COULOMETRIC TITRATION OF OXIDIZING AGENTS BY GENERATED TIN(II)

V. N. Basov, P. K. Agasyan,
B. G. Vikharev, and T. N. Testoedova

UDC 543.258

In the literature there is no information on the electrochemical generation of tin(II) from active electrodes. In view of the well-known advantages of the use of coulometric titrants generated from active electrodes we set ourselves the task of determining the optimum conditions for the production of tin(II) in this way.

In the work we used apparatus for the production of E = f(i) curves and for coulometric titration with automatic recording of the potential–time curves (with potentiometric indication of the end point) [1, 2]. We also used apparatus for coulometric titration with automatic recording of the current–time curves (with biamperometric indication of the end point). In the last case the necessary potential applied to platinum indicator electrodes, 0.3 cm^2 in area, was obtained from a 1.5-V dry battery with a 1000-Ω potential divider. The potential difference of the indicator electrode was controlled by means of an M105 millivoltmeter, and the current which arose was recorded on the chart of an ON-101 polarograph.

The generating anodes were a tin rod with 99.99% purity, 4 mm in diameter and 18 mm long, and tin amalgam. The tin electrode was inserted in a glass tube and soldered to a copper wire; the space between the glass tube and the tin was filled with paraffin wax. The amalgam was prepared by direct contact between finely divided granules of tin and mercury under a layer of hydrochloric acid solution (1:1) whileheating to 60-70°C on a water bath. It was then placed in the electrolysis cell which we designed for external generation of the titrant (Fig. 1). The need for this kind of technique arose from the incompatibility of the electrochemical and chemical processes, since the oxidizing agents are directly reduced by tin amalgam.

On the basis of the Pourbaix diagram [3] it could be supposed that in the region of pH 2-1 and at potentials of −0.3 to +0.2 V (n.h.e.) a tin anode dissolves to form Sn(II) compounds.

The current yield of Sn(II) generated electrochemically by anodic polarization of the tin electrode was determined in the following way. The electrode was submitted to anodic polarization in hydrochloric acid with various concentrations as indifferent electrolyte for a strictly defined interval of time at specified current densities. The obtained product was titrated with a standard solution of iodine with visual observation of the end point by the reaction with starch. To avoid oxidation of the tin(II) by atmospheric oxygen all the operations were carried out in an atmosphere of purified nitrogen.

TABLE 1. Current Yield of Tin(II) (η, %) during Anodic Polarization of Tin Electrode (n = 5)

i, mA/cm^2	0.01 M HCl		0.1 M HCl		1 M HCl	
	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S
0,77	160	16,2	142	9,7	153	5,0
5,8	101	2,6	113	2,7	110	2,5
15,5	91	1,5	106	1,3	110	2,9

The results are presented in Table 1. In most cases the current yield of tin(II) exceeds the amount calculated theoretically by Faraday's law. Only in the case of 0.01 M hydrochloric acid solution as indifferent electrolyte with a current density of 15.5 mA/cm^2 did the current yield amount to ~91%. This can probably be explained by passivation of the electrode. The fact that a current yield of tin(II) above the theoretical is obtained can be explained by means of the theory of the anodic disintegration of metals developed by Straumanis [4].

To eliminate the effect of anodic disintegration during the electrochemical generation of tin(II) from an active electrode

Perm Branch, All-Union Scientific-Research Institute of the Paper-Pulp Industry. Translated from Zavodskaya Laboratoriya, Vol. 38, No. 9, pp. 1060-1062, September, 1972. Original article submitted September 8, 1971.

TABLE 2. Coulometric Titration of Oxidizing Agents with Tin(II) (4 M HCl, n = 5, V = 30 ml)

Titrated oxidizing agent	Taken, mg	$\bar{x}$	s	Method of end point detection
$K_2Cr_2O_7$	2,451	2,448	0,002	Potentiometry ($i=0$)
	0,490	0,490	0,008	"
NH_4VO_3	5,810	5,79	0,02	"
	0,581	0,574	0,006	"
K_3 [Fe (CN)$_6$]	17,005	16,40	0,08	"
	0,680	0,67	0,03	"
$FeCl_3$*	8,265	8,1	0,2	"
	0,826	0,76	0,02	"
$FeCl_3$*	8,256	8,30	0,08	Biamperometry (ΔE = 100 mV)
	0,826	0,820	0,008	
K_3 [Fe (CN)$_6$]	17,005	17,00	0,08	Biamperometry (ΔE = 50 mV)
	0,680	0,68	0,02	

*Indifferent electrolyte 2 M HCl.

