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Hydrolysis of Tin(II) in Aqueous Solutions

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The hydrolysis of Sn^{2+} has been studied in various ionic media (NaNO_3 , NaCl , and artificial seawater) from 0.1 to 1 M and 20 °C by using differential pulse anodic stripping voltammetry. The shift in the potential of the stripped Sn^{2+} was determined as a function of pH (2–11) at a Sn^{4+} concentration of 5.4×10^{-7} M. These results were used to determine β_1 , β_2 , and β_3 for the hydrolysis of Sn^{2+} and β_1 and β_2 for the formation of chloro, bromo, and sulfate complexes. Our values for the hydrolysis of chloro and bromo complexes of Sn^{2+} are in reasonable agreement with the literature values. The distribution or speciation of various species of tin(II) in NaNO_3 , NaCl , and artificial seawater were determined from the calculated stability constants.

In a recent paper (1) on the voltammetric and chemical characterization of tin, it was shown that tin(IV) gives a well-defined peak corresponding to the reoxidation of $\text{Sn}(\text{Hg})$ to Sn^{2+} , in the range of pH 2–6. The electrochemical process was shown to be reversible, in agreement with some literature indications (2, 3), while the peak potential was found to shift to more cathodic potentials as the OH^- concentration was increased. The shift of the potential was found to vary linearly with pOH in various ionic media (NaNO_3) and artificial seawater. Since the slope of the straight line was approximately 0.029, it was concluded that the predominate species that occurred in the stripping process (pH 2–6) was $\text{Sn}(\text{OH})^+$. No peak was observed in alkaline conditions (–0.9 V plating potential).

The present paper describes our more recent experiments. We have found (see Figure 1) that the tin peak also occurs in alkaline conditions provided that a higher negative plating potential is applied (–1.4 V). This allowed us to make a more accurate study of the shift in the potential over a wide range of pH (2–11). An analysis of the shift in the peak potential has yielded stability constants β_1 , β_2 , and β_3 , corresponding to the formation of $\text{Sn}(\text{OH})^+$, $\text{Sn}(\text{OH})_2^0$, and $\text{Sn}(\text{OH})_3^-$. Since the concentration of tin(IV) in our results was quite low (5×10^{-7} M), we have avoided the complications due to the formation of polynuclear species (4). Our results at low pH in chloride, bromide, and sulfate solutions have yielded values for the formation of complexes of Sn^{2+} with these anions (e.g., SnCl^+ , SnCl^0).

EXPERIMENTAL SECTION

Chemicals. All the solutions were made by using Merck Suprapur chemicals. The artificial seawater (NaCl , Na_2SO_4 , KCl , NaHCO_3 , KBr , NaF , MgCl_2 , CaCl_2 , SrCl_2 , and $\text{B}(\text{OH})_3$) was prepared according to the recipe of Millero (5). The stock 1 M NaOH solution was prepared by diluting a Carlo-Erba standard solution. Stannic solutions were prepared by dilution of a Merck 1000 ppm SnCl_4 standard solution. The stock stannic solution was stabilized by adding a suitable quantity of concentrated Merck Suprapur HNO_3 to obtain a final acid concentration of 2 M. The water used in the preparation of solutions and cleaning was 10 $\text{M}\Omega\text{ cm}^{-1}$ obtained from the Millipore Milli-Q₂ system.

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Apparatus. The voltammetric measurements were performed with an AMEL 471 multipolarograph and AMEL ancillary equipment. The working electrode was a hanging drop mercury electrode (HDME). The reference electrode was an Ingold 303-NS saturated calomel electrode (SCE) and platinum was used as a counterelectrode. The pH measurements were carried out with an Orion Model 399 pH meter, equipped with Orion 91-01-00 glass electrode and 90-00-02 double-junction reference electrode. The pH meter and electrodes were calibrated with infinite dilution Normex buffers (pH 4, 7, and 10).

