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**POLAROGRAPHIC/VOLTAMMETRIC  
BEHAVIOUR OF COLLOIDAL SOLUTIONS.  
A BRIEF REVIEW**

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*Ultrasmall SnO<sub>2</sub>, TiO<sub>2</sub> and mixed Fe<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub> colloids in acidic solutions yield diffusion-controlled cathodic currents at polarized mercury electrodes, due to electroreduction of protons localized at the surface of the particles. The primarily generated hydrogen atoms reduce then the material of the particles chemically. Besides that as a parallel electrode reaction a direct reduction by electrons of Sn(IV), Ti(IV) and Fe(III), respectively, takes place.*

### **Introduction**

When atoms or molecules in solutions associate into higher aggregates, the particles thus formed lose the typical properties of individual chemical entities (molecules or ions) and behave as elements of solid phase. In polarography this was ascertained by Micka [1-5] who studied electroreduction of suspensions on the dropping mercury electrode; in order to observe the electrolytic current, he had to stir the solution during measurements so that the suspended particles could come into contact with the electrode. The dimensions of such particles are of the order of micrometers.

We had at our disposal solutions of particles thousand times smaller, of the dimensions of nanometers. These very small, so-called nano- or Q-particles [6], each of which consists of several hundred molecules, have to be prepared by a special procedure [7]; they form colloidal solutions which are optically transparent. Because of their small size, their diffusion coefficients are relatively large so that the diffusion-controlled currents due to their electrolytic reactions at the electrodes are of the order of magnitude of the currents obtained with true solutions of electroactive species.

Colloidal particles in general have the spontaneous tendency to continue increasing their size by aggregation and to sediment in the solution. This tendency can be slowed down considerably by addition of special stabilizers which themselves attach to the surface of the particles and prevent their close contact with each other. The currently used stabilizers such as sodium hexametaphosphate, poly(vinyl alcohol) [8], poly(ethylene glycol), Nafion or copolymer of styrene with maleic anhydride [9], with their big molecules prevent close contact of the particles not only with each other but also with the electrode and thus render them electroinactive. On the other hand, the ultrasmall colloids which we studied [10-13] were metal oxides  $\text{SnO}_2$ ,  $\text{TiO}_2$  and mixed  $\text{TiO}_2 + \text{Fe}_2\text{O}_3$ , and these can get stabilized by hydrogen ions in aqueous acidic solutions. The small hydrogen ions, localized at the oxygen atoms of the surface molecules of the oxide particle, not only stabilize the particle by repelling others electrostatically, but allow its approach to the electrode sufficiently close for the transfer of faradaic electrons to be accomplished, and, moreover, can participate themselves in the electrode reaction of the particle.

## **$\text{SnO}_2$ Colloids**

Figure 1 shows the comparison of cyclic voltammograms of tetravalent tin in true and in colloidal solution. The upper curve a corresponds to 1 mM  $\text{SnCl}_4$  in 1 M HCl saturated with  $\text{NH}_4\text{Cl}$ . In that medium tin(IV) forms hexachlorocomplex with the anion  $\text{SnCl}_6^{2-}$  which is partly reversibly reduced at mercury electrodes [14]; the shoulder on the positive side of the anodic peak is due to dissolution of the tin amalgam with formation of stannous oxide. The lower dashed curve b is obtained immediately after dissolution of  $\text{SnCl}_4$  to 1 mM concentration in 1 M  $\text{HClO}_4$  - only the small anodic peak (note the increased sensitivity!) indicates that the electroinactive  $\text{SnO}_2$  formed in the solution by instant hydrolysis gets partly reduced to tin amalgam at negative potentials when hydrogen ions are reduced at the electrode. However, on standing at room temperature the same solution undergoes further changes - the full curve c was obtained with the same solution after 3 weeks. The characteristic features of that voltammogram correspond to those typical for carefully prepared solutions of ultrasmall  $\text{SnO}_2$  colloids, such as is shown in Fig. 2.

