[CONTRIBUTION No. 635 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Polarographic Study of the Complex Ions of Tin in Fluoride Solutions[1]

BY WARD B. SCHAAP, JOSEPH A. DAVIS AND WILLIAM H. NEBERGALL

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Tin(II) exhibits both a cathodic and an anodic polarographic wave in fluoride solutions. The cathodic wave is reversible in acidic or neutral fluoride solutions and the data indicate that the reduction reaction is $SnF_3^- + 2e^- \rightarrow Sn(amalgam) + 3F^-$. The anodic wave is not as reversible as the cathodic wave and approaches reversibility only in acidic fluoride solutions. In the acidic solutions the anodic wave appears to be the result of the oxidation reaction $SnF_3^- + 3F^- \rightarrow SnF_6^{--} + 2e^-$. The dissociation constant of the complex ion SnF_3^- is calculated to be 1.2×10^{-10} at an ionic strength of 0.8 and 1.1×10^{-11} at $\mu = 2.5$. The dissociation constant for SnF_6^{--} is estimated to be about 10^{-25}. Freshly prepared solutions of tin(IV) in fluoride media give small irreversible reduction waves which slowly disappear as the solution stands. In perchloric acid solutions tin(II) exhibits a reversible cathodic wave and an irreversible anodic wave. Tin(IV) is not polarographically reducible in perchloric acid solution.

Introduction

No previous studies of the nature and properties of the complex ions that exist in tin(II) or tin(IV) fluoride solutions have been reported. West, Dean and Breda[2] included tin(II) as one of thirty ions used in a survey of the analytical applications of sodium fluoride as a supporting electrolyte for polarography. Although these workers measured the half-wave potentials and diffusion current constants of the anodic and cathodic tin(II) waves, they made no effort to study the species in solution.

The analogous complexes of tin(II) in chloride solutions, on the other hand, have received considerable study.[3-7] Perhaps the most careful study was that of Vanderzee and Rhodes using concentration cells. In their work evidence was found for the existence of the complex ions $SnCl^+$, $SnCl_2$ and $SnCl_3^-$ having, respectively, the stability constants 14, 50 and 48 at 25°. These constants correspond to an over-all dissociation constant of 3×10^{-5} for the trichlorostannate(II) ion, $SnCl_3^-$. The evidence for the existence of $SnCl_4^{--}$ was not strong. Vanderzee[8] reports, further, that the dissociation constant for $SnBr_3^-$ is 4.5×10^{-2}.

Several investigations of the polarography of tin(II) and tin(IV) in perchlorate solutions have been reported.[5,9,10] Apparently, tin(II) is reducible in perchloric acid solutions if a trace of chloride ion is present. Riccoboni and co-workers found also that tin(II) is reversibly reduced in solutions of lithium or potassium perchlorate. Tin(IV) is not reduced at the dropping mercury electrode below the potential of hydrogen discharge in perchloric acid solutions.[9]

In this paper we will present polarographic data obtained for the evaluation of the formulas and dissociation constants of the complexes formed by tin(II) and tin(IV) with fluoride ion. The polarography of tin(II) in perchlorate solutions will be mentioned since half-wave potentials with this non-complexing medium are used in the calculation of the dissociation constants.

Experimental

A Sargent Model XXI Recording Polarograph was used. Potential measurements were made with a Rubicon potentiometer at several points on each polarogram *versus* a bulb-type saturated calomel reference electrode. An H-type cell was used in which the solution to be studied was separated by a temporary agar plug (3% agar and 0.1 *M* $NaNO_3$) from a potassium chloride solution into which the reference electrode dipped. The resistance of such a cell was approximately 450 ohms. The two capillaries used had these characteristics (open circuit) at 25° and a mercury column height of 50.0 cm.: no. 1, m = 2.042 mg. sec.$^{-1}$ and t = 3.79 sec.; No. 2, m = 1.965 mg. sec.$^{-1}$ and t = 4.07 sec. *p*H measurements were made using the glass electrode. All polarograms were run at 25 ± 0.2°.

