

## Bromo-Complexes of Lead(II)

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The solubility of  $\text{PbSO}_4$  at  $[\text{Br}^-] < 0.32 \text{ M}$  and the solubility of  $(\text{CH}_3)_4\text{NPbBr}_3$  at  $0.48 \text{ M} < [\text{Br}^-] \leq 4.0 \text{ M}$  have been measured in  $4.00 \text{ M} [\text{HBr} + \text{H}_2\text{SO}_4]$  at  $25.0^\circ\text{C}$ . The data are consistent with the existence of  $\text{Pb}^{2+}$ ,  $\text{PbBr}^+$ ,  $\text{PbBr}_2$ ,  $\text{PbBr}_3^-$ , and  $\text{PbBr}_4^{2-}$  in solution. The step formation constants at  $25.0^\circ\text{C}$  are  $K_1 = 11.7 \text{ M}^{-1}$ ,  $K_2 = 13.4 \text{ M}^{-1}$ ,  $K_3K_4 = 17.0 \text{ M}^{-2}$ ,  $K_1K_2 = 0.278 \text{ M}^{-2}$ .

Except for one polarographic study,<sup>1</sup> information on the complexes  $\text{PbBr}_n^{2-n}$  is largely confined to values for the formation constant of  $\text{PbBr}^+$  in various media.<sup>2</sup> The fact that the solubility of  $\text{PbBr}_2$  in water is less than that of  $\text{PbCl}_2$  while in  $4 \text{ M HBr}$ ,  $\text{PbBr}_2$  gives  $0.5 \text{ M}$  solutions while  $\text{PbCl}_2$  is only  $0.012 \text{ M}$  in  $4 \text{ M HCl}$ , suggests that higher bromide complexes exist and are more stable than higher chloride complexes.

The solubility of slightly soluble lead salts has been measured as a function of bromide ion concentration in  $4 \text{ M} [\text{H}_2\text{SO}_4 + \text{HBr}]$ . The results have been interpreted using the assumption that  $\text{H}_2\text{SO}_4$  is 1:1 electrolyte.<sup>3</sup> Effects of changing  $[\text{Br}^-]$ ,  $[(\text{CH}_3)_4\text{N}^+]$ , and  $[\text{Na}^+]$  on the UV absorption spectrum of the  $\text{Pb(II)-Br}^-$  system are also reported.

## EXPERIMENTAL

$\text{PbBr}_2$  is too soluble at high  $[\text{Br}^-]$  to be useful.  $(\text{CH}_3)_4\text{NPbBr}_3$  was chosen to obtain reasonably low solubility at  $[\text{Br}^-] = 4 \text{ M}$ . When using this salt it is not possible to use perchloric acid to maintain constant ionic strength due to the low solubility of  $(\text{CH}_3)_4\text{NClO}_4$ . Sulphuric acid was used instead but the concentration of the sulphuric acid is restricted to a maximum concentration of  $3.52 \text{ M}$  above which  $(\text{CH}_3)_4\text{NPbBr}_3$  is converted to  $\text{PbSO}_4$ .

The procedure followed was to measure the solubility of  $\text{PbSO}_4$  in  $4 \text{ M} (\text{H}_2\text{SO}_4 + \text{HBr})$  for  $[\text{Br}^-] \leq 0.32 \text{ M}$  and to measure the solubility of  $(\text{CH}_3)_4\text{NPbBr}_3$  in  $4 \text{ M} (\text{H}_2\text{SO}_4 + \text{HBr})$  for  $[\text{Br}^-] \geq 0.48 \text{ M}$ . It was observed that  $\text{PbBr}_2$  in contact with  $\text{HBr}$  was very sensitive to daylight and UV radiation, free lead being formed on the surface of  $\text{PbBr}_2$  crystals. No such effect is observed with  $(\text{CH}_3)_4\text{NPbBr}_3$ .