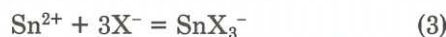
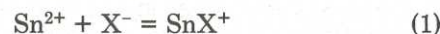
Procedure. Aliquots of 25 mL of sample, at $\text{Sn}(\text{IV})$ concentration of 5.4×10^{-7} M, were introduced into the cell, and oxygen was removed by bubbling with nitrogen. A plating potential of –1.4 V was applied for 180 s with stirring. A rest time of 12 s was employed. The stripping scan was 5 mV/s and the height of the pulse was 25 mV. After the voltammogram was recorded, the pH was measured while bubbling the samples with nitrogen. The measurements were performed at 20 °C. The same procedure was adopted for samples at various values of pH. Since the peaks of lead and tin are overlapped in the range of pH 2–4, great care was made to avoid lead contamination.

In order to investigate the effect of various ligands on the potential of Sn^{2+} , we have measured the peak potential in various ionic media (NaNO_3 , NaClO_4 , NaCl , Na_2SO_4 , NaBr , HNO_3 , HClO_4 , and artificial seawater, ASW) as a function of ionic strength at low values of pH (1.0–2.5). With the exception of NaCl , Na_2SO_4 , NaBr , and ASW, we found the peak potential to be constant from 0.1 to 1.0 M. The value of the peak potential of 0.442 ± 0.001 in NaNO_3 solutions was used as the value attributed to free Sn^{2+} . The shifts in the peak potentials from this value as a function of pH, Cl^- , Br^- , etc. were attributed to the formation of various ion pairs of Sn^{2+} . Since the Sn^{2+} peak disappeared in the pH range of 5–7.5, due to solubility limitations (1), we were not able to make reproducible measurements in this range of pH.

The use of DPASV to determine thermodynamic stability constants is possible only when the rate of formation of the complex, after the oxidation, is sufficiently fast (6). This appears to be the case for the interactions of Sn^{2+} with Cl^- , Br^- , SO_4^{2-} , and OH^- .

RESULTS AND CALCULATIONS

The shift in the peak potential, ΔE_p , at low values of pH, can be attributed to the formation of Sn^{2+} complexes



where X represents an anion such as Cl^- or Br^- . The stepwise stoichiometric association constants (β_i) are given by

$$\beta_1(\text{X}) = [\text{SnX}^+]/[\text{Sn}^{2+}][\text{X}^-] \quad (4)$$

$$\beta_2(\text{X}) = [\text{SnX}_2^0]/[\text{Sn}^{2+}][\text{X}^-]^2 \quad (5)$$

$$\beta_3(\text{X}) = [\text{SnX}_3^-]/[\text{Sn}^{2+}][\text{X}^-]^3 \quad (6)$$

where the brackets refer to concentration. The values of ΔE_p are approximately related to β_1 , β_2 , and β_3 by (6)

$$\Delta E_p = (RT/nF) \ln (1 + \beta_1[\text{X}^-] + \beta_2[\text{X}^-]^2 + \beta_3[\text{X}^-]^3) \quad (7)$$

This equation can be expressed in the form

$$F_0(\text{X}) = 1 + \beta_1[\text{X}^-] + \beta_2[\text{X}^-]^2 + \beta_3[\text{X}^-]^3 \quad (8)$$

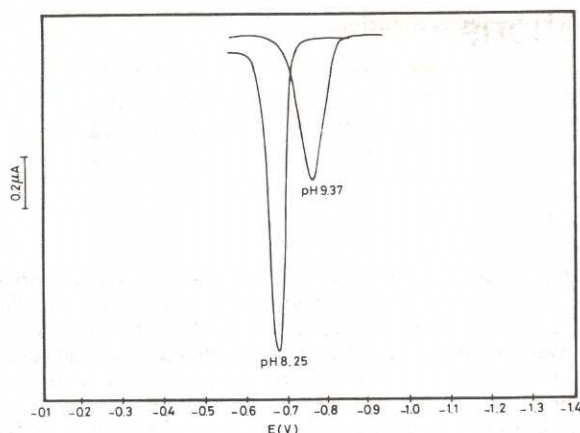


Figure 1. Voltammograms of tin (5.4×10^{-7} M) in artificial seawater with a plating potential of -1.4 V.

