METAL COMPLEXING BY PHOSPHORUS COMPOUNDS—VIII

COMPLEXING OF TIN (II) BY POLYPHOSPHATES

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Abstract—The stability of complexes of pyrophosphate and tripolyphosphate ions with Sn(II), which occur in the pH region 5–7, have been determined by equilibrating phosphate solutions at unit ionic strength with solid SnO at 25°C. The following formation constants were calculated for the simplest equilibria that are consistent with the data:

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + \text{H}_{x}\text{P}_{2}\text{O}_{7}^{-(4-z)} \stackrel{K_{1}}{=} \text{Complex}_{1}, K_{1} = 6 \times 10^{5}$$

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + 2\text{H}_{x}\text{P}_{2}\text{O}_{7}^{-(4-z)} \stackrel{\text{complex}_{1}}{=} \text{Complex}_{2}, K_{2} = 2 \times 10^{8}$$

$$K_{3}$$

$$2\text{SnO} + \text{H}_{x}\text{P}_{2}\text{O}_{7}^{-(4-z)} \stackrel{\text{complex}_{2}}{=} \text{Complex}_{3}, K_{3} = 3 \times 10^{-1}$$

where x is one or two.

Also,

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + 2\text{HP}_{3}\text{O}_{10}^{4-} \stackrel{K_{1}'}{=} \text{Complex}_{1}', K_{1}' = 1.82 \times 10^{7}$$

$$4\text{SnO} + 2\text{H}_{3}\text{O}^{+} + 2\text{HP}_{3}\text{O}_{10}^{4-} \stackrel{=}{=} \text{Complex}_{2}', K_{2}' = 4.78 \times 10^{11}$$

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + 2\text{H}_{2}\text{P}_{3}\text{O}_{10}^{3-} \stackrel{=}{=} \text{Complex}_{3}', K_{3}' = 1.0 \times 10^{5}$$

$$4\text{SnO} + 2\text{H}_{3}\text{O}^{+} + 2\text{H}_{2}\text{P}_{3}\text{O}_{10}^{3-} \stackrel{=}{=} \text{Complex}_{4}', K_{4}' = 6 \times 10^{6}$$

The constant for the hydrolysis reaction was also measured:

 $\text{SnO} + \text{H}_3\text{O}^+ \stackrel{K_h}{=} \text{Sn(OH)}^+ + \text{H}_2\text{O}, K_h = 0.53.$

The trend of the Sn(II) complexing by long chain polyphosphates with average chain lengths up to fourteen is discussed.

THE literature on metal complexing by polyphosphates was reviewed⁽¹⁾ in 1958 by VAN WAZER and CALLIS. At that time the available information was largely qualitative or at best semi-quantitative in nature. However, it was well established that most cations form soluble polyphosphate complexes.

The complexing of alkali metals^(2,3) and alkaline earth metals^(4,5) has been well defined for systems with pyrophosphate and tripolyphosphate. In the last few years, polyphosphate complexes with metal ions which hydrolyze have been characterized, e.g. Hg(I) and Hg(II)⁽⁶⁾ and Cu(II).^(7,8) In these cases the extent of the hydrolysis of the metal ion and the acid form of the polyphosphate were taken into account.

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Few studies have been reported on the complexing of Sn(II) in aqueous solutions. This situation is probably due to the extensive hydrolysis and ease of oxidation of Sn(II) as well as the extreme insolubility of the oxide. In 1958, TOBIAS⁽⁹⁾ reported the characterization of the equilibria in aqueous solutions of Sn(II) in the absence of other complexing agents, in which SILLEN's well-proven methods of potentiometry⁽¹⁰⁻¹³⁾ were employed. He accounted for the data with equilibria involving the following species: Sn^{2+} , $Sn(OH)^+$, $Sn_2(OH)_2^{2+}$ and $Sn_3(OH)_4^{2+}$.