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Solubilities were measured with the aid of a Brønsted saturator<sup>4</sup> or by shaking salt and solvent in a thermostat for 24–48 h. Saturated solutions were analyzed for total Pb(II) by diluting a sample until  $10^{-5} \text{ M} < [\text{Pb(II)}] < 10^{-4} \text{ M}$  with solutions which gave a final  $[\text{HBr}] = 4.00 \text{ M}$ . The absorbance of the diluted solutions was measured at  $25^\circ + 0.5^\circ$  with a Beckman DU, spectrophotometer using  $\epsilon = 14\,770 \text{ cm}^{-1} \text{ M}^{-1}$  at  $303 \text{ m}\mu$ . Beer's law is obeyed, but since solutions contain equilibrium mixtures of various  $\text{PbBr}_n^{2-n}$  complexes, great care was taken to control the temperature and to make  $[\text{Br}^-]$  exactly  $4.00 \text{ M}$ . Data points were duplicated by varying the number of passes through the saturator as tests of saturation.

$\text{PbSO}_4$  was recrystallized from conc.  $\text{H}_2\text{SO}_4$  by adding water. All samples were too fine for convenient use and tended to clog the Brønsted saturator.

$(\text{CH}_3)_4\text{NPbBr}_2$  was precipitated by adding saturated  $(\text{CH}_3)_4\text{NBr}$  slowly to a  $0.5 \text{ M}$  solution of  $\text{PbBr}_2$  in  $6 \text{ M HBr}$ . White, hexagonal crystals form which may be dissolved in hot hydrobromic acid and recrystallized on cooling. (Found: C 9.36; H 2.25; Br 45.81. Calc. C 9.22; H 2.32; Br 46.01). Carbon and hydrogen analyses were by the Clark Micro-analytical Laboratory. Bromine was determined by a potentiometric titration of  $\text{Br}^-$  with a standardized  $\text{AgNO}_3$  solution.

$4 \text{ M HBr}$  stock solution was constantly monitored for  $\text{Br}_2^-$  formation, by reading the absorbance *versus* a  $\text{H}_2\text{O}$ -blank.

Mixed solvents were prepared immediately before use to reduce possibilities of oxidation of  $\text{Br}^-$ . Spectra changed slightly with time, especially the UV cutoff at  $\approx 240 \text{ m}\mu$ , but blanks at  $303 \text{ m}\mu$  were sensibly zero throughout the study.  $4 \text{ M HBr}$  and  $4 \text{ M H}_2\text{SO}_4$  stock solutions were prepared from analytical grade reagents and standardized against anhydrous sodium carbonate.

The effects of substituting  $(\text{CH}_3)_4\text{N}^+$  for  $\text{H}^+$  and  $\text{Na}^+$  for  $\text{H}^+$  at constant  $[\text{Br}^-]$  on the spectrum of  $\text{PbBr}_4^{2-}$  and  $\text{PbBr}_4^{4-}$  were determined in an effort to detect possible on pair formation.

## RESULTS

The results of the solubility studies are pictured graphically in Figs. 1 and 2. The break in the curve for  $(\text{CH}_3)_4\text{NPbBr}_2$  corresponds to partial conversion of this salt to  $\text{PbSO}_4$  at low  $[\text{Br}^-]$ . Only data to the right of the break were used in calculating constants.

$\text{PbSO}_4$ . Assuming only mononuclear species the equations for analysis of the  $\text{PbSO}_4$  curve are:

$$S[\text{HSO}_4^-] = K_s \left( 1 + \sum_{n=1}^N \beta_n [\text{Br}^-]^n \right) \quad (1)$$

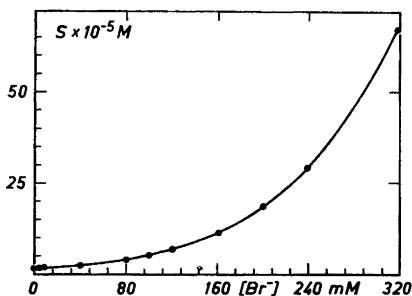


Fig. 1. Solubility of  $\text{PbSO}_4$  vs.  $[\text{Br}^-]$  in  $4.00 \text{ M} [\text{HBr} + \text{H}_2\text{SO}_4]$ .

