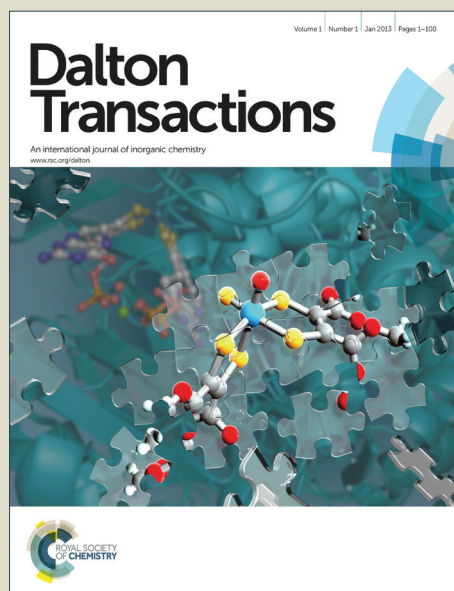


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Electrode Reactions of Iron Oxide-Hydroxide Colloids

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Small-sized FeO(OH) colloids stabilised by sugars, commercially available for the clinical treatment of iron deficiency, show two waves during cathodic polarographic sweeps, or two current maxima with stationary electrodes, in neutral to slightly alkaline aqueous medium. Similar signals are observed with Fe(III) in alkaline media, pH > 12, containing citrate in excess. Voltammetric and polarographic response reveal a strong influence of fast adsorption processes on gold and mercury. Visible spontaneous accumulation was also observed on platinum. The voltammetric signal at more positive potential is caused by Fe(III)→Fe(II) reduction, while the one at more negative potential has previously been assigned to Fe(II)→Fe(0) reduction. However, the involvement of adsorption phenomena leads us to the conclusion that the second cathodic current is caused again by Fe(III)→Fe(II), of species more shielded than the one causing the first wave. This is further supported by X-ray photoelectron spectra obtained after FeO(OH) particle adsorption and reduction on a gold electrode surface. The same analysis suggests that sucrose stabilising the colloid is still bound to the adsorbed material, despite dilution and rinsing.

Introduction

Fe(III) in the form of colloidal preparations^{1,2} has been used in the clinical treatment of acute iron deficiency since 1949.³ Coagulation is prevented by saccharides that stabilise the aggregates in which Fe(III) ions are linked by oxide and hydroxide. Phases of FeO(OH), Fe₂O₃ and Fe₃O₄ can be found in the colloidal particles.⁴⁻⁷ In preparations with sucrose, they have small diameters, 2.5 to 7 nm,^{8,9} a mass of 21 to 46 kDa¹⁰ and a poorly defined structure.^{11,12} The typical storage pH for the colloidal suspensions is 10-12, and for intravenous application they are diluted without substantial decomposition at least for one hour, despite the pH being lowered. Fe(III) in these materials is accessible to voltammetric reduction, and an electrochemical method to determine their Fe(II) content has been established.¹³⁻¹⁵ It is surprising that particles of the size mentioned, containing more than hundred Fe ions, produce easily detectable electrolysis currents, even with a dropping mercury electrode. This finding does not fit the expected low diffusion rate, compared to molecular species.

However, voltammetric signals have been obtained from Fe₂O₃ particles on tin-doped indium oxide electrodes¹⁶ and from hydrous iron oxide particles on boron-doped diamond electrodes.¹⁷ It was shown that the unexpected high currents originate from spontaneously adsorbed particles on the electrodes, which are both non-metallic.

A reagent that also stabilises Fe(III) against precipitation in alkaline solution is citrate. It is one of the strongest simple Fe(III) chelators (log K_{MLH} = 24.8¹⁸), and inhibits precipitation of iron oxides up to pH = 13.¹⁹ Polarographic studies of Fe(III) preparations with pH ≥ 12, containing citrate in excess, have been reported, and the waves obtained were assigned to the reduction of mononuclear coordination compounds.^{20,21} Ten years later, the oligo- and polymeric nature of iron citrate complexes at high pH was revealed.^{5,7,18,19} Cathodic

polarographic waves produced by alkaline Fe(III) solutions containing sucrose or mannitol were also assumed to originate from Fe(III)-sugar complexes.²²⁻²⁴

