

## Effects of Surface-active Substances on Polarographic Waves of Iron-diethylenetriaminepentaacetic Acid Complexes

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The polarographic behaviour of iron-DTPA complexes has been investigated. In the absence of surface-active substances the iron(III) complex is reversibly reduced at the dropping mercury electrode. Polarograms of mixtures of iron(II) and iron(III) yield a composite cathodic/anodic wave in the presence of excess DTPA. When Triton X-100 is added to the electrolyte, the cathodic wave is suppressed and a new irreversible wave appears at a more negative potential. In the presence of 0.1 % Triton the half-wave potential of this wave is constant independent of the pH of the supporting electrolyte. The potential at which the wave occurs is not related to the desorption of Triton, but the electrons acquire probably enough energy above  $-0.6$  V *vs* S.C.E. to reduce the complex on the solution side of the adsorbed Triton film. The wave is well defined and its height proportional to the concentration of iron(III) in the electrolyte. The analytical application of DTPA and Triton X-100 as masking agents in the determination of small amounts of iron in the presence of large amounts of copper is discussed.

In the course of a systematic study of the polarographic behaviour of diethylenetriaminepentaacetic acid (DTPA) complexes with several metals, we found that small amounts of surface-active substances seriously distorted the polarograms. When 0.01 % Triton X-100 was added to the supporting electrolyte the electrode reactions of the copper, lead, cadmium, and bismuth complexes were inhibited, the inhibition being caused by an adsorbed Triton film on the electrode. When the applied potential was increased above  $-1.3$  V *vs* SCE, the film was desorbed and the current rose to its original value.<sup>1,2</sup> The cathodic wave of the iron(III)-DTPA complex, however, was shifted only a few tenths of a volt upon addition of the same amount of Triton. The present work was carried out in order to investigate the polarographic behaviour of the iron DTPA complexes in presence and absence of surface-active substances.

## EXPERIMENTAL

*Apparatus.* Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional types of dropping mercury electrode and of electrolysis cell were used. The capillary characteristics, measured in 0.1 M potassium nitrate (open circuit) at a mercury height of 52.4 cm were:  $m = 2.998$  mg/sec and  $t = 3.62$  sec. An external saturated calomel electrode (S.C.E.), connected to the cell by means of an agar bridge, served as reference electrode. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis. All experiments were performed at  $25 \pm 0.1^\circ\text{C}$ .

The reversibility of the electrode reactions was tested by determining the slopes of the curves of  $\log i/(i_d - i)$  vs. the potentials. Corrections were made for the residual current and  $IR$  drop in the circuit. Data for the log plots were taken by manual operation of the polarograph, measuring the applied potential with a Hartmann and Braun potentiometer. Half-wave potentials of the reversible waves were taken from the logarithmic plots and were reproducible to  $\pm 2$  mV.

*Materials.* Diethylenetriaminepentaacetic acid was obtained from Geigy Chemical Corp., New York. A 0.05 M stock solution was prepared by dissolving 19.7 g DTPA and 6 g sodium hydroxide in distilled water and diluting to one liter. The solution was standardized against dipyrizozinethiocyanate according to Buděšinský.<sup>3</sup> Standard iron(III) solution was prepared by dissolving the appropriate amount of iron(III) nitrate in distilled water and diluting to one liter. The solution was standardized by the tin(II) chloride/permanganate method. The remaining chemicals were of reagent grade and used without further purification. 0.5 M acetate-, phosphate- and ammonia buffers were used as supporting electrolytes. The pH of the electrolytes was adjusted to desired value by addition of hydrochloric acid or potassium hydroxide and its pH was measured with a pH meter. Camphor, gelatin, and Triton X-100 (an alkyl-aryl-polyether alcohol obtained from Rohm and Haas Co.) were used as surface-active agents.

## RESULTS

*Wave characteristics in the absence of surface-active substances.* Polarograms of iron(III) in the presence of excess DTPA exhibit a well-defined wave, corresponding to reduction to the +2 state. No maximum occurred in the polarograms at any pH value. The plot of  $\log i/(i_d - i)$  vs. the potentials yield straight lines and the slope indicated a reversible one-electron reduction. A composite anodic/cathodic wave was obtained from mixtures of ferrous and ferric iron in DTPA medium (Fig. 1 A) and serves as further evidence for the reversibility of the system.

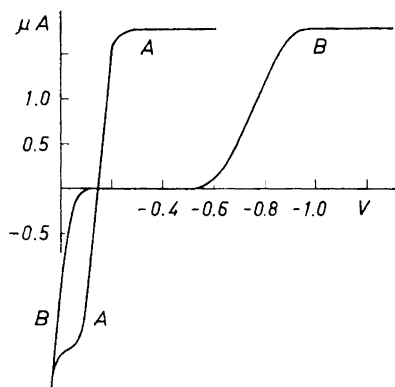


Fig. 1. Polarograms of mixtures of  $5 \times 10^{-4}$  M iron(II) and  $5 \times 10^{-4}$  M iron(III) in  $10^{-2}$  DTPA at pH 4.6. Concentration of Triton X-100: 0% (curve A) and 0.1% (curve B).