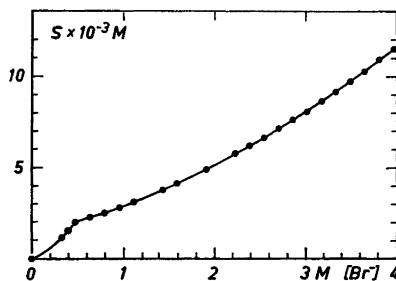


Fig. 2. Solubility of  $(\text{CH}_3)_4\text{NPbBr}_2$  vs.  $[\text{Br}^-]$  in  $4.00 \text{ M} [\text{HBr} + \text{H}_2\text{SO}_4]$ .

Remembering that the derivative  $d[\text{HSO}_4^-]/d[\text{Br}^-] = -1$  we obtain eqns. 2 and 3

$$[\text{Br}^-] = [\text{Br}^-]_0 / \left( 1 + \frac{dS}{d[\text{Br}^-]} - \frac{S}{[\text{HSO}_4^-]} \right) \quad (2)$$

$$\bar{n} = \frac{[\text{Br}^-]}{S} \frac{dS}{d[\text{Br}^-]} - \frac{[\text{Br}^-]}{[\text{HSO}_4^-]} \quad (3)$$

where

$S$  = solubility of  $\text{PbSO}_4$  in  $M$ ,

$[\text{Br}^-]_0$  = concentration of  $\text{Br}^-$  in the solvent which had not passed the saturator.

$K_s = [\text{Pb}^{2+}] [\text{HSO}_4^-]$

$\bar{n}$  = ligand number

$\beta_n = [\text{PbBr}_n^{2-n}] / [\text{Pb}^{2+}] [\text{Br}^-]^n = \prod_0^n K_n$

$K_n = [\text{PbBr}_n^{2-n}] / [\text{PbBr}_{n-1}^{3-n}] [\text{Br}^-]$

$K_s = S [\text{HSO}_4^-]$  when no bromide was present.

The first set of approximative values of the formation constants was obtained by plotting  $S [\text{HSO}_4^-] - K_s$  vs.  $[\text{Br}^-]$ , where  $[\text{Br}^-]$  originates from eqn. 2. This plot gives  $K_s \beta_1$  as a slope for a straight line formed by the first points of the curve. Using this value of  $K_s \beta_1$  the quantity  $S [\text{HSO}_4^-] - K_s - K_s \beta_1 [\text{Br}^-]$  was plotted vs.  $[\text{Br}^-]^2$  to give  $K_s \beta_2$  as a slope. This procedure was repeated until a complete set of preliminary values of  $\beta_n$  was obtained. The constants  $\beta_n$  then were recalculated until, as in Fig. 3, straight lines through the origin were obtained for all plots.

Table 1. Solubility of  $\text{PbSO}_4$ .

$[\text{Br}^-]$ M	$S[\text{HSO}_4^-] \times 10^5$ calc M <sup>2</sup>	$S[\text{HSO}_4^-] \times 10^5$ obs M <sup>2</sup>	$[\text{Br}^-]$ M	$S[\text{HSO}_4^-] \times 10^5$ calc M <sup>2</sup>	$S[\text{HSO}_4^-] \times 10^5$ obs M <sup>2</sup>
0.000	5.06	5.06			
0.004	5.30	5.44	0.120	26.44	26.46
0.008	5.54	5.71	0.160	43.8	43.8
0.040	8.74	8.75	0.200	70.6	70.6
0.080	15.45	15.41	0.239	109.4	109.8
0.100	20.30	20.28	0.318	246.2	246.6

Table 1 shows how well the calculated values of  $S$  agree with the experimental determinations. It was not possible to evaluate a value of  $\beta_6$  but the best fit was nevertheless obtained if  $\beta_6 = 742 M^{-6}$  (cf. p. 490) was introduced. At  $[\text{Br}^-] = 0.3 M$  the term  $K_s \beta_6 [\text{Br}^-]^6$  contributed  $\approx 2\%$  to the sum  $K_s (1 + \sum_{n=1}^N \beta_n [\text{Br}^-]^n)$ .  $[\text{Br}^-]$  was sensibly  $[\text{Br}^-]_0$  for all points. Thus using the calculated values of the constants  $\beta_n$  eqn. 1 is found to be