The polarographic traces obtained by reduction of Fe(III)-citrate mixtures at pH > 11 have much in common with those from alkaline colloidal Fe(III) preparations; both show only two major waves, though the one at more positive potential often lacks the clean sigmoid shape expected for a well-defined compound. The colloidal suspensions produce these polarograms even at pH = 7 and after dilution,^{10,13-15} demonstrating their stability. The position of the more positive wave is found between -0.6 and -0.9 V vs. SCE or Ag/AgCl, the more negative one between -1.0 to -1.5 V vs. SCE or Ag/AgCl. The actual positions depend on pH, electrolyte concentration, chelator or saccharide type and its concentration. The two waves have invariably been assigned to the reductions Fe(III) $\xrightarrow{1e^-}$ Fe(II) and Fe(II) $\xrightarrow{2e^-}$ Fe(0), under diffusion control, based on the half-wave potential positions. If we assume that the reductions take place in direct consecution and concern the same species diffusing towards the polarographic electrode, the limiting current of the second wave should have two times the value of the first. However, this relation is often not fulfilled. The limiting current of the second wave is frequently overestimated because it adds to the current rise caused by the solvent reduction that sets in at very negative potentials. We found that this lack of stoichiometric correlation between the two waves is also responsible for inconsistencies in modern quantitative analyses of colloidal Fe(III) by differential pulse polarography.¹⁰ In turn we studied Fe(III) colloids by using the direct approach of linear sweep voltammetry in order to obtain a better picture of the processes at the working electrode. The aim was to obtain a justifiable explanation for the persistent

non-stoichiometric two-wave pattern in voltammetric records from alkaline Fe(III) preparations.

Experimental

Reagents

Analytical grade potassium chloride and citric acid were obtained from Sigma-Aldrich, analytical grade iron(III) nitrate, sodium hydroxide, sodium acetate and nitric acid were purchased from Merck Millipore. These reagents were used without further purification. Samples of colloidal iron sucrose (Venofor[®]), iron sucrose similars (Ferri[®], FerMytan[®]) and a colloidal maghemite preparation (Feraheme[®]) were provided by Vifor Pharma. The physical properties of these materials have been described.⁸⁻¹² Ultrapure water was prepared with a Merck Millipore Advantage unit. pH was adjusted by adding concentrated NaOH solutions and monitoring with a glass electrode.

Electrochemistry

Linear sweep or cyclic voltammetry was carried out with a 7 mm² polycrystalline Au disc and a Metrohm hanging mercury drop electrode. The usual drop surface area was 3 mm². Electrolyte was prepared according to a standardised method,¹³ 1.1 M NaCH₃COO, which has pH = 8.5. The reference electrode was a Metrohm Ag/AgCl, 3 M KCl, E = 0.20 V vs. NHE. The counter electrode was a 1 cm² platinum sheet. Currents were measured with an AMEL 2049 potentiostat, controlled by an AMEL 568 function generator. Scan rates were 0.1 Vs⁻¹ and 4 Vs⁻¹. Data were acquired by a computer equipped with a 12-bit analog to digital converter board. DC Polarography was carried out with a Metrohm Autolab PGSTAT 128N and a Metrohm 663 VA stand equipped with a Metrohm Multimode mercury drop electrode.

Voltammetry procedures: the Au electrode was thoroughly polished with moist aluminium oxide powder and rinsed with water before each run. 10 ml of electrolyte were purged for 300 s with 99.99% nitrogen. The nitrogen atmosphere was maintained during the experiments. A small volume sample containing the colloid corresponding to 0.30 to 0.36 M Fe(III) was added to the electrolyte from a glass syringe, such that the resulting final concentration of Fe(III) was 1.43 mM, as required for the polarographic standard method for iron sucrose characterisation. Records were taken immediately after sample addition to the electrolyte. The Au electrode was always cleaned between scans with a polishing cloth to remove eventual deposits, except when adsorption was studied. The Hg electrode was renewed by extruding fresh drops. Polarograms were recorded with solutions prepared the same way and identical concentrations. Fe(III) citrate solutions were prepared by adding 0.36 M Fe(NO₃)₃ to stirred citrate solutions to obtain a final Fe(III) concentration of 2 mM.