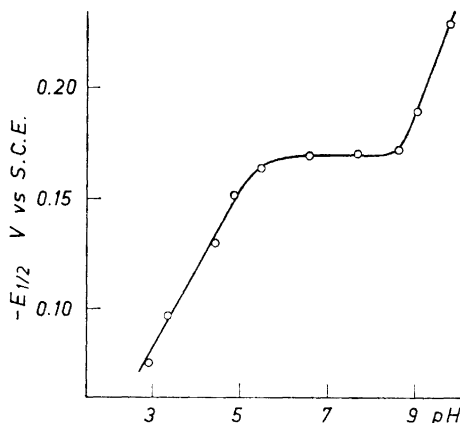
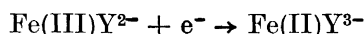


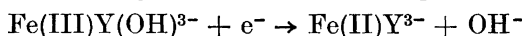
Fig. 2. Variation of the halfwave potential of the iron(III)-DTPA complex with pH of the supporting electrolyte.

By variations of the height of mercury above the capillary it was verified that the electrode reaction is diffusion controlled. The diffusion current increased linearly with increasing iron concentration at all pH values. The diffusion current constant measured in 0.2 M acetate buffer with pH 4.6, was  $I = 1.40 \pm 0.02$ .

The half-wave potential of the iron-DTPA complex shifted to more negative values with increasing pH of the supporting electrolyte. The observed half-wave potential of iron in the presence of a 10-fold excess of DTPA is plotted as a function of pH in Fig. 2. In the pH range 5.5 to 9 the observed half-wave potential was independent of both the DTPA concentration and the pH of the electrolyte. The electrode reaction in this pH range is therefore:



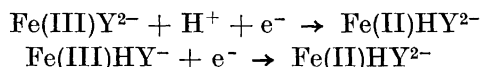
where  $\text{YH}_5$  denotes DTPA. When pH was increased above 9, the half-wave potential was still independent of the ligand concentration but it shifted 60 mV per pH unit to more negative values, according to the electrode process:



In the pH range 3 to 5.5 the slope of the plots of  $E_{1/2}$  vs. pH was 35 mV per pH unit, indicating that approximately one  $\text{H}^+$  is involved in the reduction of two iron(III) chelates. According to Vandegaer *et al.*<sup>4</sup> the following equilibrium exist in this pH range:



Hence, two reactions may occur at the electrode:



The number of  $\text{H}^+$  involved in the electrode reaction will consequently depend upon the ratio of the concentration of the two reducible species, and the average number of  $\text{H}^+$  involved in the reduction of two iron chelates will be one in accordance with the experimental value.

Mercury forms a very stable complex with DTPA and the accessible potential range in DTPA medium is limited on the positive side by the anodic dissolution potential of mercury. This potential is shifted to more negative values with increasing concentration of DTPA and increasing pH of the electrolyte. Hence, the maximum separation between the half-wave potential of the iron complex and the dissolution potential of mercury is obtained in acid medium and at a small DTPA concentration. At pH values above 6 the iron wave starts at the dissolution potential of mercury when DTPA is present in more than a ten-fold excess.

*Effects of surface-active substances.* Experiments showed that the presence of very small amounts of Triton X-100 had no influence on the current-voltage curve of the iron(III)-DTPA complex. When the Triton concentration was increased above 0.003 % in alkaline medium or above 0.007 % in acid medium, the diffusion current decreased and a new irreversible wave appeared at a more negative potential. An increase in the concentration of Triton resulted in an increase of the height of the second wave at the expense of the original one, the limiting current of the total wave remaining constant. As indicated in Fig. 1 the original wave is completely suppressed in the presence of 0.1 % Triton. A further increase in the Triton concentration had no influence on the current-voltage curve.

The half-wave potential of the second wave was independent of the excess DTPA in the electrolyte, but it shifted to more negative values with increasing amounts of Triton X-100 present and reached a limiting value at 0.1 % Triton. The observed half-wave potentials in acetate and in ammonia buffer are plotted as a function of the Triton concentration in Fig. 3. The experimental data indicate that the half-wave potential becomes independent of pH when 0.1 % Triton X-100 is present in the electrolyte.

The limiting current of the total wave appeared to be proportional to the concentration of iron, independently of the amount of Triton in the supporting electrolyte. Exactly the same diffusion current constant was obtained in the presence and in the absence of 0.1 % Triton X-100.

By variation of the height of mercury above the capillary it was verified that the electrode reaction is no longer diffusion controlled when Triton X-100 is present. The  $h$ -dependence was found to be intermediate between a diffusion controlled and a penetration controlled electrode reaction as in the case of adsorbed products.<sup>5</sup> The electrocapillary curves in Fig. 4 show that the addi-

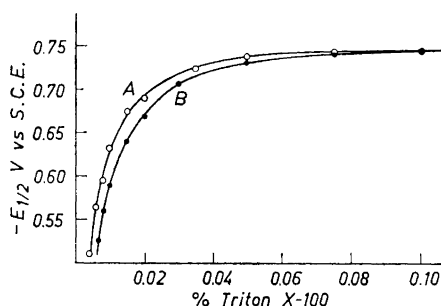


Fig. 3. Variation of the half-wave potential of the second wave with the concentration of Triton X-100. Supporting electrolytes: ammonia buffer pH 9.6 (curve A) and acetate buffer pH 4.6 (curve B).