$$S [\text{HSO}_4^-] = 5.06 (1 + 11.7[\text{Br}^-] + 157[\text{Br}^-]^2 + 2670[\text{Br}^-]^4 + 742[\text{Br}^-]^6) \times 10^{-5}$$

$$K_s = (5.06 \pm 0.10) \times 10^{-5} \text{ M}^2$$

$$K_1 = 11.7 \pm 0.5 \text{ M}^{-1}$$

$$K_2 = 13.4 \pm 0.5 \text{ M}^{-1}$$

$$K_3 K_4 = 17.0 \pm 0.8 \text{ M}^{-2}$$

$$\beta_1 = 11.7 \pm 0.5 \text{ M}^{-1}$$

$$\beta_2 = 157 \pm 6 \text{ M}^{-2}$$

$$\beta_4 = (2.67 \pm 0.11) \times 10^3 \text{ M}^{-4}$$

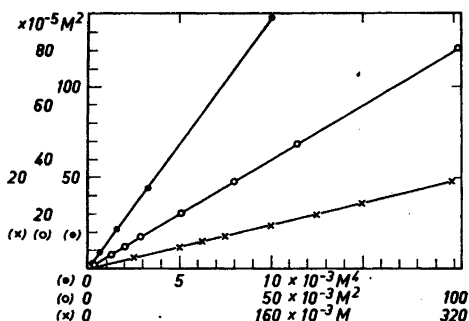


Fig. 3.  $\times$ ,  $S [\text{HSO}_4^-] - K_s (1 + \beta_2 [\text{Br}^-]^2 + \beta_4 [\text{Br}^-]^4 + \beta_6 [\text{Br}^-]^6)$  vs.  $[\text{Br}^-]$ .  
 $\circ$ ,  $S [\text{HSO}_4^-] - K_s (1 + \beta_1 [\text{Br}^-] + \beta_4 [\text{Br}^-]^4 + \beta_6 [\text{Br}^-]^6)$  vs.  $[\text{Br}^-]^2$ .  
 $\bullet$ ,  $S [\text{HSO}_4^-] - K_s (1 + \beta_1 [\text{Br}^-] + \beta_2 [\text{Br}^-]^2 + \beta_6 [\text{Br}^-]^6)$  vs.  $[\text{Br}^-]^4$ .

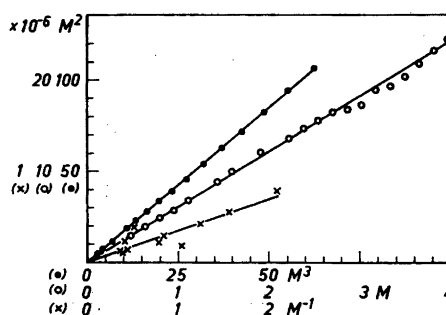


Fig. 4.  $\times$ ,  $S^2 - K_s' (\beta_4 [\text{Br}^-] + \beta_6 [\text{Br}^-]^3)$  vs.  $[\text{Br}^-]^{-1}$ .  
 $\circ$ ,  $S^2 - K_s' (\beta_2 [\text{Br}^-]^{-1} + \beta_6 [\text{Br}^-]^3)$  vs.  $[\text{Br}^-]$ .  
 $\bullet$ ,  $S^2 - K_s' (\beta_2 [\text{Br}^-]^{-1} + \beta_4 [\text{Br}^-])$  vs.  $[\text{Br}^-]^3$ .

$(\text{CH}_3)_4\text{NPbBr}_3$ . The working equations for this salt are:

$$S^2 = \frac{K_s'}{[\text{Br}^-]^3} \left( 1 + \sum_{n=1}^N \beta_n [\text{Br}^-]^n \right) \quad (1 \text{ a})$$

$$[\text{Br}^-] = [\text{Br}^-]_0 \left/ \left( 1 + 2 \frac{dS}{d[\text{Br}^-]} \right) \right. \quad (2 \text{ a})$$

$$\bar{n} = 3 + \frac{2[\text{Br}^-]}{S} \frac{dS}{d[\text{Br}^-]} \quad (3 \text{ a})$$

where  $K_s' = [(\text{CH}_3)_4\text{N}^+] [\text{Pb}^{2+}] [\text{Br}^-]^3$  and other terms have the same meaning as before. The data were analyzed in the same way as for  $\text{PbSO}_4$  although it was here more suitable to start by plotting  $S^2$  vs.  $[\text{Br}^-]^3$  which gives a preliminary value of  $\beta_6$ . The final plots are shown in Fig. 4.

