[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Polarographic Behavior of Dropping Tin Amalgam Electrodes

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The anodic behavior of tin in acid, neutral and alkaline solution has been studied polarographically with dropping amalgam electrodes. Half-wave potentials for the dissolution of tin were found to depend not only on the nature of the supporting electrolyte but also on the concentration of the amalgam. Reversible polarographic behavior is approached in the case of amalgams more dilute than 0.6 millimolar. Data are presented which substantiate an earlier observation of the author that the anodic diffusion current at dropping amalgam electrodes is not independent of the supporting electrolyte.

A new approach to the study of the dissolution behavior of metals is afforded by the polarography of dropping amalgam electrodes. The importance of the anodic behavior of tin and the interesting amphoteric, hydrolytic and complex formation properties of the metal prompted an investigation of the polarographic behavior of dropping tin amalgam anodes. The results of this investigation are reported in this paper.

Experimental

Apparatus and Materials.—The apparatus and general procedure for the polarographic study of dropping amalgam electrodes have been described.[2]

The polarograms were recorded using a Sargent–Heyrovsky Model XI polarograph.

The standard solution of stannic chloride used in the preparation of the amalgams and containing 0.303 mg. tin per ml., was prepared following the procedure employed by Lingane.[3]

The temperature was maintained at 25.0 ± 0.1° in all experiments.

Gelatin at a concentration of 0.01% was used as maximum suppressor in all solutions. Certain electrolytes were employed with and without gelatin to determine if gelatin had any undesirable effect. No deleterious effects were found either on wave form or diffusion current.

Results and Discussion

Anodic Half-wave Potentials and Polarographic Reversibility.—Typical polarographic waves for the dissolution of tin at the dropping amalgam electrode are shown in Fig. 1. Two anodic waves corresponding to the oxidation of tin to the stannic state in two 2-electron steps were found in 1 *M* hydrochloric acid, 0.5 *M* sulfuric acid, 1 *M* nitric acid, 2 *M* perchloric acid–0.5 *M* hydrochloric acid, 0.5 *M* sodium fluoride, 1 *M* sodium hydroxide and in tartrate, citrate and oxalate media. The ill-defined nature of both waves in 1 *M* sodium hydroxide (Fig. 1) clearly demonstrates the polarographic irreversibility of tin in this medium.

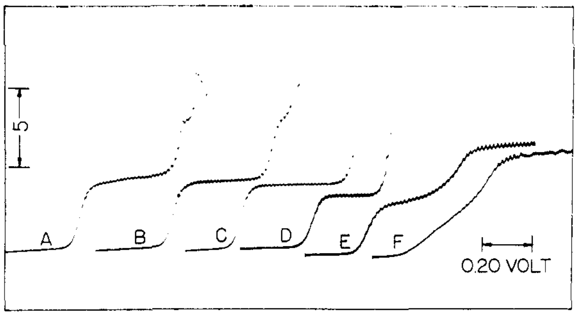

Fig. 1.—Polarograms of tin amalgams in various media: A. 2 *M* $HClO_4$–0.5 *M* HCl; B, 1 *M* HCl; C, 4 *M* NH_4Cl–1 *M* HCl; D, 4 *M* NH_4Br; E, 0.5 NaF; F, 1 *M* NaOH.

Contrary to expectations, the anodic half-wave potentials for tin amalgams in various media are not independent of amalgam concentration. The half-wave potentials for the Sn–Sn(II) waves vary discontinuously with concentration in the manner shown in Fig. 2. Amalgams more dilute than 0.6 millimolar have a steady half-wave potential which approaches the cathodic value, indicating reversible behavior in the case of very dilute amalgams. Half-wave potential data for such amalgams are presented in Table I. Since the half-wave potentials of more concentrated amalgams are shifted to more positive values, one would expect to find much less polarographic reversibility for the more concentrated amalgams. The slopes of the log $i/(i_d - i)$ *vs.* *E* plots show that this is precisely the case. Thus for a 4.72×10^{-4} molar amalgam the slope was 0.033 ± 0.002 while for a 3.60×10^{-3} molar amalgam it was 0.042 ± 0.002 (theoretical value = 0.030).