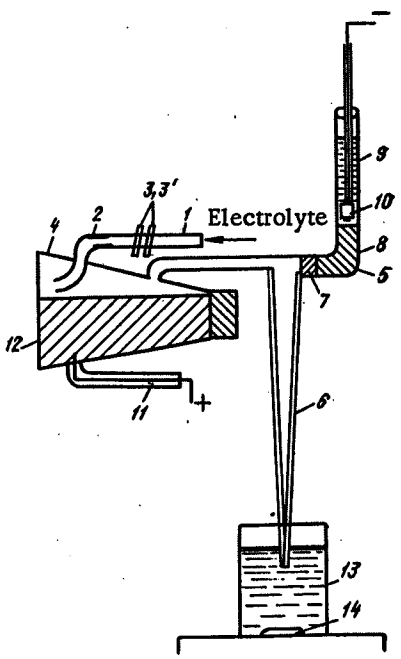

Fig. 1. Electrolysis cell for external generation of intermediate reagent: 1) Rubber tube; 2) glass inlet tube; 3) and 3') Mohr and Bunsen clamps; 4) anode compartment; 5) side tubes of electrolysis cell; 6) capillary; 7) porous plate; 8) agar-agar gel containing 5% potassium sulfate solution; 9) 5% potassium sulfate solution; 10) auxiliary platinum electrode; 11) platinum contact; 12) tin amalgam; 13) titration vessel; 14) magnetic stirrer.

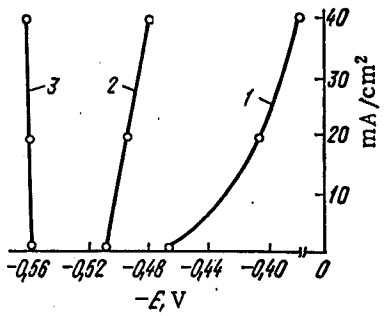

Fig. 2. The E = f(i) curves obtained with amalgam electrode (0.8% Sn in the amalgam): 1), 2), and 3) Sn(Hg) electrode in 0.01, 0.1, and 1 M HCl solutions respectively.

it is advisable to use tin amalgam as generating anode, since the difference between the standard potentials of the Sn(II)/Sn (− 0.136 V) and Hg(II)/Hg (+0.854 V) systems is considerable (0.990 V).

The current yield of Sn(II) was investigated by plotting E = f(i) curves, recorded by the commutator method, for amalgams containing 0.115, 0.154, 0.192, 0.261, 0.385, and 0.800% of tin and for mercury with 0.01, 0.1, and 1 M hydrochloric acid as indifferent electrolytes. During this operation the electrolysis cell in which the investigated amalgams were placed was attached to a laboratory shaker. The frequency of the vibrations was 1.4 Hz, and the horizontal amplitude was 30 mm. In this way the tin was made to approach the surface of the amalgam not only through diffusion but also as a result of convection. The E= f(i) curves for mercury and tin amalgam anodes are presented in Fig. 2. Similar relationships were obtained for amalgams with other concentrations of tin. Thus, in the investigated region of polarizing current densities the generation of tin(II) is 100% efficient. This was also confirmed by iodometric titration of tin(II) previously generated from an anodically polarized tin amalgam in 1 M hydrochloric acid.

To determine the optimum conditions for biamperometric detection of the end point during the titration of iron(III) in 2 M hydrochloric acid and $[Fe(CN)_3]^{3-}$ in 4 M hydrochloric acid [5] E = f(i) curves were plotted for a platinum electrode in the 0.001 M $[Fe[CN]6]^{3-}/[Fe(CN)_6]^{4-}$, Fe(III)/Fe(II), and Sn(IV)/Sn(II) systems. When i = 20 μA the degree of reversibility of the Fe(III)/Fe(II) system amounted to ~100 mV, and that of the $[Fe[Cn]_6]^{3-}/[Fe(CN-_6]^{4-}$ system amounted to ~ 50 mV. An L-shaped titration curve should therefore be expected near the

equivalence point if a potential of ~ 100 mV is applied to the two platinum indicator electrodes during titration of oxidizing agents with generated tin(II) ions, since the Sn(IV)/Sn(II) system is irreversible under these conditions.

The results from coulometric titration of model solutions of [Fe(III), $[Fe(CN)_6]^{3-}$, Cr(VI), and V(V) are presented in Table 2.

The same coulometric titrant was used to determine vanadium in a solution simulating the composition of the alloy containing 97.45% of aluminum, 2.55% of vanadium, and chromium in a specimen of steel 181 (98.4% of iron, 0.018% of sulfur, and 1.56% of chromium). Found %: 2.54 ±0.02 vanadium; 1.56 ±0.02 chromium (n = 3, α = 0.95).

LITERATURE CITED

1. P. K. Agasyan, A. I. Kostromin, and V. N. Basov, Zh. Analiticheskoi Khim., No. 2, 216 (1970).
2. P. K. Agasyan, V.N. Basov, and A. I. Kostromin, Vestnik MGU Khimiya (in press).
3. B. P. Nikol'skii (editor), Chemists' Reference Book [in Russian], Vol. 3, Izd. Khimiya (1964), p. 794.
4. M. É. Straumanis, Izv. Akad. Nauk Latv. SSR, No. 6, 613 (1967).
5. A. Berka, Ya. Vul'terin, and Ya. Zyka, New Redox Methods in Analytical Chemistry [in Russian], Izd. Khimiya (1968), pp. 186, 189.