Limited studies of the complexing of Sn(II) by chloride,⁽¹⁴⁾ bromide⁽¹⁵⁾ and pyrophosphate⁽¹⁶⁾ have been reported, but in all these studies the authors did not take into account the polynuclear species of Sn(II) which are known to exist in the pH regions investigated. Also, DAVIS⁽¹⁶⁾ found that the polarographic reduction of Sn(II) was not reversible above pH of 4. Since the polyphosphates are good complexing agents at higher pH regions where SnO is very insoluble, we selected a solubility approach for this study. In this paper, the term SnO refers to solid.

We have studied the effect of the presence of polyphosphates in solution on the equilibrium solubility of SnO. As part of this investigation, we determined the equilibrium constants for the hydrolysis of SnO in the same medium as the complexing experiments. This allows calculation of complexing constants involving soluble Sn(II) species instead of SnO.

EXPERIMENTAL

Materials. Water used in the study was deionized by ion exchange, boiled for at least 30 min and thoroughly saturated with N_3 gas. All solutions were kept under N_2 and tightly stoppered. The nitrogen saturation was repeated after each transfer. The nitrogen gas was purified by the method of Merres and Merres.⁽¹⁷⁾

Stock solutions of sodium perchlorate were prepared from Purified Sodium Perchlorate supplied by Fisher Scientific Company. High purity SnO supplied by Baker and Adamson was used throughout.

 $Na_4P_9O_7$ -10H₈O and $Na_5P_3O_{10}$ ·6H₈O which were recrystallized twice from water were used as the sources of pyrophosphate and tripolyphosphate respectively. The long chain polyphosphates were materials having $Na_9O_7O_8$ ratios of 1.34 and 1.15. Together with end group titration data, average chain lengths (\bar{n}) of 6 and 14 phosphorus atoms per molecule were assigned to these polyphosphates.

Fisher Certified Reagent KIO₃ was used to make stock solutions which were stored under nitrogen.

Apparatus. All pH measurements were made with a Beckman Expanded Scale pH meter which was standardized against standard buffer solutions, and pH was read to 0.01 pH units. The reaction vessels were rubber stoppered Pyrex[®] flasks. Agitation was achieved with a water bath shaker from Research Specialties, which was maintained at $25.0 \pm 0.2^{\circ}$ C with an auxiliary heater and control unit. Aliquots for analysis were withdrawn through a fine porosity sintered glass filter tube by means of a syringe applied to a pipette.

Computer calculations were made on an IBM 704 Computer.

Equilibrations. Solutions at various pH levels and several levels of polyphosphates were prepared in stoppered Pyrex flasks. The ionic strength was adjusted to unity with NaClO₄. One gramme of

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SnO was equilibrated with 50 ml of solution for at least twenty-four hours. This period was shown to be adequate for attainment of equilibrium because no further changes in pH or in soluble Sn(II) concentration occurred between one and three days.

Sufficient agitation was attained by adding to each flask a pool of approximately 15 g of Hg, which is inert in this system, and several glass beads. Experiments without Hg stirring yielded the same data except that longer equilibration times were required.

Aliquots were withdrawn in the manner described above. To the aliquot was added 5 ml each of concentrated HCl and starch solution, along with 50 ml of oxygen-free de-ionized water. Duplicate titrations were made with 0.0050 N KIO₃ solution containing 0.01 M KI. A blank was run for every titration, and duplicate determinations were made for each analysis. This titration of the reducing power of the solutions was found to be reproducible to ± 1 per cent over the concentrations of Sn(II) studied (10^{-2} -5 × 10^{-4} M), and independent of the concentration of polyphosphate.