TABLE I

ANODIC AND CATHODIC HALF-WAVE POTENTIALS FOR Sn–Sn(II) WAVES

Anodic values are for tin amalgams <0.6 millimolar

Supporting electrolyte	$E_{1/2}$ *vs.* S.C.E. (anodic)	$E_{1/2}$ *vs.* S.C.E. (cathodic)
0.1 *M* KCl	−0.42	-0.452^{4}
1 *M* KCl	− .45	$-\ .491^{4}$
1 *M* HCl	− .445	$-\ .47^{5}$
4 *M* NH_4Cl–1 *M* HCl	− .52	$-\ .52^{3}$
1 *M* HNO_3	− .405	$-\ .44^{5}$
0.5 *M* H_2SO_4	− .41	$-\ .46^{5}$
2 *M* $HClO_4$	− .395	$(-\ .446)^{4,4a}$
2 *M* $HClO_4$–0.5 *M* HCl	− .44	$(-\ .35)^{6,6a}$

The question immediately arises as to why this marked change in half-wave potential occurs at an amalgam concentration of about 0.6 millimolar, particularly the striking change in the case of 0.1 *M* potassium chloride. Zimmerman and Gropp[7] have shown that a single well-defined wave may on differentiation (di/dE *vs.* *E*) show not one but two or

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[1] Canadian Copper Refiners Limited, Montreal East, Quebec, Canada.

[2] N. H. Furman and W. C. Cooper, THIS JOURNAL, **72**, 5667 (1950).

[3] J. J. Lingane, *ibid.*, **67**, 919 (1945).

[4] L. Riccoboni, P. Popoff and G. Arich, *Gazz. chim. ital.*, **79**, 547 (1949).

[4a] In 1.8 *M* $LiClO_4$, $E_{1/2} = -0.446$ volt (referred to $\mu = 1$).

[5] J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 583 (1943).

[6] Lingane and Scott; I. M. Kolthoff and J. J. Lingane, "Polarography," 1st ed., Interscience Publishers, Inc., New York, N. Y., 1941, p. 263–264.

[6a] In 2 *M* $HClO_4$–0.5 *M* NaCl, $E_{1/2} = -0.35$.

[7] H. K. Zimmerman, Jr., and A. H. Gropp, *J. Phys. Colloid Chem.*, **54**, 764 (1950).

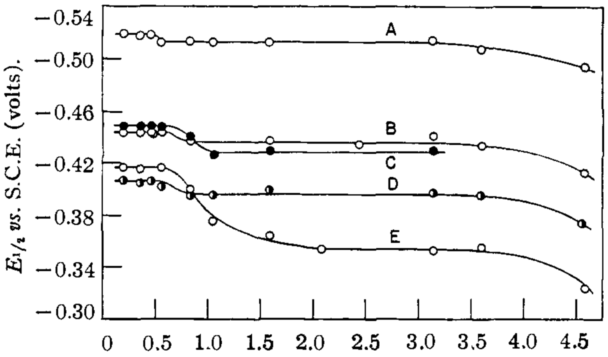

Fig. 2.—Relation between half-wave potential and amalgam concentration: A, 4 *M* NH_4Cl-1 *M* HCl; B, 1 *M* HCl; C, 1 *M* KCl; D, 1 *M* HNO_3; E, 0.1 *M* KCl.

more distinct maxima corresponding to two or more points of inflection in the original wave and indicating the existence of a separate electroactive species for each maximum. Differentiated tin-tin (II) curves for 1.84 × 10^{-4} and 8.43 × 10^{-4} molar tin amalgams in 0.1 *M* potassium chloride gave a single sharp peak in the case of the former amalgam and three maxima for the latter indicating the possible existence of three distinct tin(II) species in the case of the more concentrated amalgam. These observations are substantiated by the striking difference in the slopes of the two waves—0.030 for the more dilute amalgam *vs.* 0.115 for the more concentrated one.

Behavior in Potassium Chloride Solution.—The behavior of tin amalgams in 0.1 and 1 *M* potassium chloride is of additional interest because of the presence, in the case of certain amalgams, of three distinct polarographic waves, particularly in 0.1 *M* potassium chloride (Fig. 3). In both electrolytes the ratio ht. 2nd wave/ht. 1st wave equals 0.17 at all concentrations at which three waves are evidenced. The first wave represents, of course, the oxidation of tin to the stannous condition. The second and third waves are in all probability waves for the oxidation of two distinct stannous ion species. Evidence for the existence of more than one stannous species has already been indicated. It is doubtful that the two species result from a hydrolysis equilibrium at the electrode surface since such an equilibrium would be too rapid for the separate species to be detected polarographically.