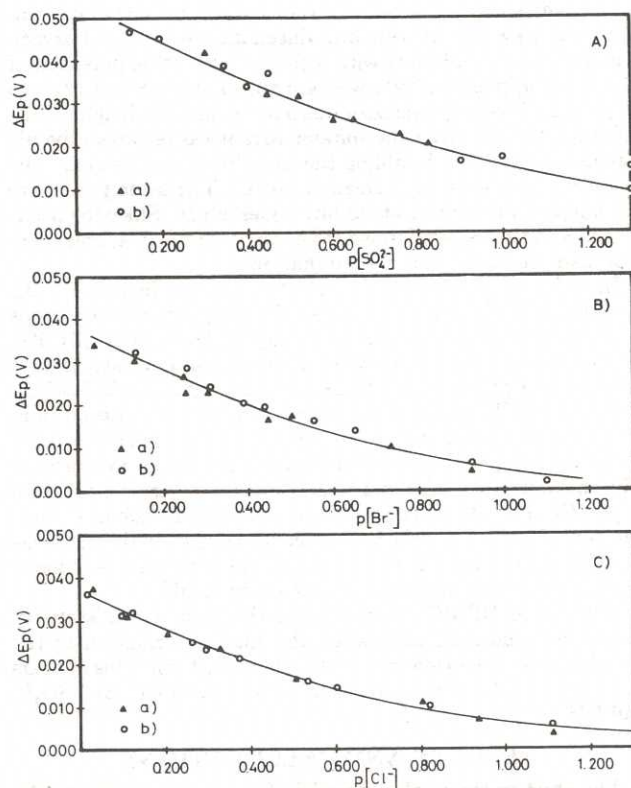


Figure 2. Values of ΔE_p (relative to SCE) vs. $p[X] = -\log [X]$ at pH 2. X represents SO_4^{2-} (A), Br^- (B), and Cl^- (C). (a) Ionic strength was kept constant to 1 M for Cl^- and Br^- and to 1.5 M for SO_4^{2-} , with the addition of a suitable quantity of NaNO_3 . (b) Ionic strength was dependent on the concentration of the added salt (NaCl , NaBr , Na_2SO_4).

where $F_0(X) = \exp[\Delta E_p(nF/RT)] = \exp(79.27\Delta E_p)$ at 20°C . The values of β_i can be estimated by examining the function $F_0(X)$ over a range of concentrations of $[X^-]$. At low concentrations of $[X^-]$, β_3 is unimportant and eq 8 becomes

$$F_1(X) = \frac{F_0(X) - 1}{[X]} = \beta_1 + \beta_2[X] \quad (9)$$

This linear equation can be used to estimate β_1 and β_2 for the formation of complexes of Sn^{2+} with anions at low values of pH (i.e., where OH^- complexes can be neglected, pH 2.0). This shift in the potential, ΔE_p , for various media containing NaNO_3 and NaCl are shown plotted vs. $p\text{Cl}$ in Figure 2. Over an ionic strength of 0.5–1.5, we were unable to see significant differences in ΔE_p at a given concentration of Cl^- . The values of $F_1(X)$ calculated from the values ΔE_p gave $\log \beta_1(\text{Cl}) = 0.73 \pm 0.1$ and $\log \beta_2(\text{Cl}) = 1.08 \pm 0.1$.

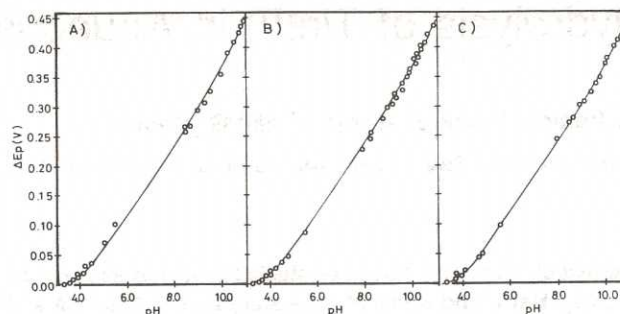


Figure 3. Values of ΔE_p (relative to SCE) vs. pH in 0.1 M (A), 0.5 M (B), and 1.0 M (C) NaNO_3 .

