The Polarographic Determination of Divalent Tin in Sodium Formate

By G. S. DESHMUKH and S. V. S. S. MURTY*

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Heyrovsky,[1] Kalousek[2] and Lingane[3] have recommended 1 molar sodium hydroxide as a supporting electrolyte for the polarographic determination of stannous tin. In this medium, Sn^{2+} gives both anodic and cathodic waves. Well-defined cathodic and anodic polarograms of stannous tin in an acetic acid - ammonium acetate buffer have been adopted for the determination of the element by Pribil[4] and Desesa[5]. The use of sodium citrate, sodium hydroxide and alkali tartrate solutions as supporting electrolytes has been indicated by Kalousek,[2] Shakhov[6] and Lingane[7]. In the latter case the half-wave potential of the anodic polarogram was found to be dependent on the pH of the solution, on the concentration of sodium tartrate, and on that of stannous tin. The symmetry of the wave was also affected by the above parameters. However, the half-wave potential of the cathodic polarogram was constant under these conditions.

A similar type of polarographic behaviour of stannous tin in sodium formate has now been observed. It has already been mentioned that

* Junior Research Fellow, C. S. I. R.

1) J. Heyrovsky and D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **7**, 198 (1935).

2) M. Kalousek, ibid., **11**, 592 (1939).

3) J. J. Lingane, *Ind. Eng. Chem. Anal. Ed.*, **15**, 583 (1943).

4) R. Pribil, Z. Roubal and E. Svatek, *Collection Czechoslov. Chem. Communs.*, **18**, 43 (1953).

5) M. A. Desesa, D. N. Hume, A. G. Glamm and D. Deford, *Anal. Chem.*, **25**, 983 (1953).

6) A. S. Shakhov, *J. Appl. Chem. U. S. S. R.*, **12**, 1555 (1939).

7) J. J. Lingane, *J. Am. Chem. Soc.*, **65**, 866 (1943).

stannous tin yields well-defined anodic and cathodic polarograms in sodium formate.[8] The behaviour of the anodic polarogram of tin is of considerable importance for its determination in the presence of other metallic elements with which it is commonly associated. The present investigation was, therefore, undertaken to obtain detailed information about the polarographic characteristics of stannous and stannic complexes in sodium formate media.

Experimental

The polarograms were recorded at 25±0.1°C with a Leeds and Northrup Electrochemograph, type E; the capillary characteristics with the open circuit were $m=3.09$ mg./sec. and $t=3$ sec. The pH of the solution was measured with a line-operated Beckmann Zeromatic pH meter.

Sodium formate of a pure-reagent-grade quality was used to prepare solutions of the desired strength. Stannous chloride solution was prepared by dissolving pure metallic tin in the requisite quantity of concentrated hydrochloric acid and storing the solution in an inert atmosphere. Nitrogen was bubbled through the solutions in order to deaerate them and the inert atmosphere was maintained to prevent the oxidation of stannous tin while the polarograms were being recorded. Freshly-prepared gelatin was used as the maximum suppressor. The pH of the solution was adjusted by means of pure formic acid.

Results and Discussion

Effect of pH.—Table I shows that the pH exerts profound effect on the half-wave potentials of the anodic polarogram. The anodic half-wave potential became more positive as the pH was decreased from 3.7 to 3.1. As the pH increased from 3.1, however, the anodic polarogram was characterized by a drawn-out wave which finally merged with the initial plateau of the cathodic polarogram at pH 5.2. The half-wave potential of the cathodic polarogram was not altered with the change in pH.

TABLE I. EFFECT OF pH ON DIVALENT TIN POLAROGRAMS

Formate concn., 1 M Gelatin, 0.005%
Concn. of Sn^{2+}, 1.584 mg.

Sample No.	pH	$E_{1/2}$, V. vs. SCE	
		Anodic	Cathodic
1	3.1	−0.17	−0.56
2	3.3	−0.185	−0.56
3	3.5	−0.195	−0.56
4	3.7	−0.23	−0.56
5	5.2	Anodic wave merged with cathodic wave	

Effect of Formate Concentration.—Variation in the formate concentration has an appreciable effect on the half-wave potential of the anodic and cathodic polarograms of stannous tin. The half-wave potential of the anodic polarogram shifted to negative potentials with the increase in the formate concentration, thus showing the formation of a more stabilized complex. The $E_{1/2}$ of the cathodic polarogram was, however, shifted to negative potentials, this shift being comparatively much less pronounced than that observed with the anodic polarogram. The diffusion current of both the polarograms was suppressed with the increase in formate concentration, especially above 1.5 M; this might be due to the increased viscosity of the medium. The results are reported in Table II.

TABLE II. EFFECT OF FORMATE CONCENTRATION ON Sn^{2+} POLAROGRAMS

pH ~3.5 Gelatin, 0.005%
Concn. of Sn^{2+}, 1.584 mg.