X-ray Photoelectron Spectroscopy

Samples of adsorbed iron sucrose were prepared on freshly polished sheets of platinum and gold. These were covered by the same solutions as used in the voltammetric experiments, 1.43 mM total Fe(III) in 1.1 M NaCH₃COO. Platinum sheets were exposed for 1 hour without application of an external

potential. Gold sheets were connected as working electrodes to the Autolab PGSTAT and submitted to repeated cathodic linear potential scans, 60 times every 30 s, from -0.1 V to -1.3 V vs. Ag/AgCl, at a rate of 0.1 Vs⁻¹. After these treatments, the metal sheets were thoroughly rinsed with distilled water and dried for 3 days over phosphorous pentoxide in a desiccator. The spectrometer was a Sigma 2 model from Thermo Scientific. It uses the Al K_α line for excitation, and the angle of detection was 50°. Path energy was set to 100 eV for survey spectra and to 25 eV for narrow range spectra. The sheets were first transferred into the ante vacuum chamber and then into the main chamber of the instrument after 24 h.

Results

Linear sweep and cyclic voltammetry

Iron sucrose preparations are routinely tested by a standardised differential pulse polarography (DPP) procedure in order to determine the Fe(II) content.¹³⁻¹⁵ Therefore, we used the supporting electrolyte of this approach but recorded linear sweep voltammograms (LSV) with stationary Hg and Au electrodes. DPP would not allow to determine charge integrals and to obtain information whether the electrode reaction is controlled by adsorption or diffusion. We also omitted nitrogen purging recommended after iron sucrose addition¹⁴ because dioxygen introduction by adding a small volume to the anaerobic electrolyte is negligible. This allowed us to probe electrochemical properties immediately after homogenization. The potential scan was started directly after iron sucrose mixing and repeated several times. We always found two cathodic waves, an extremely broad one at more positive potential and a sharper one at more negative potential (Figure 1). With each of the working electrodes, the broad wave starts at -0.5 V vs. Ag/AgCl, and the sharp wave has a peak at -1.3 V vs. Ag/AgCl for Au and -1.2 V vs. Ag/AgCl for Hg respectively. Both current maxima increase with every cycle and therefore originate from adsorbed materials. On Au, the signal grows substantially for 30 minutes and then the process slows down, but does not stop entirely even after 4 hours. During the accumulation, the sharp peak continuously shifts towards more negative values, while the maximum of the broad wave remains in place. Most interesting, the increase stagnates shortly between 2 and 10 minutes and then accelerates again. Presence of the iron colloid also facilitates solvent reduction, more pronounced on Hg than on Au, if we compare signals with blank currents in electrolyte (Figure 1). The two waves can be correlated with the two differential pulse polarographic peaks obtained with the standard method.¹⁴ If we calculate the integrals of both waves from four subsequent scans on the Au electrode, it becomes clear that they cannot be stoichiometrically related (Table 1).

Table 1. Ratio of transferred charge on the Au electrode[†]

Scan no. (Figure 1A)	1	2	3	4
Wave 1				
Wave 2	1.93	1.22	1.01	0.90

[†] Transferred charge for the two waves was determined from the current between -0.5 V and -1.3 V vs. Ag/AgCl. For details see supplementary material.