Similar measurements in NaBr and Na_2SO_4 are also shown in Figure 2. The values of $\log \beta_i$ for Br^- and SO_4^{2-} complexes obtained from eq 9 are given in Table I.

The shifts in the peak potential, ΔE_p , in various solutions of NaNO_3 as a function of pH, are shown in Figure 3. The shift in the peak potential as a function of pH can be attributed to the hydrolysis of Sn^{2+} .



The stepwise stoichiometric hydrolysis constants are given by

$$\beta_1(\text{H}^+) = \frac{[\text{Sn}(\text{OH})^+][\text{H}^+]}{[\text{Sn}^{2+}]} \quad (13)$$

$$\beta_2(\text{H}^+) = \frac{[\text{Sn}(\text{OH})_2^0][\text{H}^+]^2}{[\text{Sn}^{2+}]} \quad (14)$$

$$\beta_3(\text{H}^+) = \frac{[\text{Sn}(\text{OH})_3^-][\text{H}^+]^3}{[\text{Sn}^{2+}]} \quad (15)$$

where the concentration or activity of water is included in the β_i . The values of ΔE_p are related to the hydrolysis constants by

$$\Delta E_p = (RT/nF) \ln (1 + \beta_1/[\text{H}^+] + \beta_2/[\text{H}^+]^2 + \beta_3/[\text{H}^+]^3) \quad (16)$$

This equation can be expressed in the form

$$F_0(\text{H}^+) = 1 + \beta_1/[\text{H}^+] + \beta_2/[\text{H}^+]^2 + \beta_3/[\text{H}^+]^3 \quad (17)$$

where $F_0(\text{H}^+) = \exp[79.27\Delta E_p]$ at 20°C . In the low-pH region, only β_1 and β_2 are important, while in the high-pH region, β_1 can be neglected (6). We have determined the values of β_i for the hydrolysis of Sn^{2+} in a stepwise manner. In the low-pH region, eq 17 becomes

$$F_1(\text{H}^+) = \frac{F_0(\text{H}^+) - 1}{1/[\text{H}^+]} = \beta_1 + \beta_2/[\text{H}^+] \quad (18)$$

This equation was used to obtain values of β_1 and β_2 . Values of $-\log \beta_1 = 4.1, 3.8, 4.1$ and $-\log \beta_2 = 7.6, 8.0, 7.7$ were obtained, respectively, for 0.1, 0.5, and 1.0 M NaNO_3 .

In the high-pH region, one can use the estimated values of β_1 to transfer eq 17 to the linear form

$$\frac{F_1(\text{H}^+) - \beta_1}{1/[\text{H}^+]} = \beta_2 + \beta_3/[\text{H}^+] \quad (19)$$

Table I. Values of Stability Constants of Sn(II) with Various Ligands in Aqueous Solutions

ligand	media	$\log \beta_1(X)$	$\log \beta_2(X)^a$	$\log \beta_3(X)$
H_2O	0.1 M $NaNO_3$	-4.1 ± 0.2^b	-7.9 ± 0.2	-17.5 ± 0.2
	0.5 M $NaNO_3$	-3.8 ± 0.2	-7.9 ± 0.2	-17.7 ± 0.2
	1.0 M $NaNO_3$	-4.1 ± 0.2	-7.8 ± 0.2	-17.6 ± 0.2
	0.5 NaCl	-3.1 ± 0.2	-8.2 ± 0.2	-17.8 ± 0.2
	ASW ($I = 0.7$)	-3.1 ± 0.2	-8.2 ± 0.2	-17.2 ± 0.2
Cl^-	1.0 M $NaNO_3$	0.73 ± 0.1	1.08 ± 0.1	
Br^-	1.0 M $NaNO_3$	0.60 ± 0.1	1.13 ± 0.1	
SO_4^{2-}	1.0 M $NaNO_3$	1.29 ± 0.1	1.65 ± 0.1	
H_2O, Cl^-	0.5 NaCl and ASW	-2.9 ± 0.2		
H_2O, M^{2+}	0.5 NaCl and ASW			-16.2 ± 0.2

^a The values of β_2 for the hydrolysis of Sn(II) are the average values obtained from eq 18 and 19. ^b The errors are the standard errors of the least-squares fits.