Over this region of  $[\text{Br}^-]$ , the dominant change is formation of  $\text{PbBr}_3^{4-}$ . Scatter is observed in the plot vs.  $[\text{Br}^-]$ , which gives  $K_s' \beta_4$  as a slope, where  $\text{PbBr}_6^{4-}$  is the dominant species. The presence of  $\text{PbBr}_2$  in solution is barely felt before  $(\text{CH}_3)_4\text{NPbBr}_3$  is converted to  $\text{PbSO}_4$  as evidenced by the bad scatter of the plot vs.  $[\text{Br}^-]^{-1}$ . The plots give the following form to eqn. 1a

$$S^2 = (0.352[\text{Br}^-]^{-1} + 6.11[\text{Br}^-] + 1.701[\text{Br}^-]^3) \times 10^{-6}$$

from which

$$K_3K_4 = 17.4 \pm 0.6 \text{ M}^{-2} \text{ and } K_5K_6 = 0.278 \pm 0.006 \text{ M}^{-2}$$

From the combined studies

$$\begin{aligned} \beta_1 &= 11.7 \pm 0.5 \text{ M}^{-1} & K_s &= (5.06 \pm 0.10) \times 10^{-5} \text{ M}^2 \\ \beta_2 &= 157 \pm 6 \text{ M}^{-2} & K_s' &= (3.0 \pm 0.2) \times 10^{-8} \text{ M}^5 \\ \beta_4 &= (2.67 \pm 0.11) \times 10^3 \text{ M}^{-4} \\ \beta_6 &= (7.4 \pm 0.4) \times 10^2 \text{ M}^{-6} \end{aligned}$$

Table 2. Solubility of  $(\text{CH}_3)_4\text{NPbBr}_3$ .

$[\text{Br}^-]_0^a$ M	$10^3 S_{\text{calc}}$ M	$10^3 S_{\text{obs}}$ M	$[\text{Br}^-]_0^a$ M	$10^3 S_{\text{calc}}$ M	$10^3 S_{\text{obs}}$ M
0.48	1.96	1.97	2.56	6.61	6.61
0.64	2.21	2.21	2.72	7.09	7.09
0.80	2.49	2.48	2.88	7.58	7.53
0.96	2.74	2.78	3.04	8.08	8.01
1.12	3.05	3.05	3.20	8.61	8.58
1.44	3.74	3.74	3.36	9.15	9.13
1.60	4.10	4.13	3.52	9.70	9.65
1.92	4.87	4.91	3.68	10.27	10.24
2.24	5.71	5.71	3.84	10.84	10.84
2.40	6.13	6.14	4.00	11.43	11.43

<sup>a</sup>  $[\text{Br}^-] < 0.8$  lower

The agreement on  $K_3K_4$  for the two salts is gratifying. Table 2 shows how well solubility calculated using the constants given, agree with observed solubilities. Fig. 5 shows the regions of existence of various  $\text{PbBr}_n^{2-n}$  complexes.

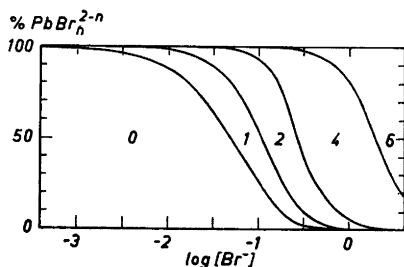


Fig. 5. Regions of existence of  $\text{PbBr}_n^{2-n}$  complexes in 4.00 M  $[\text{HBr} + \text{H}_2\text{SO}_4]$ .