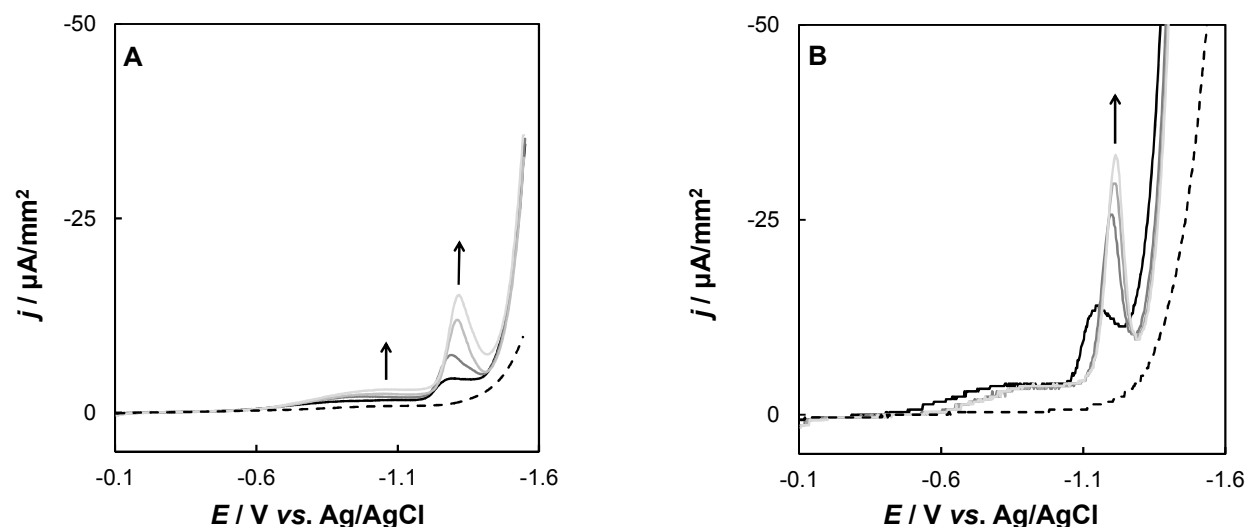


Figure 1. Linear sweep voltammograms of 20 μl iron sucrose added to 10 ml 1.1 M sodium acetate, obtained on an Au electrode (A) and on a Hg electrode (B). Sweep rate: 0.1 Vs^{-1} . Four successive scans, time between records is 30 s. The dashed line represents the current without iron sucrose added.

If the first wave would represent $\text{Fe(III)} \xrightarrow{1e^-} \text{Fe(II)}$, and the second $\text{Fe(II)} \xrightarrow{2e^-} \text{Fe(0)}$ from the same deposit, the ratio of integrals should be 0.5 and constant. This contradiction, together with the concomitant changes in shape, supports an assignment to subsequent reductions of different Fe(III) species instead of two different oxidation states. The combined findings can only be explained by the accumulation of iron colloid on the electrode surface. We demonstrated that substantial particle adsorption on Hg takes place even during the polarographic drop life of 0.4 s used for iron sucrose characterization.¹⁴ The current peak shapes obtained under this condition are unambiguously typical for reactions of material confined to the electrode surface.²⁵ Details can be found in supplementary materials. The adsorption can even be made visible to the naked eye by exposing a platinum sheet for one hour to an iron sucrose solution of 1.43 mM Fe(III). The metal acquires a brown-golden hue that can only be removed by concentrated acids or mechanical abrasion.

In cathodic voltammetric scans of a freshly prepared acidic solution of $\text{Fe(NO}_3)_3$, which was added to the 1.1 M acetate electrolyte of pH = 8.5, a broad wave starting at -0.3 V is obtained with an Au electrode, similar to iron sucrose, while no sharp second wave is found. A strong cathodic current appears below -1.2 V, and this cannot be caused by a $\text{Fe(II)} \xrightarrow{2e^-} \text{Fe(0)}$ reduction alone, because it is much higher than two times the first wave (Figure 2). The current wave between -0.8 V and -1.2 V found in absence of Fe(III) is obtained in the 1.1 M acetate electrolyte even after extensive polishing of the Au electrode.

All voltammograms obtained on Au and Hg electrodes exhibit increased hydrogen evolution currents at more positive potential when a Fe(III) sample is added to the electrolyte (Figures 1 and 2). Since Fe(0) is not soluble in Hg, it has to remain on the surface if formed, like on Au. This electropositive product is capable to sustain a catalytic cycle:

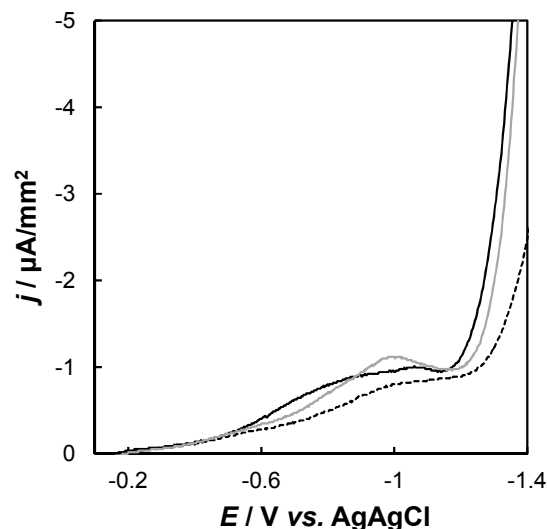
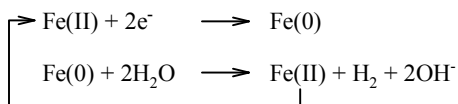


Figure 2. Linear sweep voltammograms of 20 μl 0.36 M Fe(III) nitrate in 1.1 M sodium acetate, Au electrode, sweep rate 0.1 Vs^{-1} . Dashed line: without Fe(III), solid grey: after Fe(III) addition, solid black: After 5 min.

