

The Complex Equilibria of Pb^{2+} with 3-Bromo-5-sulfosalicylate Ions

YING-HUA LEE

Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, P.O. Box, S-402 20 Göteborg 5, Sweden

The equilibria between lead(II) and 3-bromo-5-sulfosalicylate ions, HC^{2-} , have been studied at 25 °C in 3 M sodium (perchlorate) medium, by means of potentiometric titrations using both glass and lead amalgam electrodes. The total concentrations of Pb^{2+} and HC^{2-} ranged from 0.25 to 1 mM and from 0 to 35 mM, respectively. The pH range was 3–7.

The data have been evaluated with a graphical method, and the results refined with the generalized least squares program LETAGROP ETITR. The four main complexes formed between Pb^{2+} and HC^{2-} are $PbHC$, $Pb(HC)_2^{2-}$, PbC^- , and PbC_2^{4-} with the following formation constants: $\log \beta_{011} = 1.116 \pm 0.006$, $\log \beta_{012} = 1.931 \pm 0.013$, $\log \beta_{-111} = -4.875 \pm 0.004$ and $\log \beta_{-212} = -11.187 \pm 0.018$. The $PbOH^+$ species was also present in the solutions studied.

The present study was undertaken in order to determine the complex formation constants between Pb^{2+} and 3-bromo-5-sulfosalicylate ion, HC^{2-} , in aqueous solutions. No previous work on the equilibrium in aqueous solutions between Pb^{2+} and salicylic acid or its derivatives has been carried out to the author's knowledge. Owing to the relatively slight solubility of $Pb^{2+}-HC^{2-}$ complexes and the hydrolysis of Pb^{2+} , low concentrations of Pb^{2+} and a high precision method are necessary for such an investigation.

In the present investigation, the potentiometric method with a computerised automatic titrator was employed. The hydrolysis of Pb^{2+} was accounted for. This has been investigated previously by Olin.¹

The most common symbols are listed below for reference:

| | |
|-------------------------------|--|
| B | total concentration of lead. |
| b | concentration of free lead. |
| E_g | emf of cell with glass electrode. |
| E_{am} | emf of cell with lead amalgam electrode. |
| η | $\log B/b$. |
| β_{pqr} | equilibrium constants. |
| U_E | $\sum (E_{am(calc)} - E_{am(exp)})^2$. |
| V_0, H_0, B_0, C_0 | Volume, H, B and C in the solution ($S_0' + S_1$). |
| V_T, H_T, B_T, C_T | Volume, H, B and C in the buret solution T . |
| $C, c, H, h, \sigma, (\beta)$ | see Ref. 3. |

EXPERIMENTAL

Chemicals. Sodium perchlorate, perchloric acid, sodium hydroxide and disodium 3-bromo-5-sulfosalicylate solutions were prepared and analysed as described elsewhere.^{2,3}

Lead perchlorate. $Pb(ClO_4)_2$ solutions were prepared by dissolving PbO (Baker *p.a.*) in $HClO_4$ (Merck *p.a.*) as described by Olin.¹ Lead was determined by precipitation as lead sulfate.¹ The analytical hydrogen concentration of the stock solution was determined potentiometrically, using Gran's extrapolation method⁴ to evaluate the equivalence point.

Lead amalgam was prepared by dissolving bright lead metal (Merck silberfrei) in mercury. The concentration of lead in the amalgam was 0.4 % (by weight). The amalgam was stored under *ca.* 20 mM $HClO_4$ in a closed vessel filled with nitrogen.

Emf measurements and apparatus. The experiments were carried out as two series (I and II) of potentiometric titrations at 25 °C in nitrogen atmosphere. The two different types of titrations performed were:

1. The total concentration of Pb^{2+} , B , was kept constant and the total concentration of HC^{2-} , C , was increased by addition of Na_2HC solution, while pH varied from 2.5 to 4.