RESULTS AND DISCUSSION

Solubility of SnO in non-complexing solutions

Data on the solubility of SnO at an ionic strength of 1.0 at 25° C were obtained as a function of pH by iodometric determination of total Sn(II) in solution and potentiometric pH determination. The ionic strength was maintained at 1.0 with sodium perchlorate. The initial adjustments of pH were made with 1 M NaClO₄. The equilibrium data are shown in Table 1 and also by the dashed curves in Figs. 1 and 4. On the basis of the species found by TOBIAS⁽⁹⁾ in similar media, the following chemical equilibria are expected to occur:

$$\mathrm{SnO} + \mathrm{H}_{3}\mathrm{O}^{+} \stackrel{\mathrm{K}_{h}}{=} \mathrm{Sn(OH)^{+}} + \mathrm{H}_{2}\mathrm{O} \tag{1}$$

$$\text{SnO} + 2\text{H}_3\text{O}^+ \stackrel{K_1}{=} \text{Sn}^{2+} + 3\text{H}_2\text{O}$$
 (2)

$$SnO + Sn^{2+} + H_2O \stackrel{K_1}{=} Sn_2(OH)_2^{2+}$$
 (3)

$$\text{SnO} + 2\text{Sn}^{2+} + 3\text{H}_2\text{O} \stackrel{\text{A}_k}{=} \text{Sn}_3(\text{OH})_4^{2+} + 2\text{H}^+$$
 (4)

$(Sn^{2+}) \times 10^{2}$, (M)	pН	$(Sn^{2+}) \times 10^{3}$, (M)	pН
4.75	1.82	2.98	2.50
3.64	1.91	2.46	2.54
2.34	2.03	1.92	2.60
1.70	2.13	1.55	2.65
1.26	2.16	0.993	2.72
0.836	2.24	0.773	2.79
0.719	2.33	0.521	2.90
0.351	2.45		

Table 1.—Solubility of SnO at 25.0°C and $\mu = 1.0$

and

Based upon the equilibria (1-4), the total soluble Sn(II) is given by the following

expression: $(Sn(II)) = (Sn^{2+}) + (Sn(OH)^{+}) + 2(Sn_2(OH)_2^{2+}) + 3(Sn_3(OH)_4)^{2+}$ (5)

where the parentheses represent concentrations of the species present and (Sn(II)) represents the total tin concentration in solution. The relationship between the total soluble Sn(II) and the hydrogen ion activity, the antilog of (-pH), is as follows:

$$(Sn(II)) = K[H^+] + (K_i + 2K_iK_j + 3K_i^2K_k)[H^+]^2$$
(6)

where [H+] represents the hydrogen ion activity as calculated from the measured pH.

The coefficients in Equation (6) were determined from the experimental data by the least squares method on an IBM 704 computer. The equation is reduced to the following:

$$(Sn(II)) = (0.53 \pm 0.10)[H^+] + (1.96 \pm 0.10) \times 10^2[H^+]^2$$
(7)

Although the magnitude of K_i , K_j and K_k cannot be individually determined, the quantity in parentheses is 196 \pm 10. Equation (7) shows that if the data can be extrapolated to higher pH regions, the predominant species above pH of 4 is Sn(OH)⁺.

Complexing media

The ionic strength was kept constant at 1.0 with sodium perchlorate. Perchlorate was used because it has little tendency to form complexes as do the other common anions such as Cl⁻, Br⁻, SO₄²⁻, etc. Also, it was found that perchlorate oxidation of Sn(II) occurs very slowly under the conditions of these experiments, e.g. the half-life at 50°C is about two weeks while no oxidation was detected after one day at 25°C. The sodium ion was used rather than tetramethylammonium since the tetramethylammonium perchlorate is too insoluble. Although sodium ions are known to form weak complexes with polyphosphates,^(2,3) no attempt was made to correct for their effect on the complexing data. However, a pH region was chosen to minimize the sodium ion effect, as discussed below.

The pH region of 5–7 is most useful for studying complexing of Sn(II) by pyrophosphate. Below pH 5, an insoluble tin pyrophosphate forms. The region between pH 4 and 7 was used for tripolyphosphate. In more acidic regions of pH, hydrolysis becomes important and above pH of 7 the complexing of sodium ions by polyphosphates becomes more significant. Also, at higher pH values, the solubility of SnO in small concentrations of polyphosphates becomes too low for precise measurement.

