cos \theta_2$; $\cos \theta_1$ is the electrode wettability at the reaction onset, $\cos \theta_2$ is the electrode wettability 1 min after (from Fig. 11), and η is the solution kinematic viscosity.

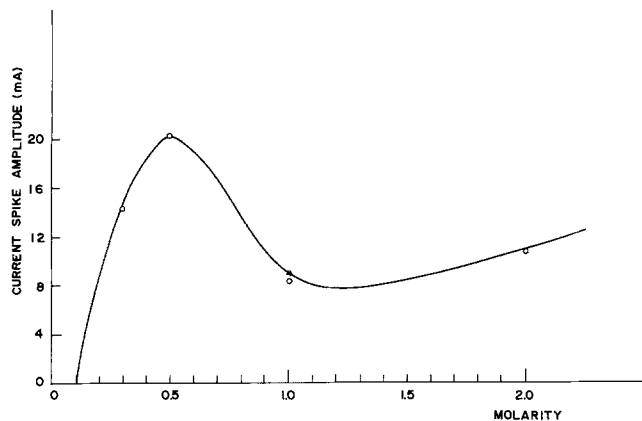


Fig. 10. Most anodic current spike (obtained in cathodic scans starting at +500 mV vs. SCE and a sweeping rate of 2 mV/s) as a function of sulfuric acid concentrations.

sion as a function of sulfuric acid concentration divided by the kinematic viscosity. This curve shows the same functional behavior as the electrocorrosion current as a function of sulfuric acid concentration, indicating that $\Delta\gamma$ is the driving force for solid and solution mass transfer around the electrode. It is thus a decisive factor in the rate of the corrosion reaction. The same functional behavior is obtained by plotting the current spike amplitude as a function of molarity (Fig. 10).

Interfacial tension at an immersed electrode surface may be nonuniform (and thus a gradient may exist) due to three reasons: electrode (chemical, morphological, and electrical) inhomogeneity, electrolyte composition nonuniformity (due to nonuniform product accumulation and convection); and electrode coating with solid or colloidal reaction products. Interfacial tension gradients are thus to be expected and should lead to movement of solid particles and liquid, in the interfacial region. We can evaluate these gradients by observing the contact angle vs. time curves, in Fig. 11. These curves refer to bare, clean metal

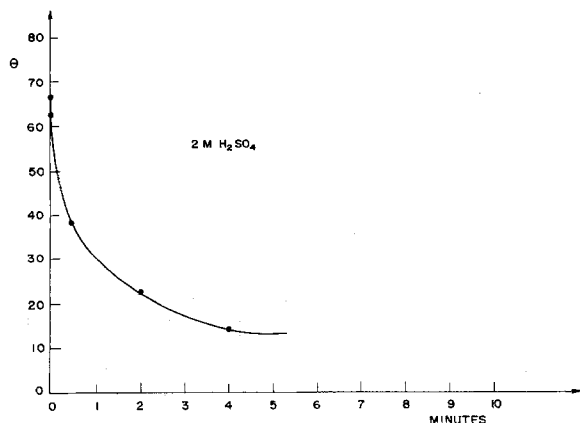
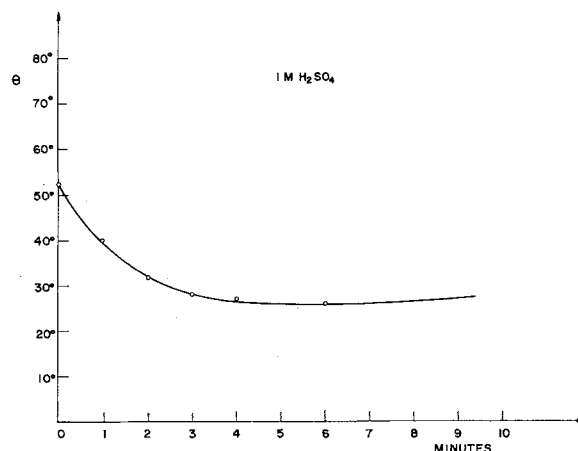
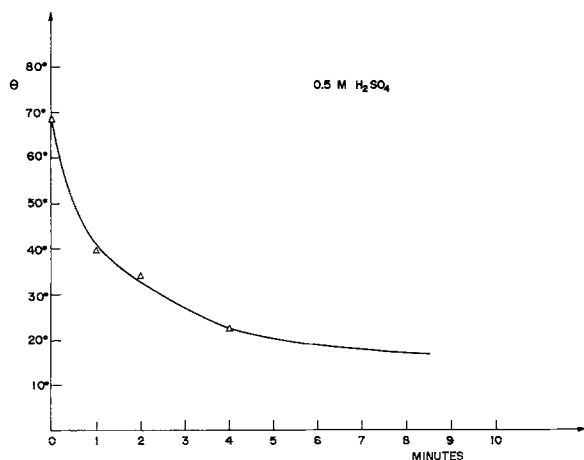
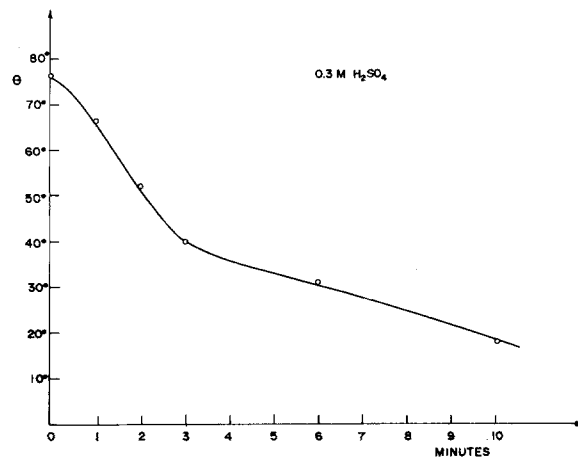
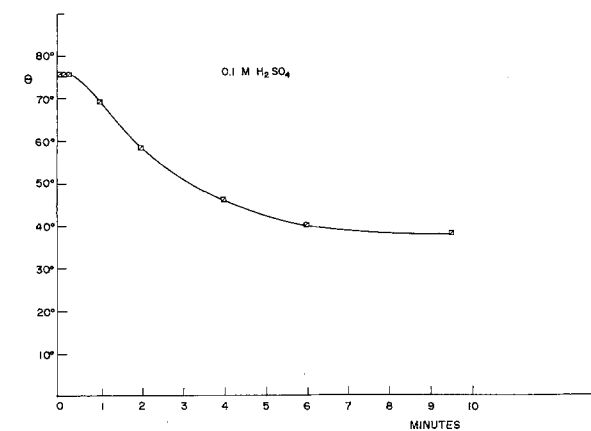