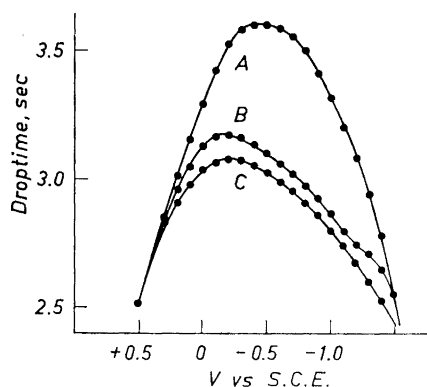


Fig. 4. Electrocapillary curves of  $10^{-3}$  M iron(III) and  $10^{-2}$  M DTPA in ammonia buffer pH 9.4. Concentration of Triton X-100: 0 % (curve A), 0.01 % (curve B) and 0.1 % (curve C).

tion of Triton X-100 to the supporting electrolyte causes a large decrease in the drop-time of the capillary and serve as further evidence for a strong adsorption of Triton.

The effect of camphor which also is strongly adsorbed at the dropping mercury electrode was investigated using acetate- and phosphate buffers as supporting electrolytes. In acid medium the iron DTPA wave was seriously distorted in the presence of camphor and no wave height or half-wave potentials could be measured. In neutral and alkaline medium, however, the original wave was completely suppressed upon addition of camphor and a well defined irreversible wave appeared at a more negative potential. In the presence of 0.1 % camphor the half-wave potential of this wave is  $-0.50$  V vs S.C.E. and the limiting current exactly the same as in the absence of camphor.

A few experiments with gelatin was also performed using acetate buffer with pH 4.6 as supporting electrolyte. The experiments indicated that the current voltage curve of the iron(III)-DTPA complex is not affected by the presence of 0.001 to 0.05 % gelatin.

#### DISCUSSION

The effect of Triton on the current-voltage curve of the iron(III)-DTPA complex may be explained in the following way. At low Triton concentrations the electrode is only partly covered with an adsorbed film. Hence, the electrode reaction may involve two processes. The original reversible reduction proceeds at the uncovered surface and a penetration controlled reaction at the covered surface. With increasing Triton concentration the surface coverage and the contribution of the penetration controlled reaction increases. Accordingly, the height of the original wave decreases and that of the second one increases. In the presence of sufficiently large amounts of the surface active agent, a complete coverage of the mercury surface is obtained from the beginning of the drop formation and only the second wave is observed on the polarogram. The shift in half-wave potential of the second wave with increasing amounts of Triton present (Fig. 3) is probably due to an increase in the thickness of the adsorbed film.

The potential range at which the second wave occurs is not related to a desorption of Triton. The desorption potential is approximately 0.8 V more negative than the potential at which the wave begins to rise. Apparently, at potentials more negative than  $-0.6$  V, the electrons acquire enough energy to reduce the iron(III) chelate to a lower oxidation state on the solution side of the adsorbed layer.

It is of interest to note that the presence of Triton affects not only the cathodic process but also the anodic one. The anodic wave of the iron(II)-DTPA complex is shifted to more positive values upon addition of Triton X-100. As indicated in Fig. 1 the anodic wave is completely masked by the dissolution wave of mercury when 0.1 % Triton is present in the electrolyte. Similar results have been reported by Tanaka *et al.*<sup>6</sup> who studied the effect of polyoxyethylene lauryl ether on the trioxalatoferrate system.

The effect of camphor in alkaline medium appears to be similar to that of Triton. The penetration current occurs, however, at more negative potentials in the presence of Triton than in the presence of the same amount of camphor, and may be due to a more tightly packed structure of the Triton film than that of camphor.

*Analytical application of Triton X-100 as a masking agent.* In non-complexing media copper is reduced at a more positive potential than iron and large amounts of copper interfere in the determination of the latter. In slightly acid EDTA medium, however, the iron(III) complex is reduced about 0.2 V in advance of the copper complex, and EDTA has been recommended as masking agent in the determination of small amounts of iron.<sup>7</sup> The cathodic wave of iron occurs at more positive potentials than that of copper also in DTPA medium. The separation between the two waves is, however, very small in acid medium, and at pH values above 6 the dissolution wave of mercury interferes when DTPA is present in a large excess.

When 0.1 % Triton X-100 is incorporated in a DTPA supporting electrolyte, the wave of the iron(III) complex occurs approximately 0.6 V in advance of the waves due to copper, cadmium, lead and bismuth which are reduced to the amalgams at the desorption potential of Triton. The iron wave is well-defined in this medium and the height of the wave is proportional to the concentration of iron. The half-wave potential is constant, independent of the pH of the electrolyte and well separated from the dissolution wave of mercury. Hence, DTPA and Triton X-100 should be very useful as masking agents in the polarographic determination of small amounts of iron.

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