Table II. Comparisons of the Stability Constants of Sn(II) Obtained in This Study with Literature Data

ligand	media	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	ref
H_2O	$NaNO_3$	-4.0	-7.9	-17.6	this study
	$NaClO_4$	-3.9	-7.6	-16.7	Baes and Mesmer (7)
	$NaClO_4$	-3.9			Tobias (4)
	$HCl + NaOH$	-2.1	-7.1	-16.6	Garret and Heiks (8)
	$HClO_4$	-1.7			Gorman (9)
Cl^-	$NaClO_4$	-1.7			Vanderzee and Rhodes (10)
	$NaNO_3$	0.73	1.08		this study
	$NaClO_4$	1.2	1.7	1.7	Vanderzee and Rhodes (10)
Br^-	$NaClO_4$	1.1	1.8	1.5	Duke and Courtenay (11)
	$NaNO_3$	0.60	1.13		this study
	$NaClO_4$	0.76	1.2	1.4	Vanderzee (12)

This linear equation was used to obtain the values of $-\log \beta_2 = 8.1, 7.7, 7.9$ and $-\log \beta_3 = 17.5, 17.7, 17.6$, respectively, at 0.1, 0.5, and 1.0 M $NaNO_3$. the values of β_2 and β_3 obtained in this manner were found to be insensitive to the value selected for β_1 .

The values of β_1, β_2 , and β_3 for the hydrolysis of Sn^{2+} are independent of ionic strength (0.1–1.0 M) within the experimental error of our measurements. If the total data set is fit to eq 18 and 19, we obtain values of β_1, β_2 , and β_3 equal to the average values given in Table II.

Measurements of the hydrolysis of Sn^{2+} were also made in 0.5 M NaCl and 0.7 M ionic strength artificial seawater (ASW). The values of ΔE_p as a function of pH are shown in Figure 4. The values of ΔE_p as a function of pH in NaCl and ASW include the effects of competing interactions of Sn^{2+} with Cl^- , Br^- , and SO_4^{2-} . The shift in the potential is given by

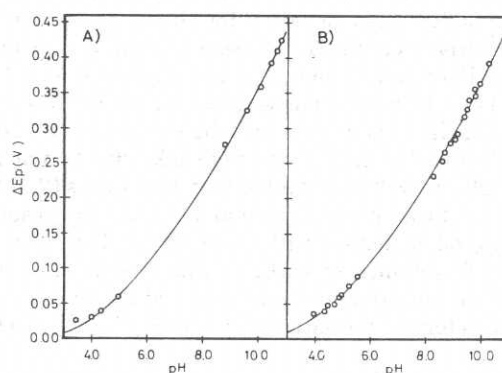
$$\Delta E_p = (1/79.27) \ln (1 + \sum \beta_i [X]^i + \beta_1/[H^+] + \beta_2/[H^+]^2 + \beta_3/[H^+]^3) \quad (20)$$

where the summation is made over all the anions (Cl^- , Br^- , and SO_4^{2-}) able to form complexes with Sn^{2+} . For 0.5 M NaCl at a pH 2.0, eq 20 gives $\Delta E_p = 0.024$ V compared to the measured value of 0.025 V. With $[Cl^-] = 0.560$ M, $[SO_4^{2-}] = 0.029$ M, and $[Br^-] = 0.001$ M for ASW, eq 20 at pH 2.0 gives $\Delta E_p = 0.027$ V compared to the measured value of $\Delta E_p = 0.028$ V. Thus, the values of β_i for the interactions of Sn^{2+} with Cl^- , Br^- , and SO_4^{2-} in binary solutions are valid in artificial seawater.