Pyrophosphate complexes

The data are summarized in Fig. 1, where the dashed curve represents the solubility of SnO in non-complexing media and the solid curves its solubility in solutions with four levels of pyrophosphate-added. A maximum appears in these curves because of the formation of a Sn(II) pyrophosphate precipitate below pH of 5 and the greater insolubility of SnO at higher pH.

The precipitate which forms below pH 5 has a Sn(II): pyrophosphate ratio of 1.50 which corresponds to the empirical formula $Sn_3(HP_2O_7)_2 \cdot xH_2O$. This material is amorphous to X-rays and was not further characterized. Therefore, data below pH of 5 are not useful for determination of complexing constants. Above pH 5.3, chemical analysis showed that the equilibrium solid phase is $SnO \cdot xH_2O$ and contained no phosphorus.

Although Equation (7) indicates that the most predominant uncomplexed tin species above a pH of 4 is $Sn(OH)^+$, other ionic forms cannot be completely ruled out. Therefore, equilibria will be written in terms of SnO. The corresponding equilibrium constants for the equilibria in terms of $Sn(OH)^+$ can be calculated with the use of Equation (1).

Some important qualitative observations can be made from the data of Fig. 1. Evidence for the existence of polynuclear species is given by the maxima in Fig. 1, which occur at concentrations in solution of total Sn(II): total pyrophosphate ratios of 1.58 in 0.0050 M, 1.33 in 0.0150 M, and 1.04 in both 0.0500 M and 0.0750 M pyrophosphate. Not only are the ratios greater than unity, but the magnitude decreases with increasing pyrophosphate concentration. There must be at least two complexes present to qualitatively explain this behaviour.



FIG. 1.—Complexing of Sn(II) by pyrophosphate:
(a) The mole ratio of Sn(II) in solution-to-total pyrophosphate added (left ordinate) as a function of pH at four levels of pyrophosphate concentration; □-0.0750 M, ○-0.0500 M, △-0.0150 M and ●-0.0050 M.
(b) The solubility of SnO in non-complexing media represented by the dashed curve (right ordinate).

Additional information about the formation of the complexes between Sn(II) and polyphosphates was obtained by the following study. The pH of the solutions of polyphosphate equilibrated with SnO were back titrated with acid to the original pH which existed before the SnO was added. In this way data were obtained on the moles of hydroxide released per mole of Sn(II) complexed. Table 2 shows that the hydroxide released per mole of complexed Sn(II) is 0.5 ± 0.1 for both the pyrophosphates and tripolyphosphate systems. The net reaction giving rise to the observed pH change is given by:

$$a \operatorname{SnO} + a/2H_3O^+ + bH_xP_2O_7^{-(4-x)} = \operatorname{Complex}$$
 (8)

For pyrophosphate molar concentrations of 0.005 M and 0.0015 M, the ratio of total Sn(II):total pyrophosphate in solution was between one and two, implying the existence of complexes with ratios of *a*:*b* larger than one. Figure 1 also shows the ratio depends on ligand concentration at a given pH, indicating the existence of complexes with different numbers of ligands per complex. The simplest equilibria that can explain these two qualitative observations are for 2:1 and 2:2 Sn(II):pyrophosphate complexes:

$$2\mathrm{SnO} + \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{H}_{x}\mathrm{P}_{2}\mathrm{O}_{7}^{-(4-x)} \stackrel{K_{1}}{=} \mathrm{Complex}_{1}$$
(9)

$$2SnO + H_{3}O^{+} + 2H_{x}P_{2}O_{7}^{-(4-x)} \xrightarrow{K_{2}} Complex_{2}$$
(10)

The ability of these expressions to conform quantitatively with the data is seen in the following discussion.