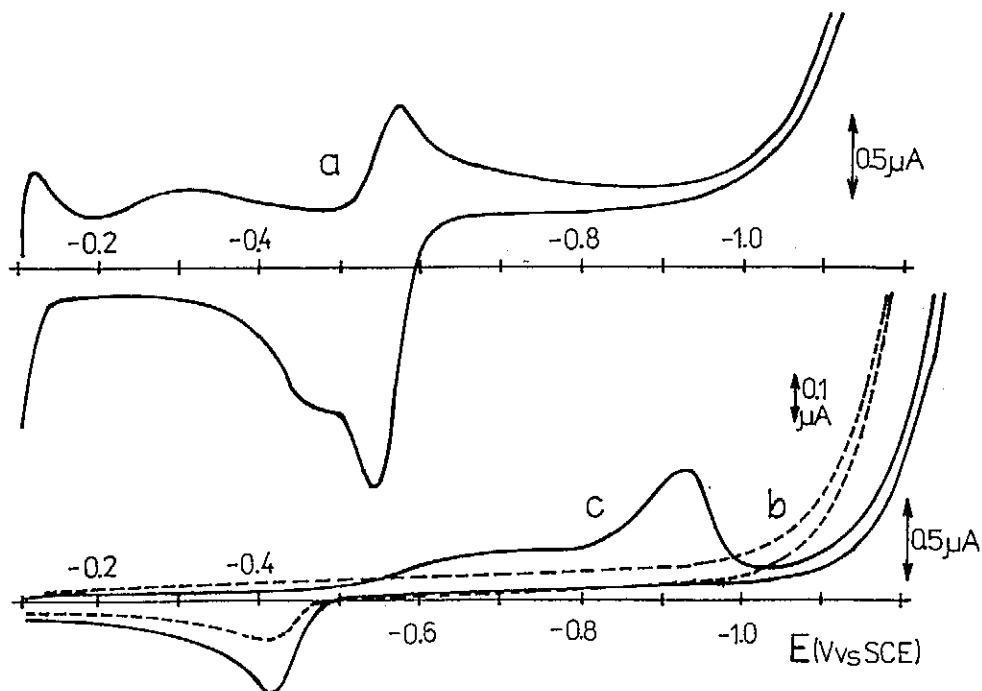


Fig. 1 Cyclic linear voltammetric curves of 1 mM  $\text{SnCl}_4$  in: a) 1 M HCl saturated with  $\text{NH}_4\text{Cl}$ ; b) 1 M  $\text{HClO}_4$  immediately after dissolution; c) 1 M  $\text{HClO}_4$  after 3 weeks of standing at room temperature. HMDE, deaerated solutions, curves recorded from positive to negative potentials and back at scan rate  $100 \text{ mV s}^{-1}$

The  $\text{SnO}_2$  colloids were found to be relatively stable in 1 M  $\text{HClO}_4$  solutions [11]; the full curve in Fig. 2 represents a cyclic voltammogram of  $5 \times 10^{-5} \text{ M}$  colloidal  $\text{SnO}_2$  in that supporting electrolyte which acts at the same time as stabilizer. In the cathodic branch of the curve the drawn-out shoulder as well as the more negative peak denote electrode processes leading to the same product – the tin amalgam, the electrolytic dissolution of which is marked by the prominent anodic peak. In the potential range of the cathodic shoulder the primary electrode reaction is electroreduction of hydrogen ions on the surface of the particles. The thus produced hydrogen atoms reduce the tin dioxide chemically into metallic tin which readily dissolves in mercury while the particle is in contact with the electrode. At potentials of the negative peak the reduction of tin dioxide occurs directly by electrons transferred from the electrode. The dotted and dashed curves in Fig. 2 were obtained after addition of 5 and 10  $\mu\text{l}$  respectively of 17.9 mM  $\text{SnCl}_2$  into 20.5 ml of solution. The round cathodic peak at the beginning of the shoulder corresponds to electroreduction of the added  $\text{Sn}^{2+}$  ions to metallic tin. From the increase of the anodic peak and from the concentrations of divalent and tetravalent tin it can be estimated, on the assumption that with the mean diameter of 2.5 nm the average particle contains