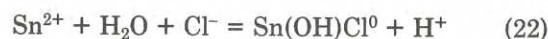
The values of β_1 and β_2 for the hydrolysis of Sn^{2+} in NaCl and ASW in the low pH range (3.0–5.0) can be determined from

$$F_1(H^+) = \frac{F_0(H^+) - 1 - \sum \beta_i [X]^i}{1/[H^+]} = \beta_1 + \beta_2/[H^+] \quad (21)$$

where $F_0(H^+) = \exp(79.27 \Delta E_p)$. Values of $\log \beta_1 = -3.1 \pm 0.2$ and $\log \beta_2 = -8.2 \pm 0.2$ were determined from eq 21 for NaCl and ASW. The values of β_2 in NaCl and ASW are equal to the value found in $NaNO_3$ within experimental error. The

Figure 4. Values of ΔE_p (relative to SCE) vs. pH in 0.5 M NaCl (A) and in artificial seawater (B).

higher values of β_1 in NaCl and ASW can be attributed to the formation of a mixed complex



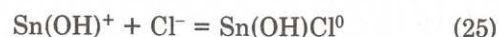
The mixed hydrolysis constant is given by

$$\beta_{H_2O, Cl} = \frac{[Sn(OH)Cl][H^+]}{[Sn^{2+}][Cl^-]} \quad (23)$$

The value of $\beta_{H_2O, Cl}$ is related to β_1^* in NaCl and ASW and β_1 in $NaNO_3$ by

$$\beta_1^* = \beta_1 + \beta_{H_2O, Cl}[Cl] \quad (24)$$

Equation 24 gives $\log \beta_{H_2O, Cl} = -2.9 \pm 0.2$. The constant for the formation of $Sn(OH)Cl^0$



is given by $\beta_{Sn(OH)Cl} = \beta_{H_2O, Cl}/\beta_1 = 10^{1.14} = 13.8$. Since our measurements were not made over a wide range of Cl^- concentrations, these values of $\beta_{H_2O, Cl}$ and $\beta_{Sn(OH)Cl}$ must only be considered to be a reasonable estimate.

In the high-pH region, one can use the estimated values of β_1^* in NaCl and ASW to convert eq 20 to the linear form (eq 19, where $F_1(H^+)$ is given by eq 21 and $\beta_1 = \beta_1^*$). This linear equation gives $\log \beta_2 = -8.1 \pm 0.2$, -8.3 ± 0.2 , and $\log \beta_3 = -17.8 \pm 0.2$, -17.2 ± 0.1 , respectively, for 0.5 M NaCl and ASW. The values of β_2 and β_3 in NaCl and ASW are equal to the values found in NaNO_3 within the experimental error of the measurements. The higher value of β_3 in ASW compared to the values in NaCl and NaNO_3 could be related to the formation of a mixed complex



where $\text{M}^{2+} = [\text{Mg}^{2+}] + [\text{Ca}^{2+}] + [\text{Sr}^{2+}] = 0.065 \text{ M}$.

The value of the mixed hydrolysis constant $\beta_{(\text{H}_2\text{O})_3\text{M}}$ is related to the β_3^* in ASW and β_3 in NaNO_3 by

$$\beta_3^* = \beta_3 + \beta_{(\text{H}_2\text{O})_3\text{M}}[\text{M}^{2+}] \quad (27)$$

Equation 27 gives $\log \beta_{(\text{H}_2\text{O})_3\text{M}} = -16.2 \pm 0.2$. The constant for the formation of $\text{MSn}(\text{OH})_3^+$



is given by $\beta_{\text{MSn}(\text{OH})_3} = \beta_{(\text{H}_2\text{O})_3\text{M}}/\beta_3 = 10^{1.5} = 32 \pm 10$. Further measurements of the hydrolysis of Sn^{2+} in $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ solutions are needed to confirm these estimates of $\beta_{(\text{H}_2\text{O})_3\text{M}}$ and $\beta_{\text{MSn}(\text{OH})_3}$.