Polarography

In order to obtain an impression of the timescale on which Fe(III) colloid adsorption affects electrode behaviour, we studied polarography of iron sucrose compared to Fe(III) in the same concentrated acetate solution. We recorded DC polarograms instead of applying the differential pulse technique of the standard method, because this conceals the limiting current levels which are the true measure for concentration in polarography. Two waves were obtained from freshly dissolved Fe(III) and iron sucrose of the same total Fe(III) concentration, see Figure 3. The drop time of the polarographic electrode was varied to reveal eventual influences of adsorption phenomena. The values of the limiting currents in Figure 3A and 3B clearly express the different degree of condensation; they are distinctly smaller for iron sucrose. In both cases, deviations from the appearance of diffusion determined polarograms and the predictions of the Ilkovič^{26,27} equation are observed: with iron

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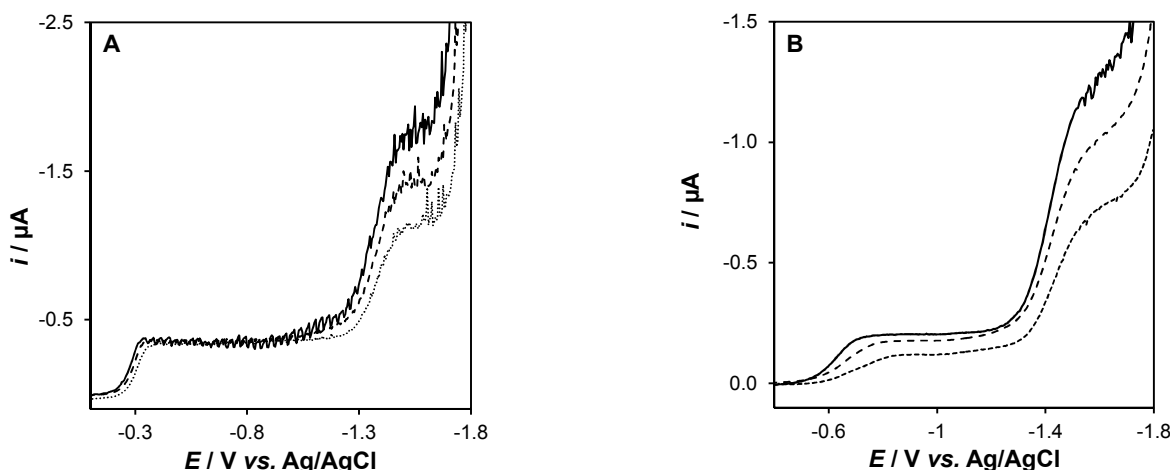


Figure 3. DC polarograms of A: 20 μl 0.36 M Fe(III) in 10 ml 1.1 M CH_3COONa ; B: 20 μl iron sucrose in 10 ml 1.1 M CH_3COONa . pH adjusted to 7 with HNO_3 . Drop time: solid line 1.6 s, dashed line 0.8 s, dotted line 0.4 s.

sucrose both limiting currents are not proportional to $t^{1/6}$ and the half-wave potentials shift towards more positive values with increasing drop time. With freshly prepared acidic Fe(III) solution added to the acetate electrolyte, the half-wave potentials do not shift as much as with iron sucrose, but the limiting current of the more positive wave is not at all a function of drop time. With increasing drop time, the flow rate of the mercury becomes unstable, resulting in short-term current variations. Furthermore, for both samples the shape of the transition from the first limiting current into the second wave changes with drop time. All these phenomena can be attributed to on-going adsorption processes, because they depend on the contact time of the electrode with the solution.

X-ray Photoelectron Spectroscopy

When dilute 1.43 mM iron sucrose is allowed to deposit on a Pt sheet, it forms a visible brownish layer within an hour. After extensive rinsing and drying, the Fe 2p X-ray photoelectron spectrum represented by the dashed line in Figure 4 was obtained. The binding energies of the $p_{3/2}$ and the $p_{1/2}$ maxima are similar to those of freshly prepared FeO(OH) or goethite,^{28,29} and the satellite pattern fits an Fe(III) species.³⁰ The visible layer is so thick that Pt features are absent in the spectrum.