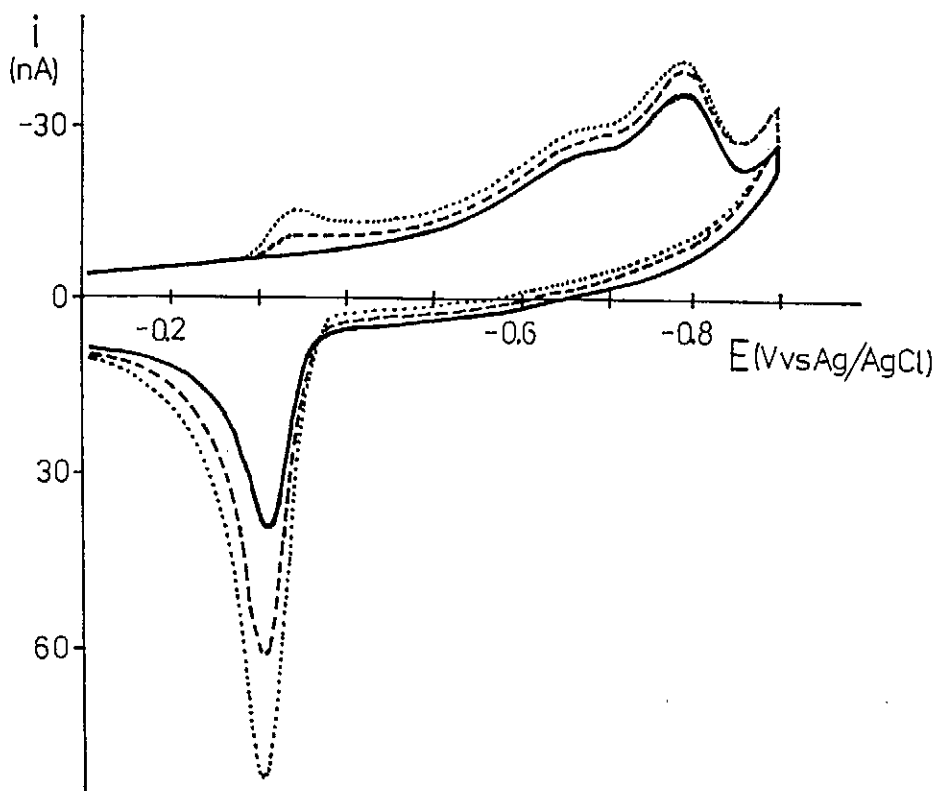


Fig. 2 Cyclic linear voltammetric curves of deaerated  $5 \times 10^{-5}$  M colloidal  $\text{SnO}_2$  in 1 M  $\text{HClO}_4$ . Dashed and dotted curves: to 20.5 ml of solution added 5 and 10  $\mu\text{l}$  of 17.9 mM  $\text{SnO}_2$ , respectively. HMDE, curves recorded from positive to negative potentials and back at scan rate  $50 \text{ mV s}^{-1}$

about 200 molecules, that in the  $\text{SnO}_2$  colloidal particle on average about 1 in 8  $\text{SnO}_2$  molecules gets reduced to Sn.

The above estimate is only approximate, as our solutions were polydisperse, i.e., the sizes of the colloidal particles were not all identical; they followed a certain statistical distribution depending on the details of the preparation procedure and on the composition of the solution. The size of the particle determines to a large extent its electrochemical properties [10]: the rate of diffusion through the diffusion coefficient, the number of electrons exchanged with the electrode and the potential at which the electrode reaction takes place. Hence, the polarographic and the voltammetric curves obtained with colloidal solutions must be regarded as certain envelopes, or sums, of individual virtual curves due to all groups of particles of equal sizes present in the solution according to the actual distribution. The special character of these curves gives them a shape conspicuously different from that of true solutions of electroactive species: the polarographic curves are strongly drawn-out and the voltammetric curves are with bulges instead of with the usual sharp peaks.