Standard tin(II) solutions were prepared by two methods. The first consisted in direct weighing of Metal and Thermit Co. C.P. stannous oxide into the air-free perchloric acid solution and then warming the mixture on a steam-bath until dissolution was complete. The other method involved dissolving the readily soluble crystalline stannous fluoride (anhydrous), prepared in this Laboratory,[11] in the fluoride or perchloric acid solutions. Somewhat higher and more consistent values of i_d/C were obtained with this second method, presumably due to a decreased extent of oxidation made possible by the decreased time of handling. It was found essential to remove dissolved air as completely as possible from solutions before introducing the tin(II) compound, since at the low concentrations of tin used (usually about 10^{-3} *M*) a major portion of the tin(II) would be oxidized by the dissolved oxygen. Air was removed by bubbling purified nitrogen through the solutions.

Crystalline sodium stannate was used for the preparation of tin(IV) solutions. All tin(IV) solutions were prepared fresh immediately before using.

Stock solutions of sodium fluoride and potassium fluoride were prepared from the C.P. chemicals and standardized by conductometric titration with standard hydrochloric acid solution. Adjustments of the ionic strengths of the potassium fluoride solutions were made with a stock solution of potassium nitrate and adjustments in the case of sodium fluoride solutions were made with a sodium nitrate solution.

Results and Discussion

Perchlorate Solutions.—For the calculation of instability constants of complex ions from polarographic data, it is desirable to know the half-wave potential for the reduction of the hydrated ion in a non-complexing solution. In this study, we chose

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[1] From a thesis submitted by Joseph A. Davis to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Master of Arts, August, 1952.

[2] P. W. West, J. Dean and E. J. Breda, *Collection Czechoslov. Chem. Communs.*, **13**, 1 (1948).

[3] M. Prytz, *Z. allgem. anorg. Chem.*, **172**, 147 (1928).

[4] M. Gorman and P. A. Leighton, THIS JOURNAL, **64**, 719 (1942).

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

[6] F. Duke and W. G. Courtenay, *Iowa State J. Sci.*, **24**, 397 (1950).

[7] C. E. Vanderzee and D. E. Rhodes, THIS JOURNAL, **74**, 3552 (1952).

[8] C. E. Vanderzee, *ibid.*, **74**, 4806 (1952).

[9] I. M. Kolthoff and J. J. Lingane, "Polarography," First Ed., Interscience Publishers, Inc., New York, N. Y., 1946, p. 263.

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

[11] W. H. Nebergall, J. C. Muhler and H. G. Day, THIS JOURNAL, **74**, 1604 (1952).

to measure the half-wave potentials for the reduction of tin(II) in perchlorate solutions at the same values of ionic strength as were used with the fluoride solutions.

The polarograms of tin(II) in perchloric acid solution show both cathodic and anodic waves. The cathodic waves are well-formed and reversible, corresponding to the two-electron reduction of the hydrated stannous ion to the metal (amalgam). The anodic waves, which are due to the oxidation of tin(II) to tin(IV), are rather poorly developed and are irreversible. The results are given in Table I.

TABLE I

RESULTS FOR CATHODIC AND ANODIC TIN(II) WAVES IN PERCHLORATE SOLUTIONS

Added $HClO_4$, *M*	Ionic strength[a] (μ)	$E_{1/2}$ (*vs.* S.C.E.), volts	Reversibility test slope[b]
	Cathodic waves		
0.04	0.8	−0.409	0.032
.40	0.8	− .423	.031
.80	0.8	− .432	.028
.04	2.5	− .410	.030
.20	2.5	− .411	.037
.40	2.5	− .421	.029
1.00	2.5	− .433	.031
2.00	2.5	− .447	.032
2.40	2.5	− .449	.032
	Anodic waves		
0.04	0.04	0.007	0.081
.10	.1	.043	.052
.50	.5	.109	.040
1.00	1.0	.136	.041
2.00	2.0	.178	.039
3.00	3.0	.182	.042

[a] Ionic strength was adjusted to the indicated values with $NaClO_4$ in the case of the solutions used in the study of the cathodic waves. [b] These slopes were obtained from a plot of $E_{d.e.}$ *versus* log $(i_d - i)/i$ according to the equation $E_{d.e.} = E_{1/2} + 0.059/2 \log (i_d - i)/i$.