The reliability of these values of β_i can be examined by comparing the calculated and measured values of ΔE_p (using eq 7, 16, and 20). The smooth curves shown in Figures 2–4 were obtained in this manner. The average deviations were found to be less than $\pm 0.001 \text{ V}$ for all the systems studied.

The hydrolysis of $\text{Sn}(\text{II})$ has been studied by a number of workers. Baes and Mesmer (7) have recently selected what they feel are the most reliable values for the hydrolysis constants of $\text{Sn}(\text{II})$. Their selection is based on the experimental work of Tobias (4) and Garrett and Heiks (8). A comparison of their selected values and other literature values (9, 10) with the results of this study is given in Table II. Our results for β_1 are in good agreement with the results of Tobias (4). The values of β_1 obtained by earlier workers are in error due to the high concentrations of $\text{Sn}(\text{II})$ used and the failure to make corrections for the formation of $\text{Sn}_2(\text{OH})_2^{2+}$ and $\text{Sn}_2(\text{OH})_4^{2-}$ (7).

Our value for β_2 is in reasonable agreement with the value obtained by Garrett and Heiks (8) extrapolated to 1 M (7). For β_3 we obtain a value that is smaller than that obtained by Garrett and Heiks (8). This difference could be due to the formation of polymeric species of $\text{Sn}(\text{II})$ at the high concentrations (0.004–0.3 M) used by Garrett and Heiks (8). Since the values of β_i obtained for the hydrolysis of $\text{Sn}(\text{II})$ by Garrett and Heiks (8) were indirectly derived from solubility data of $\text{SnO}(\text{s})$ at high concentrations of $\text{Sn}(\text{II})$, we feel that our values are more reliable.

Comparisons of our values of stability constants for interactions of $\text{Sn}(\text{II})$ with Cl^- and Br^- and literature values are also given in Table II. Our values of β_1 and β_2 for the formation of SnCl^+ and SnCl_2^0 are lower than those found by Vanderzee and Rhodes (10) and Duke and Courtenay (11). This difference is probably due to the formation of polymeric species of $\text{Sn}(\text{II})$ at the higher concentrations used in these studies. Our values for β_1 and β_2 for the formation of SnBr^+ and SnBr_2^0 are in good agreement with the values obtained by Vanderzee (12). We did not find it necessary to use a β_3 to fit our data for all the systems we studied. To the best of our knowledge, results for the β_i for $\text{Sn}(\text{II})$ -sulfate interactions are not available in the literature.

To summarize, we have determined the hydrolysis constants of $\text{Sn}(\text{II})$ in NaNO_3 solutions from 0.1 to 1.0 M, as well as the stability constants of $\text{Sn}(\text{II})$ with Cl^- , Br^- , and SO_4^{2-} in 0.5 M

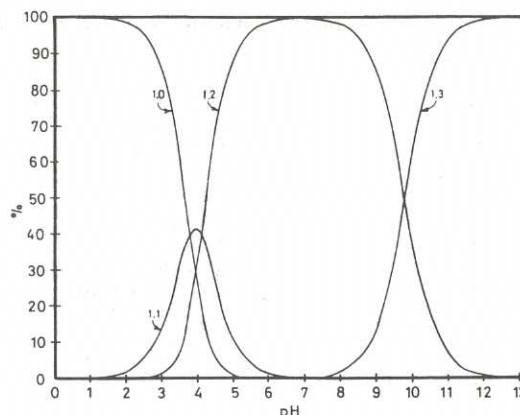


Figure 5. Distribution of various species of tin(II) as a function of pH in NaNO_3 (0.1–1 M). The numbers refer to the values of x and y of the species $\text{Sn}_x(\text{OH})_y$.

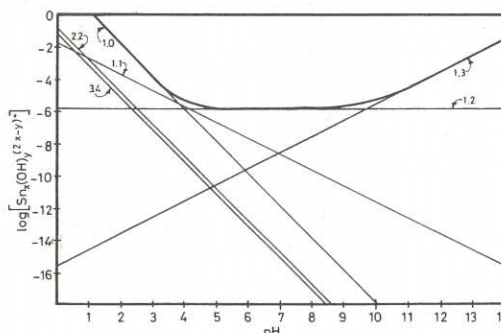


Figure 6. Distribution of hydrolysis products (x , y) in NaNO_3 solution saturated with SnO .