## TiO<sub>2</sub> Colloids

The ultrasmall TiO<sub>2</sub> colloids [12] are considerably more stable than those of SnO<sub>2</sub>, also in dilute acidic solutions, and so their properties can better be studied. In Fig. 3 there are compared the mean polarographic currents due to

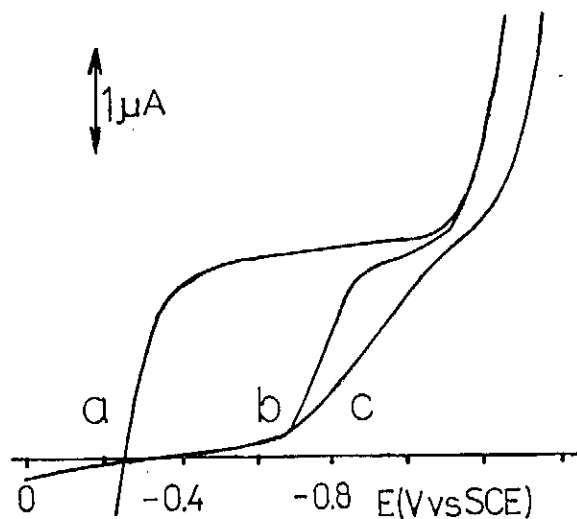


Fig. 3 D. c. polarographic curves (mean currents) of Ti(IV) reduction in various deaerated solutions: a) 4.7 mM (TiCl<sub>3</sub> + TiCl<sub>4</sub>) in 1 M H<sub>3</sub>PO<sub>4</sub> ; b) 2.2 mM TiO<sup>2+</sup> in 0.1 M HClO<sub>4</sub>; c) 10 mM coll. TiO<sub>2</sub> in 10 mM HClO<sub>4</sub>

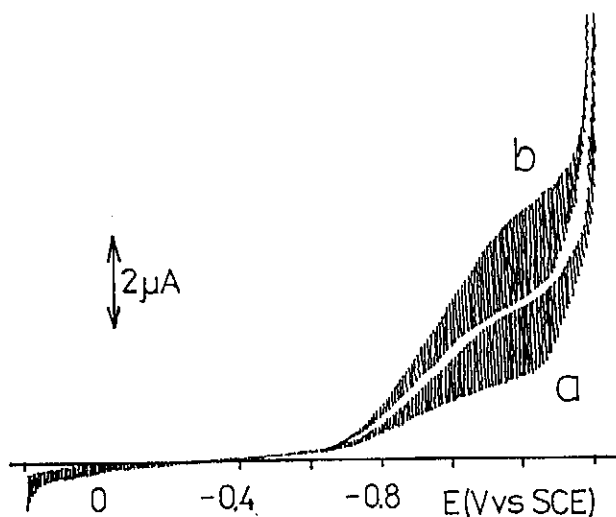


Fig. 4 D. c. polarographic curves of deaerated 10 mM solution of colloidal TiO<sub>2</sub> before (a) and after (b) addition of NaClO<sub>4</sub> to 0.1 M concentration. Damping of current oscillations reduced to minimum

reduction of Ti(IV) to Ti(III) in 3 different solutions: a reversible reduction of a phosphate complex in 1 M  $\text{H}_3\text{PO}_4$  [15], an irreversible reduction of  $\text{TiO}^{2+}$  in 0.1 M  $\text{HClO}_4$  [16] and the reduction of colloidal  $\text{TiO}_2$  in 0.01 M  $\text{HClO}_4$ . The latter reduction proceeds irreversibly in polarography, but in cyclic voltammetry at higher scanning rates it appears as partly reversible. As in the case of  $\text{SnO}_2$  colloids, it starts by reduction of  $\text{H}^+$  ions at the particle surfaces and at more negative potentials it goes over to direct reduction of  $\text{TiO}_2$  by electrons. In the presence of complexing agents in the solution some of the surface  $\text{TiO}_2$  molecules change into surface Ti(IV) complexes and as such get reduced, partly reversibly, at the corresponding potentials. Thanks to the stability of  $\text{TiO}_2$  colloids in acid solutions of different compositions, it is possible to follow, on the polarographic and voltammetric curves, the effects of the particle and electrode double layers on the electrode process. Figure 4 demonstrates the increase of the polarographic reduction wave of  $\text{TiO}_2$  colloids caused by addition of an indifferent electrolyte to the solution. This increase depends specifically on the kind and charge of the added ions and with further additions of electrolytes it diminishes and finally changes into decrease, which is due to flocculation of the colloids by high concentrations of salts.