It should be noticed that the reversibility test slopes for the cathodic (reduction) waves are very close to the theoretical value, 0.0296, over the entire range of perchloric acid concentration, whereas the anodic (oxidation) waves show a large variation in slope, approaching the reversible value of 0.0296 only at the higher acid concentrations. This situation indicates that it is the extreme hydrolysis of the tin(IV) ion produced at the anode that is responsible for the irreversibility of the anodic wave and that the extent of this hydrolysis decreases with increasing acidity. This explanation also accounts for the large positive shift in the half-wave potential of the irreversible anodic wave with increasing acid concentration.

From a consideration of the data the value −0.410 volt was taken to be the half-wave potential for the reduction of the hydrated stannous ion in the non-complexing perchlorate medium. This value agrees reasonably well with the standard electrode potential, −0.382 volt (*vs.* S.C.E.), calculated by Latimer[12] from thermal data and with the value −0.387 measured by Haring and White[13] for the couple $Sn = Sn^{+2} + 2e^-$.

Tin(IV) was found not to be polarographically reduced in perchloric acid solution confirming a previous report.[9]

Fluoride Solutions.—To obtain the data necessary for the study of the fluoride complexes of tin(II), a series of polarograms was run with solutions containing about 6×10^{-4} *M* tin(II), from 0.005 to 0.75 *M* sodium fluoride and sufficient sodium nitrate to maintain the ionic strength at a constant value of 0.8 throughout the series. Since potassium fluoride is more soluble than sodium fluoride, a second series was run using potassium salts. In this series the concentration of potassium fluoride was varied from 0.10 to 2.5 *M* and sufficient potassium nitrate was added to maintain the ionic strength constant at 2.5. In both series the *p*H was maintained above 5.0, making it unnecessary to take into account the two ionization constants of hydrofluoric acid (see below).

Both cathodic and anodic tin(II) waves were observed in these fluoride solutions. The cathodic waves are reversible and correspond to the reduction of the fluoro complex to the amalgam. The data for the cathodic waves in the sodium fluoride and potassium fluoride solutions are given in Table II.

TABLE II

RESULTS FOR CATHODIC TIN(II) WAVES IN NEUTRAL FLUORIDE SOLUTIONS

Fluoride ion concn., *M*	*p*H	$E_{1/2}$ (*vs.* S.C.E.), volts	Reversibility test slope	Calcd. dissociation constant $\times 10^{10}$
Series A: sodium fluoride–sodium nitrate soln. at μ = 0.8				
0.005	5.3	−0.506	0.031	0.72
.010	5.4	− .528	.034	1.02
.025	5.7	− .558	.034	1.56
.10	6.4	− .611	.034	1.59
.15	6.6	− .627	.030	1.27
.20	6.8	− .640	.035	1.36
.25	6.9	− .650	.034	1.22
.30	7.0	− .656	.036	1.36
.35	7.1	− .663	.033	1.21
.40	7.2	− .669	.034	1.14
.45	7.2	− .673	.035	1.15
.50	7.4	− .683	.038	0.74
.55	7.5	− .683	.031	0.98
.60	7.6	− .688	.036	0.86
.65	7.6	− .686	.044	1.26
.70	7.7	− .691	.036	1.09
.75	7.6	− .693	.036	1.14
Series B: potassium fluoride–potassium nitrate soln. at μ = 2.5				
0.10	6.7	−0.640	0.032	0.17
0.40	7.5	− .698	.034	.12
0.70	7.6	− .720	.034	.11
1.00	8.0	− .724	.040	.11
1.30	8.1	− .746	.039	.10
1.60	8.3	− .746	.039	.18
1.90	8.5	− .764	.042	.08
2.20	8.6	− .773	.044	.06
2.50	8.6	− .772	.039	.09

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(12) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, pp. 148–150.