Sample No.	Concn. of formate M	$E_{1/2}$, V. vs. SCE	
		Anodic	Cathodic
1	0.3	−0.13	−0.525
2	0.5	−0.155	−0.54
3	1.0	−0.185	−0.555
4	1.5	−0.19	−0.575
5	2.0	−0.215	−0.59
6	2.5	−0.23	−0.605

Effect of Stannous Tin Concentration.—The anodic half-wave potential shifted to positive potentials with the increase in stannous tin concentration. For example, with 1 molar sodium formate and at pH 3.0 with 0.005% gelatin, the anodic half-wave potentials of 0.514, 1.028, 2.056, 3.084 and 4.112 mM were, respectively, −0.185, −0.175, −0.15, −0.09 and −0.035 V. vs. SCE. On the other hand, the cathodic half-wave potential in the above experiments remained constant at −0.57 V. (cf. Fig. 1).

These results indicate that the oxidation of the stannous formate complex was thermodynamically irreversible at the dropping electrode. The irreversibility was confirmed by investigating polarograms of stannic tin in formate media. In formate solutions stannic tin does not show a reduction wave, whereas, if the stannic-stannous system is reversible, a reduction wave would be observed with stannic formate solutions at the same potential at which the anodic wave occurs with the stannous formate solutions. The irreversibility of the

8) G. S. Deshmukh and Y. D. Kane, *J. Sci. Ind. Research*, **21B**, 135 (1962).

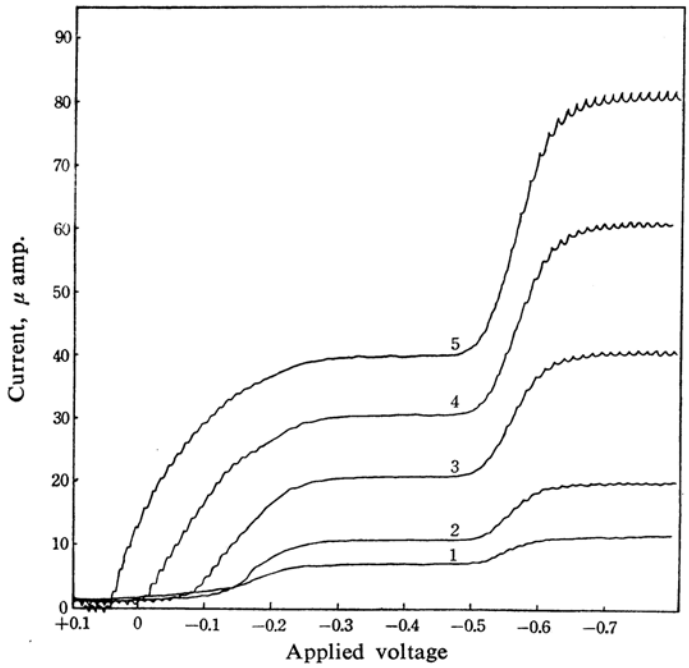

Fig. 1. The polarograms of (1) 0.514 (2) 1.028 (3) 2.056 (4) 3.084 and (5) 4.112 mM Sn^{2+} in 1 M sodium formate. pH=3.0 Gelatin=0.005%

anodic polarogram was also increased with the concentration of Sn^{2+}, as is evidenced by the increase in the difference between $E_{3/4}$ and $E_{1/4}$. Thus, with 1 molar formate at pH 3.0 with 0.005% gelatin, the difference between $E_{3/4}$ and $E_{1/4}$ of the anodic polarogram of 1.028, 2.056, 3.084 and 4.112 mM was 60, 80, 100 and 120 mV. vs. SCE respectively, but for the cathodic polarogram it was constant, the values always being 50 mV. For a thermodynamically-reversible wave, the expected value should be 28 mV. This shows that the cathodic wave was also irreversible.

Calibration curves were drawn with 1 molar sodium formate at pH 3.0 ± 0.1. It was observed that the diffusion current was directly proportional to the concentration of tin for both the anodic and cathodic polarograms between 10^{-5} to 10^{-4} M.

Summary

Well-defined cathodic and anodic polarograms of stannous tin in sodium formate have been reported. The diffusion current is directly proportional to the concentration of stannous tin between 10^{-5} to 10^{-4} M. The anodic half-wave potential of tin is shifted to positive values with the increase in the concentration of Sn^{2+}, whereas the cathodic half-wave potential is constant. The anodic polarogram is highly irreversible. The cathodic polarogram is also irreversible. The irreversibility of the anodic polarogram is increased with the concentration of stannous formate. This is evidenced by a corresponding increase in the difference between $E_{3/4}$ and $E_{1/4}$. Above pH 5.0 the anodic polarogram merges with the cathodic polarogram, thereby limiting the polarographic determination of Sn^{2+} to the pH value 3～5. The $E_{1/2}$ of the anodic polarogram shifts to negative potentials when the pH was increased, whereas that of the cathodic wave is constant. The polarogram with equal wave heights obtained in 1 molar sodium formate at pH 3.0 with 0.005% gelatin has been taken for the determination of tin.

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Department of Chemistry
Banaras Hindu University
Varanasi-5, India