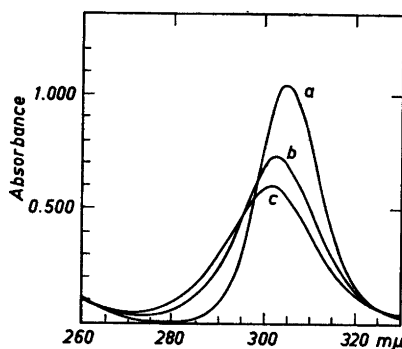


Fig. 6. UV absorption spectra of  $5.00 \times 10^{-5}$  M  $\text{Pb(II)}$  in a. 8.7 M  $\text{HBr}$  b. 4.00 M  $\text{HBr}$  c. 2.00 M  $\text{HBr} + 2.00$  M  $\text{HClO}_4$ .

*Spectra.* In Fig. 6 the effect of  $[\text{Br}^-]$  on the Pb(II) spectrum is observed. The curve with the highest peak is probably the  $\text{PbBr}_6^{4-}$  spectrum unless complexes of  $n > 6$  are formed. The peak is at  $305 \text{ m}\mu$  where the molar absorbance ( $\epsilon$ ) is  $20\,750 \text{ cm}^{-1} \text{ M}^{-1}$ .  $\text{PbCl}_6^{4-}$  has a peak at  $272 \text{ m}\mu$  and  $\epsilon = 14\,910 \text{ cm}^{-1} \text{ M}^{-1}$ .<sup>5</sup> Since no isosbestic point was observed for  $[\text{Br}^-] \leq 4.0 \text{ M}$  it is obvious that more than 2 complex species play an important part. For such a case the present data were not considered accurate enough to allow the evaluation of equilibrium constants. Spectra of  $\text{PbBr}_n^{2-n}$  of low  $n$  are inaccessible because of the opacity of  $\text{Br}^-$  in solution at  $\lambda < 250 \text{ m}\mu$ .

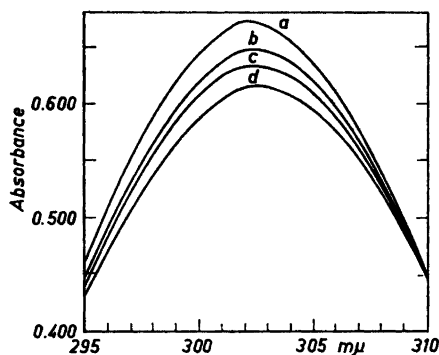


Fig. 7. UV absorption spectra of  $5.00 \times 10^{-5} \text{ M}$  Pb(II) in  $3.52 \text{ M}$   $[\text{HBr} + (\text{CH}_3)_4\text{NBr}]$ . Molarity of  $(\text{CH}_3)_4\text{N}^+$ : a. 0.00; b. 0.48; c. 0.80; d. 1.20.

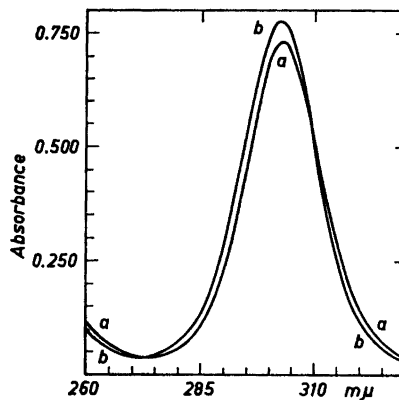


Fig. 8. UV absorption spectra of  $5.00 \times 10^{-5} \text{ M}$  Pb(II) in a.  $4.00 \text{ M}$  HBr; b.  $4.00 \text{ M}$  NaBr.

The effect on the  $\text{PbBr}_4^{2-} - \text{PbBr}_6^{4-}$  spectrum of substituting  $(\text{CH}_3)_4\text{N}^+$  and  $\text{Na}^+$  for  $\text{H}^+$  is shown in Figs. 7 and 8. Neither change is consistent with a change in activity of  $\text{Br}^-$  alone. The spectral shifts are very small indicating that ion pair formation is very slight or else has little effect on the spectrum or both. The shift on adding  $(\text{CH}_3)_4\text{N}^+$  is compatible with the formation of the pair  $[(\text{CH}_3)_4\text{NPbBr}_6^{3-}]$  with a formation constant of 0.1. The fact that  $(\text{CH}_3)_4\text{N}^+$  has no effect on  $\text{BiBr}_6^{3-}$  spectra<sup>9</sup> suggests that ion pair formation between  $(\text{CH}_3)_4\text{N}^+$  and large anions is negligible in solutions of high ionic strength unless the charge on the anion is 4 or more.