Behavior in Perchloric Acid Solution.—In 2 *M* perchloric acid solution Lingane and Scott[6] found no polarographic waves for either stannous or stannic tin. However, when chloride ion was added waves appeared. These observations were corroborated by Nickelson and Randles[8] who found that a mere trace of chloride ion sufficed for the polarographic reduction of tin(II) in perchloric acid. Riccoboni, Popoff and Arich[4] obtained cathodic waves for stannous tin in potassium perchlorate and lithium perchlorate solutions which had been carefully analyzed to establish the absence of any trace of chloride ion. However, these authors did not report on the behavior of tin in perchloric acid.

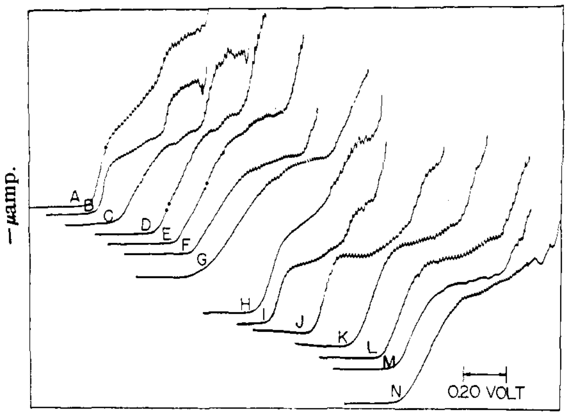

Fig. 3.—Polarograms of tin amalgams in 0.1 *M* potassium chloride (A-G) and 1 *M* potassium chloride (H-N); concentration of amalgams (moles per liter): A, H, 3.65 × 10^{-4}; B, I, 5.65 × 10^{-4}; C, J, 8.43 × 10^{-4}; D, K, 1.06 × 10^{-3}; E, L, 2.08 × 10^{-3}; F, M, 3.60 × 10^{-3}; G, N, 4.58 × 10^{-3}.

In the anodic polarography of tin amalgam electrodes, tin is oxidized to the stannous state in 2 *M* perchloric acid, a well-defined wave being formed whose height is proportional to the amalgam concentration. When the supporting electrolyte is made 0.5 molar in hydrochloric acid, two waves are formed (Fig. 1) and the half-wave potential of the Sn–Sn(II) wave changes from −0.39 to −0.44 volt *vs.* S.C.E. which value is the same as that for tin amalgams of comparable concentration in 1 *M* hydrochloric acid. Hence an approach to reversible behavior is indicated in perchloric acid–hydrochloric acid medium.

Behavior in Acid Tartrate Medium.—In acid tartrate solutions the dissolution of dilute tin amalgams occurs with the formation of two reasonably well-defined waves. However, in the same media, more concentrated amalgams, *e.g.*, 2.5 millimolar, produce two waves and a pronounced minimum in the vicinity of the oxidation potential of the stannous tartrate complex. This minimum which becomes deeper and broader with increasing *p*H is analogous to the minimum which Lingane[9] observed at the dropping mercury electrode for tin in tartrate media below *p*H 9. The change in half-wave potential with *p*H for the tin–tin(II) wave is about independent of amalgam concentration although the actual half-wave potentials are shifted to more negative values with increasing amalgam concentration. This shift is quite marked in the case of the Sn(II)–Sn(IV) wave and is similar to that observed for the same wave at the dropping mercury electrode. Thus for the Sn(II)–Sn(IV) wave in 0.1 *M* tartrate solution between *p*H 3 and 5

$$E_{1/2} = -0.065 - 0.044\,p\text{H (volt } vs. \text{ S.C.E.)}$$

at an amalgam concentration of 4.88 × 10^{-4} molar. When the concentration is raised to 2.44 × 10^{-3} molar, the relation becomes $E_{1/2} = 0.115 - 0.057$ *p*H. The relative *p*H dependency of tin, copper and bismuth amalgams in acid tartrate medium is shown in Fig. 4.

Anodic Diffusion Current and its Dependence on Supporting Electrolyte.—Diffusion current con-

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[8] A. S. Nickelson and J. E. B. Randles, "Polarographic and Spectrographic Analysis of High Purity Zinc Alloys for Die Casting," British Ministry of Supply, London, 1945, p. 12.