(pH) _i *	(pH)eq.†	mmoles H^+ added to restore pH_{eq} to pH_1	mmoles Sn(II) complexed	Moles hydroxide released per mole Sn(II) complexed
	te:			
6.63	7.82	0.0108	0.0174	0.62
6.21	7.32	0.0116	0.0224	0.52
5.88	6.97	0.0157	0.0267	0.59
5.64	6.73	0.0128	0.0290	0.44
5.36	6.43	0.0170	0.0332	0-51
5.14	6-27	0.0170	0.0365	0.44
				Mean (0.52)
Tripolyphosp	hate:			
4.53	6.88	0.0213	0.0339	0.63
4.57	6.81	0.0207	0.0350	0.59
3.99	6.46	0.0195	0.0384	0.51
3.74	6.29	0.0215	0.0416	0.52
2.98	5.78	0.0250	0.0463	0.54
				Mean (0.55)

TABLE 2.—HYDROXIDE RELEASED PER Sn(II) COMPLEXED

* This is the initial pH of the solutions containing 0.05 M polyphosphate, NaClO₄ and HClO₄ before addition of SnO.

† This is the equilibrium pH of solutions in * after adding the SnO and equilibration.

At pyrophosphate concentrations of 0.05 M or higher, Fig. 1 shows the maximum ratio of total Sn(II) to total pyrophosphate is only slightly greater than unity, which indicates that Equation (10) must predominate in this region of pyrophosphate concentration. The graphical test of the fit of that data to this equation is shown in Fig. 2. Equation (10) requires a linear relationship between the left side of Equation (11) and $[H^+]$ i.e.

$$\frac{(\text{Sn(II)})}{2(\text{H}_x\text{P}_2\text{O}_7^{-(4-x)})^2} = K_2[\text{H}^+]$$
(11)

Figure 2 is a log-log plot, whose slope confirms the unit order dependence on hydrogen ion activity, shown in Equation (11) and gives a value of $2 \pm 1 \times 10^8$ for K_2 . The free pyrosphosphate concentration in this case is the quantity obtained by subtracting the total Sn(11) concentration from the total pyrophosphate concentration. Because the two forms of pyrophosphate HP₂O₇³⁻ and H₂P₂O₇²⁻ co-exist in this pH region, the linearity of the Fig. 2 suggests that their complexing behaviour is not distinguishable by these data.

The constant K_1 is evaluated from data where Complex₁ and Complex₂ co-exist, i.e. 0.0050 M and 0.0150 M pyrophosphate. K_1 is obtained by plotting the left side of Equation (12) against the hydrogen ion activity:

$$\frac{(\text{Sn(II)}) - 2 (\text{Complex}_2)}{2(\text{H}_x \text{P}_2 \text{O}_7^{-(4-x)})} = K_1[\text{H}^+]$$
(12)

Figure 3 gives the plot of the data at 0.0150 M and 0.0050 M pyrophosphate. The slope of the line gives the value of $6 \pm 3 \times 10^5$ for K_1 . Because an intercept does



FIG. 2.—Graph of the log of the left side of equation (11) against pH: \Box -0.0500 M, O--0.0750 M pyrophosphate.



FIG. 3.—Plot of the left side of equation (12) against [H⁺]: \bigcirc —0.0150 M and \square —0.0050 M pyrophosphate.

occur in Fig. 3, another equilibrium must exist which shows zero hydrogen ion dependence such as:

$$2\text{SnO} + H_x P_2 O_7^{-(4-x)} \xrightarrow{K_3} \text{Complex}_3$$

 K_3 obtained from the intercept is 0.3 ± 0.2 . Therefore, the complete description of the data of Fig. 3 is given by the following:

$$\frac{(\text{Sn(II)}) - 2(\text{Complex}_2)}{2(\text{H}_x\text{P}_2\text{O}_7^{-(4-x)})} = K_1[\text{H}^+] + K_3$$
(13)

Tripolyphosphate complexes

Figure 4 shows data for the Sn(II)-tripolyphosphate system.

Between pH of 2 and 3, there is a measurable amount of uncomplexed Sn(II) in 0.0050 M tripolyphosphate media, which accounts for the rise of the dotted curve. The



FIG. 4.—Complexing of Sn(II) by tripolyphosphate: (a) The mole ratio of Sn(II) in solution-to-total tripolyphosphate added (left ordinate) as a function of pH at four levels of tripolyphosphate concentration: \Box —0.0500 M, \odot —0.0300 M, Δ —0.0150 M, \oplus —0.0050 M.