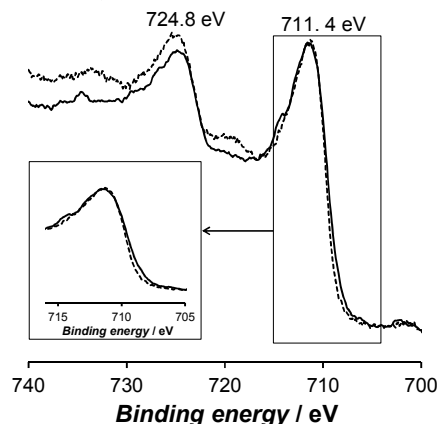


Figure 4. XPS Fe 2p region for FeO(OH) adsorbed on Pt (dashed line), and on Au with simultaneous exposure to reducing potentials (solid line).

When iron sucrose is allowed to adsorb to an Au sheet electrode and is concomitantly and repeatedly reduced by cathodic linear scans to -1.3 V vs. Ag/AgCl, the Fe 2p X-ray photoelectron spectrum shown as solid line in Figure 4 is obtained. It is again dominated by FeO(OH) characteristics. Obviously, only a small fraction of the adsorbed Fe(III) is reduced by electrolysis. The Fe(III) satellite of the $2p_{3/2}$ peak is diminished, and a weak satellite appears closer to the $2p_{3/2}$ maximum, the rising edge of which is shifted somewhat to lower energy, see inset in Figure 4. These changes indicate formation of some Fe(II) but do not provide evidence for deposition of metallic Fe which would produce a sharp peak at 707 eV.³⁰ Besides Fe and substrate related maxima, O 1s and C 1s peaks were observed. The C 1s signal is probably caused by co-deposition of sucrose. This implies that it could not be washed away with water and must be bound rather tightly to the FeO(OH) particles, which is in agreement with its colloid stabiliser properties.

Discussion

Signatures of the adsorption phenomena on metal electrodes we report here can be recognised in studies from 1946 on. The process was unambiguously identified much later, but for non-metallic electrodes.^{16,17} Polarographic experiments with iron(III) solutions of pH ≥ 12 , containing citrate in excess, date back to Lingane and Meites.^{20,21} Polarograms of 2 mM Fe(III) in presence of 0.5 M citrate are shown in Figure 5.²¹ The author stated that the second wave in trace (zz), at -1.5 V, is twice as high as the one at -0.9 V. However, the height of the wave at -1.5 V cannot be estimated easily because it combines with the solvent reduction current. Since this contribution is not limited by diffusion, we fitted an exponential function to provide a baseline (dotted curve). When the latter is subtracted from curve (zz), we obtain a normal polarographic wave (dashed curve) which has about the same height as the one at -0.9 V, but a steeper rise. Despite the stoichiometric ratio misfit, the wave at -1.5 V was assigned to $\text{Fe(II)} \xrightarrow{2e^-} \text{Fe(0)}$.

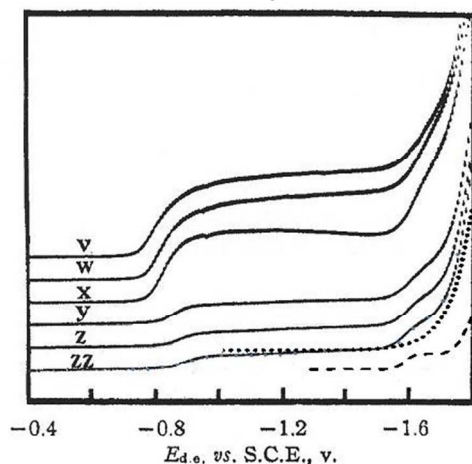


Figure 5. Polarograms of Fe(III) in 0.5 citrate, taken from Ref. ²¹, at pH (v) 12.02, (w) 12.25, (x) 12.55, (y) 12.78, (z) 12.89, (zz) 13.09. Concentration of total Fe(III) was always 2 mM. Dotted line: exponential fit for the solvent reduction current. Dashed line: net second wave, obtained by subtraction of the fitted baseline.