Table 1. Summary of the titrations in 3 M Na(ClO₄). Concentrations in mM.^a

| Titr. No. | H_0' | B_0' | H_1 | C_1 | $H_{T_1+T_2}$ | B_{T_1} | C_{T_1} | C/B |
|-----------|--------|---------|---------|--------|---------------|-----------|-----------|-------|
| Series I | | | | | | | | |
| 1 | 0.5987 | 0.3007 | -0.0135 | 0 | -0.001 | 0.5046 | 179.78 | |
| 2 | 0.6065 | 0.60175 | -0.0135 | 0 | 0.0112 | 1.0049 | 179.78 | |
| 3 | 1.547 | 1.1998 | 0.2995 | 0 | 0.3300 | 2.0010 | 180.57 | |
| Series II | | | | | | | | |
| 1 | 0.6065 | 0.60175 | -0.0133 | 179.78 | -2.478 | 1.004 | 60.00 | 60 |
| 2 | 0.6065 | 0.61795 | -0.0124 | 120.06 | -2.468 | 1.004 | 40.01 | 40 |
| 3 | 0.6065 | 0.60175 | -0.0127 | 90.06 | -3.099 | 1.005 | 29.97 | 30 |
| 4 | 0.6065 | 0.60175 | -0.0132 | 60.16 | -3.110 | 1.005 | 19.95 | 20 |
| 5 | 0.6065 | 0.60175 | -0.0132 | 29.95 | -4.130 | 1.004 | 10.25 | 10 |
| 6 | 0.5987 | 0.3007 | -0.0133 | 179.78 | -2.490 | 0.5046 | 59.89 | 120 |
| 7 | 0.5987 | 0.3007 | -0.0124 | 120.06 | -2.525 | 0.5046 | 39.92 | 80 |
| 8 | 0.5853 | 1.2050 | -0.0133 | 179.78 | -2.524 | 2.0100 | 60.23 | 30 |

^a In each titration equal volumes, V_T ml, of the buret solutions T_1 and T_2 were added to 60.02 ml of an initial solution which consisted of 50.02 ml S_0' and 10 ml S_1 solution.

2. Both B and C were kept constant, while pH was increased from 3 to 6 or 7 by the addition of NaOH solution until precipitation occurred or a desired amount of titrant had been added.

Since a slightly soluble precipitate was formed between Pb^{2+} and HC^{2-} ions at pH < 5, the values of B and C were chosen to be less than 1 mM and 40 mM, respectively, in order to be able to carry out the titrations and to have a sufficient amount of complex formed in the solutions. All the solutions were made 3 M in Na^+ by adding $NaClO_4$ to keep the activity factors constant.

A summary of the titrations is given in Table 1. In the titration series II, the C/B ratio was varied from 10 to 120. All the solutions listed in Table 1 were prepared with boiled doubly distilled water and N_2 gas was passed through the solutions for half an hour before use. The solutions containing NaOH were freshly prepared under N_2 atmosphere.

The hydrogen ion, h , and lead ion concentrations, b , were measured with a Jena type U glass electrode and a lead amalgam electrode (ca. 0.4 %), respectively.

The apparatus used for emf measurements is similar to that described in the author's previous work.³

From the measured emf, E_g and E_{am} , h and b were calculated using the following relations:

$$E_g = E_{og} + 59.156 \log h + E_j \quad (1)$$

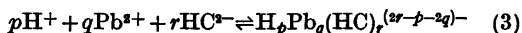
$$E_{am} = E_{oam} + 29.578 \log b + E_j \quad (2)$$

where E_{og} and E_{oam} are constants for the electrodes used and E_j is the liquid junction potential, which can be expressed as $E_j = jh$,

where j is approximately -17 mV/M in 3 M $NaClO_4$.

Each titration was carried out in three steps: First, E_{og} and E_{oam} were determined from the potential of the initial solution S_0' , containing no HC^{2-} ions, by inserting the analytical concentrations H_0' and B_0' in eqns. (1) and (2). A certain amount of the solution S_1 containing HC^{2-} was then added to the titration vessel to achieve the required $C = C_{T_1}/2$ and $B = B_{T_1}/2$. In the titration series I, the solution S_1 contains only 3 M $NaClO_4$. It took usually $\frac{1}{2}$ to 1 h to reach equilibrium again. The titrations were then continued by adding equal volumes of T_1 and T_2 solutions until a desired amount of titrant had been added.