(13) M. M. Haring and J. C. White, *Transactions Electrochem. Soc.* LXXIII, 211 (1938).

The anodic waves, arising from the oxidation of the tin(II) species to tin(IV), are not well defined and are not reversible in neutral fluoride solutions. The data for these waves are given in Table III.

TABLE III

RESULTS FOR ANODIC TIN(II) WAVES IN NEUTRAL AND ACIDIC FLUORIDE SOLUTIONS

pH	Fluoride ion concn.,[a] M	$E_{1/2}$ (*vs.* S.C.E.), volts	Reversibility test slope	$K_{d\text{IV}}/K_{d\text{II}}$[b] $\times 10^{15}$
Neutral fluoride soln. ($\mu = 0.5$)				
5.9	0.05	−0.217	0.096	
6.0	.07	− .224	.081	
6.1	.09	− .217	.097	
6.2	.10	− .242	.073	
6.5	.15	− .263	.080	
6.6	.20	− .285	.089	
6.8	.25	− .309	.092	
Acidic fluoride solns. ($\mu = 0.1$ to 0.2)				
3.55	0.058	−0.214	0.042	2.2
3.30	.049	− .199	.040	4.8
2.70	.022	− .174	.039	2.9
2.00	.005	− .117	.038	3.0

[a] In the acidic fluoride solutions the actual fluoride ion concentration was calculated using the two ionization constants of hydrofluoric acid. [b] Ratio of the dissociation constant of the tin(IV) fluoro complex to that of the tin(II) fluoro complex calculated from the polarographic data.

Separate experiments, the data from which are not reported here, showed that at constant fluoride concentration the $E_{1/2}$ values for the cathodic waves are independent of tin(II) concentrations and also that changes in pH in the range 5.6 to 7.1 at constant fluoride concentration do not appreciably affect the $E_{1/2}$ values for the cathodic waves. These observations indicate, respectively, that the tin(II) complex in fluoride solutions is not polynuclear and that basic complexes are not important in these neutral solutions containing excess fluoride. It should be noted that a qualitative indication of the strength of the tin(II) fluoro complex is the failure of stannous hydroxide to precipitate from neutral fluoride-containing solutions in spite of its low K_{sp} of 1.5×10^{-26}.

A plot of the half-wave potentials of the reversible cathodic waves *versus* the logarithm of the concentration of fluoride ion was made in order to determine the composition of the tin(II) complexes. Over a wide range of fluoride concentration (about 0.01 to 2.0 M) the slopes of the plots with both the NaF and the KF solutions agreed well with that expected for a coördination number of three, *i.e.*, $3(-0.059/2) = -0.089$, indicating that the predominant complex in this concentration range is SnF_3^- and that the cathodic reaction is $SnF_3^- + 2e^- \rightarrow Sn(amalgam) + 3F^-$.

An attempt was made to apply the method of Hume and Deford[14] to the data in order to study the lower complexes. However, the trifluoro complex appears to be stable and predominant even at very low fluoride concentrations so that no additional information was obtained over the range of fluoride concentration shown in Table II.

The dissociation constants given in Table II were calculated at each fluoride concentration assuming the complex to be SnF_3^- and using the difference between the $E_{1/2}$ with the fluoride solution and the value −0.410 obtained as the half-wave potential with the non-complexing perchlorate solutions. In the case of the sodium fluoride–sodium nitrate solutions at $\mu = 0.8$, the value of the over-all dissociation constant was calculated to be 1.2×10^{-10} ($\sigma = \pm 0.24$). In the case of the potassium fluoride–potassium nitrate solutions at $\mu = 2.5$, the value calculated for the dissociation constant was 1.1×10^{-11} ($\sigma = \pm 0.4$). No attempt was made to convert the fluoride ion concentrations to activity values.