(b) The solubility of SnO in non-complexing media represented by the dashed curve (right ordinate).

data below pH of 4 was not considered in the calculation of equilibrium constants because in the more acidic regions, hydrolysis of the polyphosphate becomes important.

One obvious difference between the tripolyphosphate and the pyrophosphate systems is the absence of precipitate formation between Sn(II) and tripolyphosphate. Another difference is the independence of the total Sn(II): total tripolyphosphate ratio in solution with changing tripolyphosphate concentration over the pH range investigated. The maximum ratio of 1.14 indicates that at least two complexes are formed in this system also. The simplest equilibria that are consistent with these observations are for the formation of 1:1 and 2:1 Sn(II) tripolyphosphate complexes. However, the data of Table 2 show that the moles of hydroxide released per mole of complexed tin is 0.5. The following equilibria are the simplest having integral coefficients and

the above Sn: tripolyphosphate ratios:

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + 2\text{HP}_{3}\text{O}_{10}^{4-\frac{K_{1}}{2}} \text{Complex}_{1}$$

$$2\text{SnO} + \text{H}_{3}\text{O}^{+} + 2\text{H}_{2}\text{P}_{3}\text{O}_{10}^{3-\frac{K_{3}}{2}} \text{Complex}_{2}$$

$$4\text{SnO} + 2\text{H}_{3}\text{O}^{+} + 2\text{HP}_{3}\text{O}_{10}^{4-\frac{K_{3}}{2}} \text{Complex}_{3}$$

$$4\text{SnO} + 2\text{H}_{3}\text{O}^{+} + 2\text{H}_{2}\text{P}_{3}\text{O}_{10}^{3-\frac{K_{4}}{2}} \text{Complex}_{4}$$

The simplicity of this set of equilibria introduced by their common dependence on the square of the ligand concentration makes possible the calculation of equilibrium



FIG. 5.—Sn(II) complexed by polyphosphate solutions containing 2.0 g/l anhydrous sodium polyphosphate: O—sodium pyrophosphate, $\langle -\rangle$ —sodium tripolyphosphate, $\bar{n} = 6$, Δ —sodium polyphosphate with $\bar{n} = 14$.

constants by computer. The values calculated are: $1.82 \pm 0.02 \times 10^7$, $4.78 \pm 0.06 \times 10^{11}$, $1.0 \pm 0.3 \times 10^5$ and $6 \pm 4 \times 10^6$, for K_1' , K_2' , K_3' and K_4' , respectively.

Equilibria in which two tripolyphosphate species, $H_2P_3O_{10}^{3-}$ and $HP_2O_{10}^{4-}$, combine to form complexes with tin were not considered, although a correct dependence on hydrogen ion concentration could also be given by such expressions. Such complexes would be probable only where comparable amounts of both species of free tripolyphosphate exist in solution. This situation occurs only over a very narrow pH region, whereas the equilibria written above describe the data over the whole pH region of 4-7.

Complexing by other polyphosphates

The complexing ability of higher chain-length polyphosphates was studied to establish the trend with chain length. For this purpose, complexing by polyphosphates with average chain lengths of 6 and 14 was investigated. No attempt was made to calculate equilibrium constants, for the longer chain members, because of the difficulty in assigning formulae to their complexes.

Figure 5 shows data giving the total amount of tin complexed per 0.1 g of anhydrous polyphosphate in 50 ml of solution. The data clearly indicate the trend of less efficient complexing with increasing chain length. The curve for pyrophosphate terminates at a pH value of 5 because precipitation commences at about that point.

It is to be noted that the general decline in amount of complexed tin with increasing pH is due to the increased insolubility of the SnO rather than the weakening of the complex. The lessening of the effect of chain-length with increasing chain-length is consistent with other properties of the polyphosphates such as the decreasing difference in the last two acidity constants.⁽¹⁸⁾ This effect also suggests the greater importance of end phosphorus atoms over middle phosphorus atoms in the complexing of Sn(II) by long chain polyphosphates.

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