[9] J. J. Lingane, THIS JOURNAL, **65**, 866 (1943)

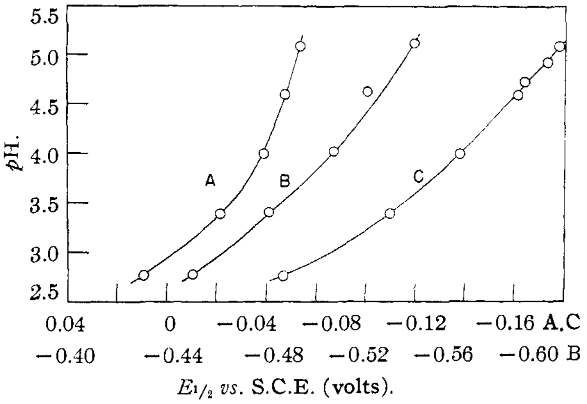

Fig. 4.—Relation between half-wave potential of Cu-Cu(II), Sn-Sn(II) and Bi-Bi(III) waves and *p*H in 0.1 *M* tartrate solution: A, 2.30×10^{-3} molar copper amalgam; B, 2.44×10^{-3} molar tin amalgam; C, 4.94×10^{-4} molar bismuth amalgam.

stant data for dropping tin amalgam electrodes in various media have been reported.[10] These and numerous additional data substantiate an earlier observation, disputed by Stromberg,[11] that the anodic diffusion current at dropping amalgam electrodes is not independent of the supporting electrolyte.[2] That the electrolyte is not without effect on the anodic current is illustrated in the case of tin amalgams by the slight but significant decrease in current obtained when a 2 *M* perchloric acid solution is made 0.5 *M* in hydrochloric acid.

In Table II a comparison of diffusion current constants for tin amalgams in different supporting electrolytes is presented.

TABLE II

RATIO OF DIFFUSION CURRENT CONSTANTS IN VARIOUS MEDIA TO THAT IN 1 *M* HCl

Range of amalgam concn.—1.8×10^{-4} to 4.6×10^{-3} molar

Amalgam	4 *M* NH_4Cl-1 *M* HCl	0.5 *M* H_2SO_4	1 *M* HNO_3	2 *M* $HClO_4$
1	0.99	1.03	1.15	1.14
2	1.02	1.05	1.02	1.06
3	0.98	1.03	1.02	1.06
4	1.01	1.04	1.00	1.07
5	1.03	1.05	1.03	1.09
6	0.98	1.03	1.02	1.06
7	0.98	1.03	1.03	1.07

Since the anodic diffusion current constant changes markedly with changes in $t^{1/6}/m^{1/3}$ as shown by Strehlow and von Stackelberg[12] and Turner and Winkler,[13] the corresponding $t^{1/6}/m^{1/3}$ values were calculated and found to be strictly comparable except in the case of amalgam No. 1 where the $t^{1/6}/m^{1/3}$ values in 1 *M* nitric acid and 2 *M* perchloric acid were substantially smaller than the value in 1 *M* hydrochloric acid, hence the high diffusion current constant ratios—1.15 and 1.14, respectively. From the data presented here and the fact that I_D values could be obtained with a standard deviation of ±0.05 one may conclude that, on the average, the anodic diffusion currents for tin amalgams in the electrolytes: 1 *M* hydrochloric acid, 4 *M* ammonium chloride-1 *M* hydrochloric acid, 0.5 *M* sulfuric acid, 1 *M* nitric acid and 2 *M* perchloric acid, are, for any one amalgam and for comparable $t^{1/6}/m^{1/3}$ values, in the ratio $1.00:1.00_5:1.03_6:1.02:1.06_3$, respectively. This variation in diffusion current cannot be attributed to different $t^{1/6}/m^{1/3}$ values; neither can it be attributed to differences in drop size since the average mass of the amalgam drop in 1 *M* hydrochloric acid was larger than the drop masses in other media.

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[10] W. C. Cooper and N. H. Furman, THIS JOURNAL, **74**, 6183 (1952).

[11] A. G. Stromberg, *Doklady Akad. Nauk S.S.S.R.*, **85**, 831 (1952).

[12] H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[13] R. C. Turner and C. A. Winkler, *Can. J. Chem.*, **29**, 469 (1951).