Similar interpretations were given for reduction waves caused by Fe(III) in alkaline citrate solution before²⁰ and basic Fe(III) solutions containing sucrose^{22,23} or mannitol.²⁴ Besides the expected shift of the first wave towards more negative potential, the polarograms in Figure 5 show two unusual variations with increasing pH. The height of the more positive wave decreases with increasing pH, and concomitantly the second wave develops, though the total Fe(III) concentration is constant. Since no immediate precipitation occurs, the current drop of the first wave can only be explained by a diminished diffusion coefficient or conversion to a different soluble or colloidal species. Possible causes are an increase in viscosity or in molecular size. It is not expected that a pH change by 0.5 will produce a substantial change in viscosity, so the iron containing species must have grown in size. Actually, switching from pH=12.5 to 12.8 appears to induce a fundamental change in Fe(III) species, supported by the visual observation that a yellow Fe(III) citrate solution of pH=12 turns colourless when brought to pH=13. The Fe(III) species in the yellow solutions are known to be oligomeric.^{7,18} Decolouration is most likely caused by replacement of citrate as a ligand by hydroxide. This hypothesis is further supported by the observation that after 10

or more minutes, a red precipitate starts to form. Another oddity in the polarograms is the shift of half-wave potential of the second wave towards more positive values with increasing pH, while the rise of the solvent reduction current moves towards more negative potential, as expected. We conclude that the second wave cannot be caused by dissolved mono- or oligonuclear Fe(II) species, because they would be stabilized against reduction as pH is increased. All observations point at the reduction of polynuclear Fe(III), the chemical potential of which is lowered upon adsorption to the electrode surface. We repeated some of these experiments with the stationary mercury electrode, instead of a polarographic setup, for better recognition of adsorption effects. As in the experiments of Lingane and Meites, a distinct second wave appeared only at pH ≥ 12 (Figure S2). An additional change was the sharpening of the first wave at pH 13, which is an indicator of beginning adsorption. Details can be found in supplementary material.

Iron sucrose and maghemite clusters are prepared at pH conditions similar to those of the polarographic studies on Fe(III), mentioned above, in presence of citrate or sugars. These colloidal suspensions are stable if stored at pH ≥ 10 and decompose only slowly when brought into neutral or slightly alkaline solution.⁸ Their cathodic sweep voltammograms obtained with stationary electrodes show a broad and irregular wave from -0.6 V to -1.1 V vs. Ag/AgCl and a well-defined one at more negative potential. We could show that both waves are caused by material adsorbed to the electrode (Figure 1). The integrals of the waves obtained on stationary electrodes do not support the stoichiometry of subsequent $\text{Fe(III)} \xrightarrow{1e^-} \text{Fe(II)}$ and $\text{Fe(II)} \xrightarrow{2e^-} \text{Fe(0)}$ reduction. Since the signals originate from an adsorbed layer, the ratio should be 1:2 because of mass conservation. We find 1:3 at very short electrode exposure time and fast scan rate (Figure S1), and a variation from about 2:1 to 1:1 with longer time and slow scan rate (Figure 1 and Table 1). The signal is obviously very dependent on the time the electrode is exposed to the sample. Therefore we conclude that we most likely observe reductions of different Fe(III) species instead of consecutive reduction of Fe(III) to Fe(0) via Fe(II). The shape and width of the first wave implies that the species causing the current are not uniform, while the second wave originates from a more homogeneous material. A similar two-peak pattern with adsorption signatures was obtained by cyclic voltammetry applied to a 1:1 mixture of Fe(III) and ethylenediaminetetraacetate, at pH = 9.³¹ A further sign of fast spontaneous adsorption of hydrous iron oxide particles are the considerable voltammetric currents obtained even with small total Fe(III) concentrations.

According to the standard determination method for Fe(II) in iron sucrose¹³⁻¹⁵ it is suggested to record differential pulse polarograms (DPP) of a sample diluted in sodium acetate electrolyte of pH = 8.5,¹³ or acetate buffer of pH = 7.¹⁵ The motivation is that Fe(II) is believed to cause toxic effects upon infusion of the drugs. It is not clear from the history why DPP was chosen as the standard technique, because sensitivity is not an issue here. Under the assumption that two different reactions are observed, the signals would be comparable only if they would exhibit identical kinetics. Two peaks, of which the first often shows various irregularities, are obtained, and from the difference of their heights the Fe(II) concentration is calculated. Differential pulse polarograms of iron sucrose similars reported by Toblli *et al.*¹⁰ show peaks of almost identical height, which leads to negative Fe(II) concentrations with the proposed computation scheme.¹³⁻¹⁵ We conclude that the electrode processes in this case are also affected by

adsorption, because except for the detection method, conditions are identical to our DC polarography experiments. No references of the origin of these methods are given in the US Pharmacopeia. We suppose that the assignment of the polarographic waves dates back to studies on alkaline Fe(III) solutions in presence of sucrose and mannitol.²²⁻²⁴ As in the Fe(III) citrate studies, it is assumed that the second wave is twice as high as the first, though it was admitted that this ratio could be obtained only under certain conditions. Křivánek, for example, interpreted the original 1:1 ratio he measured to be caused by a polarographic maximum of the second order in the first wave, and added gelatine to suppress it. In turn the current ratio changed to 1:2, but only for a limited Fe(III) concentration range.²²