The stable coördination number of three for the tin(II) complex is interesting in view of its electronic configuration. Tin(II) has two 5s electrons, leaving the three p-orbitals vacant and capable of accepting electron pairs. Apparently, in this fluoro complex the most stable configuration is the sp^3 hybrid involving the lone electron pair and the three pairs of electrons "shared" (unequally) with the fluoride ions. This pyramidal configuration with its C.N. of three is preferred over the tetrahedral complex, which is the usual configuration of "ionic type" complexes with C.N. less than six. It is unusual that the number of tin(II) orbitals available for covalent bonding determines the coordination number of the fluoro complex, especially since the highly electronegative fluoride ions favor ionic type bonding. Also, it should be noted that the order of stability of the halide complexes of tin(II) is F > Cl > Br and that this order is opposite that observed with most metals having an outer 18-electron shell (*e.g.*, Cu, Ag, Cd, Hg, Tl), but parallels that of zinc.

An attempt was made to study tin(IV) complexes by running polarograms with fluoride solutions containing dissolved sodium stannate. It was found that such solutions when freshly prepared give temporary, poorly defined and irreversible reduction waves at approximately −1.2 volt. The diffusion currents for these waves are much lower than expected and if the solutions are allowed to stand for several days the waves disappear completely due to gradual hydrolysis and precipitation of the tin(IV) from solutions.

Alternatively, a series of polarograms was obtained using acidified fluoride solutions containing tin(II) in the hope that the anodic waves would be more nearly reversible in the acidic solutions, thus making it possible to obtain some information concerning the tin(IV) complexes formed as oxidation products. Solutions were made up containing 0.1 M potassium fluoride and varying amounts of perchloric acid. The actual concentration of free fluoride ion, $[F^-]$, was calculated for each solution using the two ionization constants of Broene and DeVries[15] for hydrofluoric acid. For the equilibrium $HF = H^+ + F^-$, $K_1 = 6.71 \times 10^{-4}$ and for the equilibrium $HF_2^- = HF + F^-$, $K_2 = 0.259$.

The total fluoride concentration, ΣF, is given by the expression $\Sigma F = [F^-] + [HF] + 2[HF_2^-]$. Combining this with the two equilibrium expres-

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(14) D. DeFord and D. Hume, THIS JOURNAL, **73**, 5321 (1951).

(15) H. H. Broene and T. DeVries, *ibid.*, **69**, 1644 (1947).

sions above, the following quadratic equation is obtained which can be solved for the concentration of unassociated "free" fluoride ion, $[F^-]$, if the total added fluoride concentration, the pH and the ionization constants are known.[16]

$$\Sigma F = [F^-] + [H^+][F^-]/K_1 + 2[H^+][F^-]^2/K_1K_2$$

The results from the polarograms obtained with acidic fluoride solutions are presented in Table III along with results from neutral fluoride solutions.

The reversibility test slopes show that in neutral fluoride solutions the anodic reaction is definitely irreversible. However, in the acidic fluoride solutions the slopes approach the theoretical value of 0.0296 (for a two-electron reaction) much more closely. If it is assumed that the observed $E_{1/2}$ values in the acidic solutions correspond to the reversible values, or very nearly so, then the data from the polarograms in the fluoride solutions of low pH can be used in the calculation of the formula and dissociation constant of the tin(IV) complex.