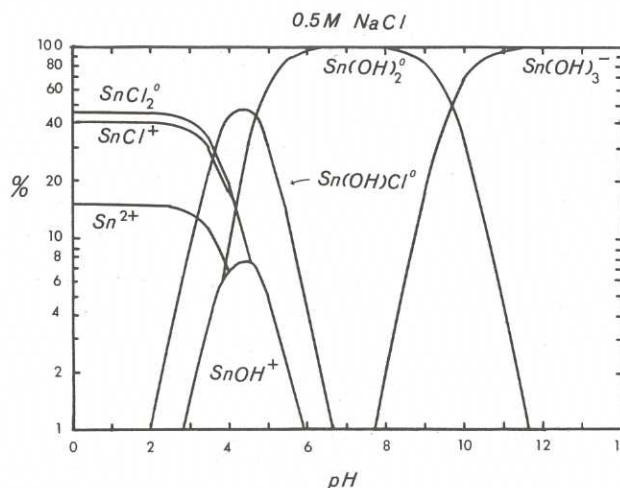


Figure 7. Distribution of various species of tin(II) as a function of pH in 0.5 M NaCl.

NaNO_3 . Since we were able to determine these constants in very dilute solutions of $\text{Sn}(\text{II})$, we have been able to avoid the complications of earlier work due to the formation of polymeric forms of $\text{Sn}(\text{II})$, $\text{Sn}_2(\text{OH})_2^{2+}$, and $\text{Sn}_3(\text{OH})_4^{2+}$ (4).

The values of hydrolysis constants of Sn^{2+} in NaNO_3 , NaCl, and ASW determined in this study can be used to determine the speciation of $\text{Sn}(\text{II})$ in these solutions. The speciation of Sn^{2+} at low concentrations as a function of pH at 20 °C and in NaNO_3 is shown in Figure 5. Our results have been combined with the solubility data of Garrett and Heiks (8) and the polynuclear constants of Tobias (4) to yield the speciation of $\text{Sn}(\text{II})$ saturated with SnO at an ionic strength of 0.5 M (see Figure 6). The effects of adding NaCl and ASW to the speciation are shown in Figures 7 and 8. The addition of NaCl

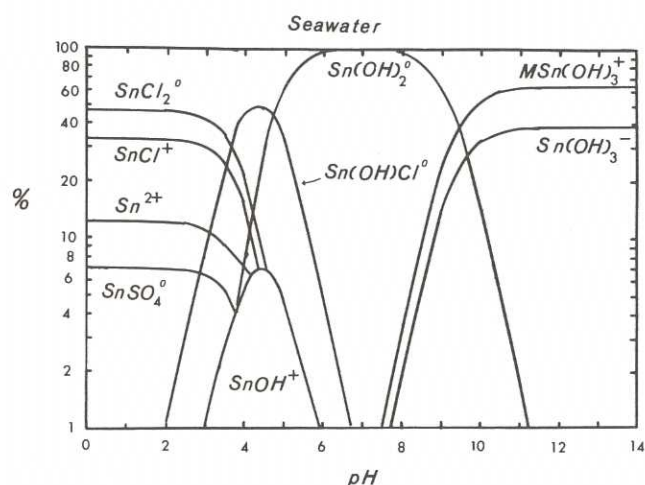


Figure 8. Distribution of various species of tin(II) as a function of pH in artificial seawater ($I = 0.7 \text{ M}$).

changes the forms of Sn(II) in the low-pH range but has little effect above a pH of 7. In seawater at pH 8.1 (the value for average seawater), the predominate forms of Sn(II) are Sn(OH)_2^0 (93.8%), Sn(OH)_3^- (2.4%), and MSn(OH)_3^+ (3.8%).

ACKNOWLEDGMENT

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