One could argue that on the time scale of polarographic drop life, with the electrode surface being periodically renewed, adsorption would play only a minor role and truly dissolved material could be measured selectively. For the determination of Fe(II) in iron sucrose this would mean that only a small fraction of total Fe(III) and Fe(II) would be detected, because most of the colloid is intact even after hours. It can be decomposed quickly only in very acidic solution or by an excess of reducing agents.^{8,32} The contribution from Fe(II) would be higher than proportional because it is expected to be more soluble than Fe(III) at high pH. It turns out that hydrous iron oxide adsorption to metal electrodes is a fairly fast process that can influence polarographic response even at a drop time of 0.4 s, which is the typical low end available with commercial equipment (Figure 3B and supplementary material). Even freshly prepared Fe(III) added to slightly alkaline acetate solution shows severely anomalous polarograms (Figure 3A).

X-ray photoelectron spectroscopy of adsorbed iron sucrose revealed that Fe metal is not deposited during electrolysis at potentials down to -1.3 V vs. Ag/AgCl, a range in which the characteristic reduction waves of the material appear. The Fe 2p spectra imply that there is formation of Fe(II), but even this is far from being quantitative. We conclude that the iron sucrose particles are bound as entities to the surface, and only Fe(III) close to the electrode surface is accessible to electrochemical reduction. Moreover, it appears that a substantial amount of sucrose remains bound to the oxide particles after adsorption, because C 1s photoelectron emission is observed. This is somewhat surprising because it has been shown that sucrose is not coordinated directly to Fe(III) centres in the colloidal preparations.³³

We suggest that the two significant voltammetric waves, obtained by a cathodic scan in alkaline Fe(III) solutions (pH > 12) with chelators, or Fe(III) aggregated into clusters prior to dilution at lower pH, share the same origin. In some cases, the wave at more positive potential shows features that imply an origin from multiple but similar species. This is most easily recognised with differential pulse polarography.¹⁰ Fe(III) in a freshly prepared solution of pH = 8.5 initially does not show the pattern, but it starts to develop towards this after a few minutes (Figure 2). It cannot be entirely excluded that $\text{Fe(II)} \xrightarrow{-2e^-} \text{Fe(0)}$ contributes to the second wave in polarographic recordings, because if Fe(II) is added to a neutral or slightly alkaline iron sucrose solution in inert atmosphere, it contributes to the second current wave. However, the added Fe(II) is expected to be in a thermodynamic state not as stable as Fe(II) produced by reduction of Fe(III) bound in the particulate material.

Adsorbed FeO(OH) colloids on metal surfaces appear to contain at least two distinctly different states of Fe(III). This could be explained by a low weight fraction and clusters; or,

instead of a low weight component, the periphery of the clusters could represent the more easily reduced species. The two waves would be caused by the subsequent reduction of these two different major Fe(III) fractions to Fe(II). The material causing the second wave must contain Fe(II) produced at the potential of the first wave, but this conversion is incomplete because XPS shows mainly Fe(III) after many reduction cycles. The onset potential of the second reduction is probably so negative because the contact area to volume ratio becomes poor with increasing particle size. The observation that colloids larger than iron sucrose particles cause smaller currents is a sign that there is only a limited range of size that allows FeO(OH) particles to be electrochemically active without deliberate fixation on an electrode. Further investigations on small hydrous iron oxide clusters by electrochemical techniques could lead to new characterization methods of their redox properties and spontaneous adsorption/deposition behaviour.

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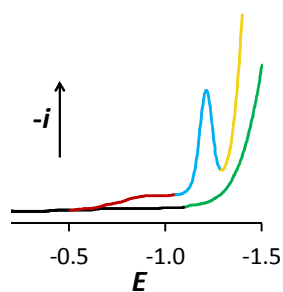
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Scalable TOC graphics (4 x 4 cm) and TOC text



FeO(OH) colloids adsorb spontaneously on conductors and undergo three subsequent voltammetric reductions.