When the $E_{1/2}$ values for the anodic waves obtained with the acidic solutions are plotted against the logarithm of the "free" fluoride ion concentration, the experimental points fall closely along a line of slope −0.089, indicating a difference of three in the number of fluoride ions complexed by the tin(II) and the tin(IV). This is an entirely reasonable result and indicates that the oxidation reaction occurring at the electrode in acidic fluoride solutions is

$$SnF_3^- + 3F^- \longrightarrow SnF_6^{--} + 2e^-$$

Taking the standard potential of the reaction $Sn^{+2} \rightarrow Sn^{+4} + 2e^-$ to be −0.092 volt (*vs.* S.C.E.)[12] and considering this to represent the oxidation potential of tin(II) in a non-complexing medium, then from the shift in $E_{1/2}$ values in acidic fluoride solutions the ratio of the dissociation constant of the tin(IV) complex to that of the tin(II) complex is calculated to be 3×10^{-15}. From this ratio and the previously calculated value of 10^{-10} for the dissociation constant of SnF_3^-, an over-all dissociation constant of about 10^{-25} is calculated for the complex ion SnF_6^{-2}.

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BLOOMINGTON, INDIANA

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[16] The accuracy of this equation was tested by comparing the $E_{1/2}$ values for the reversible cathodic waves obtained with fluoride solutions of low pH, for which the concentration of the "free" fluoride ion was calculated by means of this equation, wth the $E_{1/2}$ values obtained with approximately neutral fluoride solutions for which no correction for association was needed. The values of the half-wave potentials for solutions of corresponding fluoride ion concentration agreed within several millivolts. Furthermore a plot of the $E_{1/2}$ values (for the cathodic waves in the acidic fluoride solutions) *versus* the logarithm of the free fluoride ion concentration (calculated with this equation) gave a straight line, the slope of which again corresponded closely to that expected for a coördination number of three, *i.e.*, the reaction, $SnF_3^- + 2e^- \rightarrow Sn(Hg) + 3F^-$.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Determination of Molecular Weights of Vapors at High Temperatures. I. The Vapor Pressure of Tin and the Molecular Weight of Tin Vapor[1]

BY ALAN W. SEARCY[2] AND ROBERT D. FREEMAN

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An apparatus is described with which molecular weights of vapors can be determined at temperatures of 1200 to 2200°K. and at pressures of 10^{-6} to 10^{-4} atm. The molecular weight of a vapor is calculated from simultaneous measurements of the vapor pressure by the Knudsen effusion method and by direct determination of the force resulting from effusion of the vapor. The molecular weight of tin vapor is found to be 91 ± 29 in the range 1600–1900°K., confirming the fact that tin vapor is essentially monatomic. The heat of sublimation of tin at 298°K. is calculated to be 71.9 ± 2.0 kcal.

Recent investigations which have established the existence of such unexpected gaseous molecules as $(Al_2S)_x$,[3] $BeO \cdot (H_2O)_x$[4] and Ge_4[5] attract attention to the meagerness of our knowledge of the compositions and structures of gaseous molecules at high temperatures. Most techniques for obtaining information about gaseous species are unreliable or prohibitively difficult to apply at temperatures much above 1000°. As a result, investigators of reactions at higher temperatures are usually forced to assume, with little supporting evidence, that gaseous reaction products are atoms, spectroscopically familiar diatomic molecules, or simple molecules with stoichiometries of known condensed phases. Uncertainty about the composition of reaction products imposes a severe limitation on the usefulness of thermodynamic data for high temperature calculations.

In most reactions yielding gaseous products, knowledge of the molecular weight of the products would permit almost certain identification of the molecular species formed. A promising method for simultaneous determination of the vapor pressure of a substance and of the molecular weight of its vapor has been developed by Mayer[6] and Volmer.[7] However, they and later workers[8–10] have employed the method only at temperatures at-

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[1] Work supported by the Office of Naval Research. Based on a dissertation submitted by R. D. Freeman in partial fulfillment of the requirements for the Ph.D. degree at Purdue University.

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[7] M. Volmer, *ibid.*, Bodenstein Festband, 863 (1931).

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[10] G. Wessel, *Z. Physik*, **130**, 539 (1951).