### Mixed Colloids

When a part of the  $\text{TiO}_2$  molecules in the particles is replaced by ferric oxide,  $\text{Fe}_2\text{O}_3$  [13], the polarographic and voltammetric curves start from the beginning at positive potentials by a cathodic current of reduction of Fe(III), as shown in Fig. 5. When measured at potential of  $-0.5$  V vs. SCE, the current is directly proportional to the concentration of colloids as well as to the percentage of iron in the particles; with higher proportion of  $\text{Fe}_2\text{O}_3$  in the particles a "streaming maximum" appears on polarographic as well as on voltammetric curves, which is typical of true solutions of Fe(III). Such a kind of reduction of colloids occurs by acceptance of electrons from the electrode by molecules in the whole volume of the particle. When measured at the potential of  $-1.2$  V, on the other hand, the dependence of the current on concentration of the colloids gradually changes: at low percentages of iron oxide in particles it increases to a limit, which indicates that the electrode reaction proceeds mainly at the surface of the particles, as is typical for pure  $\text{TiO}_2$  colloids; at high  $\text{Fe}_2\text{O}_3$  percentages the dependence becomes linear. From comparison of the polarographic/voltammetric curves of solutions of colloids with different percentages of iron oxide it appears that the structure of such colloids depends on the Fe/Ti ratio: when it is low, the surface of the particles is occupied prevalingly by  $\text{TiO}_2$  molecules, when it is high, these molecules are displaced towards the particle interior.

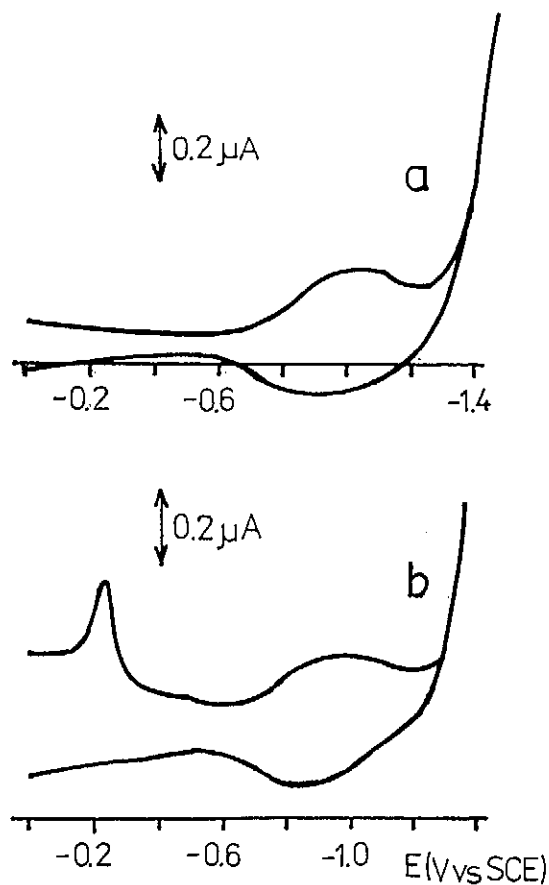


Fig. 5 Cyclic linear voltammetric curves of deaerated 10 mM solutions of mixed  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  colloids in 10 mM  $\text{HClO}_4$ . Colloids contain a) 12.5 % Fe; b) 62.5 % Fe. HMDE, curves recorded from positive to negative potentials and back at scan rate  $100 \text{ mV s}^{-1}$

## Conclusion

Our polarographic and voltammetric experience with ultrasmall colloids brought a strong motivation for continued research which promises to bring new information for electrochemistry as well as for colloid science.

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