Table 3. Comparison of the formation constants of the Pb-Br system.

Medium	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$	$K_6$	Reference
4 M $[\text{HBr} + \text{H}_2\text{SO}_4]$	11.7	13.4	17.0		0.278		this work
4 M $[\text{LiBr} + \text{LiClO}_4]$	35	13	4.5	2.9	0.05	0.5	10
4 M $[\text{NaBr} + \text{NaClO}_4]$	32	9.6	6.0	1.1	1.0	—	11
1 M $[\text{NaBr} + \text{NaClO}_4]$	13	2.1	5.6				1

## DISCUSSION

Kivalo<sup>1</sup> finds  $\beta_1 = 13.0$ ,  $\beta_2 = 27$ , and  $\beta_3 = 153$  in 1 M (NaBr + NaClO<sub>4</sub>) using polarographic techniques. If both studies are accurate, changing from 1 M Na<sup>+</sup> to 4 M H<sup>+</sup> profoundly affects the distribution of PbBr<sub>n</sub><sup>2-n</sup> complexes.  $\beta_1$  at zero ionic strength has been found to be 56 by spectrophotometric analysis.<sup>8</sup> Later published studies, a potentiometric investigation<sup>10</sup> in 4 M [LiClO<sub>4</sub> + LiBr] using a lead-amalgam electrode and a solubility study<sup>11</sup> in 4 M [NaClO<sub>4</sub> + NaBr] are more in agreement with this work as far as the constants  $K_2$ ,  $K_3$  and  $K_4$  are concerned. A comparison of the data is shown in Table 3.

Table 4. Comparison of formation constants.

[H <sup>+</sup> ] = 4.0 M							
Species	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$	$K_6$	Reference
PbBr <sub>n</sub> <sup>2-n</sup>	11.7	13.4		17.0		0.278	this work
PbCl <sub>n</sub> <sup>2-n</sup>	10	29		1.4			5
SnBr <sub>n</sub> <sup>2-n</sup>	?	8			2.1?		6
SnCl <sub>n</sub> <sup>2-n</sup>	28	8	1.0	0.7	—	—	7
[Li <sup>+</sup> ] = 4.0 M							
PbBr <sub>n</sub> <sup>2-n</sup>	35	13	4.5	2.9	0.05	0.5	10
PbCl <sub>n</sub> <sup>2-n</sup>	17	3.1	2.3	0.17	0.2	—	12

Table 4 compares formation of PbBr<sub>n</sub><sup>2-n</sup> with PbCl<sub>n</sub><sup>2-n</sup> and with SnCl<sub>n</sub><sup>2-n</sup> and SnBr<sub>n</sub><sup>2-n</sup>. Chloride and bromide complexes of low  $n$  are comparable in stability with  $\beta_2$  for chloride slightly higher than  $\beta_2$  for bromide. It might be worthwhile to consider that other investigations<sup>10,12</sup> show an opposite trend, with  $\beta_2$  for bromide higher than  $\beta_2$  for chloride. For  $n > 2$  the bromide complexes are decidedly stronger. This indicates that covalent effects predominate for complexes of negative charge while electrostatic effects predominate for complexes which are positive or neutral. The smaller, harder, Sn<sup>2+</sup> ion combines more strongly with one or two halides than does Pb<sup>2+</sup> but is less inclined to form complexes of negative charge. The shift of the UV band of PbBr<sub>6</sub><sup>4-</sup> to higher wavelengths than that observed for PbCl<sub>6</sub><sup>4-</sup> is consistent with the greater covalent character of bromide as compared with the chloride complexes. The relative instability of negative complex ions of odd  $n$  is notable.

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