Fig. 11. Iron electrode sulfuric acid solution contact angles as a function of time; (a, top left) 0.1; (b, top right) 0.3; (c, middle left) 0.5; (d, middle right) 1; (e, left) 2M H_2SO_4 .

surfaces being transformed by contact with reagent. Zero-time contact angles are 50°-80° and drop to values below 30° in a few minutes. As wetting changes with time, we have to acknowledge that it will also change from point to point, at the electrode surface, because the extent of reaction and the degree of product accumulation at different points cannot be the same. Two contiguous regions may thus present differences in θ amounting to some tens of degrees, depending on their actual compositions.

Now, we should consider the concentration effects. Added surfactants or acid will adsorb at the existing solid surfaces: both bare metal and reaction products (iron oxide, iron sulfate). Extent of adsorption will depend on the nature of the surface and on absorbate concentration. In the case of surfactants, we should expect that high concentrations will lead to saturation or to hemimicelle formation, so that the various solid surfaces will have their surface tension differences covered up. This means that low detergent concentration may both increase or decrease interfacial tension gradients; high concentrations should decrease them. Liquid circulation around the electrode and corrosion rates should vary accordingly, as indeed we found in this work.

Regarding sulfuric acid concentration changes, there is a major difference: we should not expect cover up of solids, due to the fact that at least bare patches of metal should not be saturated with the reactive acid. Indeed, the corrosion rates *vs.* acid concentration curve has a maximum, but the corrosion rate is still high at the higher acid concentration.

A major difficulty which is already seen in the process of creating a detailed model to evaluate convective liquid displacement around the electrode is that we need values for $\Delta\gamma$ and thus for interfacial tensions; since we are looking at reaction transients, the relevant γ 's are dynamic, not equilibrium ones.

Manuscript submitted April 6, 1987; revised manuscript received Feb. 26, 1988.

Instituto de Física and Instituto de Química, UNICAMP, assisted in meeting the publication costs of this article.

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A Mathematical Model for the Electrodeposition of Alloys on a Rotating Disk Electrode

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ABSTRACT

A general multiple electrode reaction model for electrodeposition of alloys on a rotating disk electrode is presented. Included in the model are mass transport equations with the effect of ionic migration, Butler-Volmer kinetic rate expressions, and the mole fractions of the individual components in the solid state. The model shows that the effect of ionic migration is important and that plating variables such as applied potential, pH, and bulk concentration can be included. Two examples (Ni-P and Ru-Ni-P) are used to illustrate the predictions of the model.

One of the less expensive and most popular techniques for preparing alloys is electrodeposition (1). Electrodeposition from aqueous electrolyte solutions has considerable advantages over the other means of production of alloys because the technique is relatively easy, technically simple, fast and productive, and for certain systems is the only method of preparation. Therefore, it is desirable to determine the operating conditions under which a certain alloy can be made. A mathematical model which includes the effect of ionic migration is presented here as an aid to do this.

Two purely theoretical cases are presented here as examples of how the model may be used. These are the electrodeposition of Ni-P and Ru-Ni-P. Nickel-phosphorus alloys have received considerable attention (2-10) due to their ferromagnetic and metallic properties. The structure of Ni-P was investigated by Tyan and Toth (7); they found that alloys with a phosphorus composition greater than Ni-P_{0.144} appeared to be amorphous. The dependence of the amorphous structure on the contents of the plating bath is supported by the work of Okamoto and Fukushima (5) and by Vafaei-Makhsous (6). Analysis of the data from these experimental studies suggests that a theoretical model may be helpful in determining the operating conditions of a cell

to produce such an alloy. The electrochemical reactions that are used here for electrodeposition of Ni-P are shown in Table I. The chemical species added are assumed to be NiSO₄, H₃PO₂. The evolution of hydrogen is included and is written as shown because it is the reaction that occurs as the potential of the working electrode is made more and more negative. To demonstrate the versatility of the model, the electrodeposition of a tertiary system Ru-Ni-P is also studied theoretically. The plating bath for this alloy contains NiSO₄, NiCl₂, H₃PO₂, and RuCl₃. Table II lists the electrochemical reactions that are assumed to participate in the deposition of Ru-Ni-P. The electrochemical system used to model these processes is that for a rotating disk electrode (RDE), which is used because of the simplicity of the system and its well-understood hydrodynamics (11, 12).

Table I. Reactions for Ni-P deposition

No.	Electrochemical reaction	Standard electrode potential, (V) ^a
1.	Ni ²⁺ + 2e ⁻ → Ni	-0.23
2.	H ₃ PO ₂ + H ⁺ + e ⁻ → P + 2H ₂ O	-0.51
3.	2H ⁺ + 2e ⁻ → H ₂	0.00

^aTaken from Ref. (30).

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