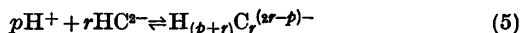
In evaluating the complex formation constants, H^+ , Pb^{2+} , and HC^{2-} were chosen as components. The general equilibria and the formation constants are



$$\beta_{pqr} = [H_pPb_q(HC)_r^{(2r-p-2q)-}] / h^{-p} b^{-q} c^{-r} \quad (4)$$

respectively. Since the pH ranged from 2.5 to 7, both the proton association equilibria of HC^{2-} and the hydrolysis equilibria of Pb^{2+} must be taken into consideration in the calculations of the complex formation constants.

For the $H^+ - HC^{2-}$ equilibria



the results obtained in the author's previous work were used.^{2,3} The values of β_{101} , β_{102} , β_{202} , and β_{-101} for reactions (5) are given in Table 4.

In the hydrolysis of Pb^{2+}

Table 2. Equilibrium constants for the hydrolysis of Pb(II) calculated by LETAGROP.

| | This paper | Olin ¹ |
|---------------------|---------------------|-------------------|
| $\log \beta_{-110}$ | -7.962 ± 0.236 | -7.9 ± 0.1 |
| $\log \beta_{-440}$ | -19.149 ± 0.010 | -19.25 ± 0.1 |
| $\log \beta_{-430}$ | -22.629 ± 0.042 | -22.87 ± 0.1 |
| $\log \beta_{-860}$ | -42.103 ± 0.046 | -42.14 ± 0.1 |

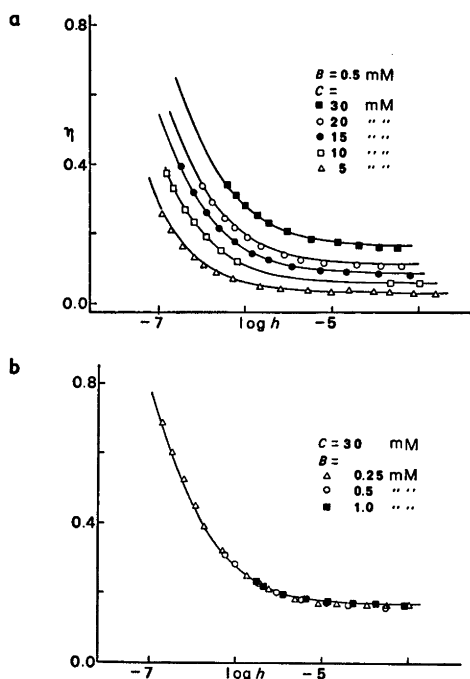
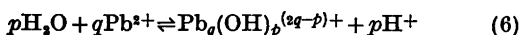


Fig. 1. Experimental data $\eta(\log h)_{B,C}$ in 3 M Na(ClO₄) medium. $\eta = \log B/b$. The curves have been calculated with the final equilibrium constants β_{pqr} (cf. Table 4) using HALTAFALL.¹⁰



the main species are PbOH^+ , $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_3(\text{OH})_4^{3+}$ and $\text{Pb}_6(\text{OH})_6^{4+}$.¹ As a check, emf titrations to investigate the hydrolysis of Pb(II) were performed in a similar way as those described above for the complex formation between Pb^{2+} and HC^{2-} . The values of β_{-pq0} thus obtained were in good agreement with those obtained by Olin (cf. Tables 2).

TREATMENT OF DATA

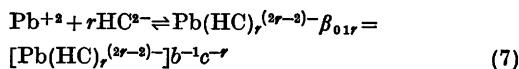
The experimental data plotted as $(\eta, \log h)_{B,C}$, are presented in Fig. 1a–b (where $\eta = \log B/b$).

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From Fig. 1a–b it is seen that η is a function of both C and $\log h$ but is independent of the value of B . It is apparent that the mononuclear mixed complexes $\text{H}_p\text{Pb}(\text{HC})_r^{(2r-p-2)-}$ are the predominant species in the concentration region studied.

The formation constants of the main complexes were determined graphically and the results were refined with the generalized least squares program LETAGROP ETITR.^{5,6} LETAGROP was also used to investigate the formation of other possible complexes.

Graphical method. It is apparent from Fig. 1b that η varies slightly with pH at pH < 4.5, but increases with the values of C . The most probable complexes at pH < 4.5 are thus $\text{Pb}(\text{HC})_r^{(2r-2)-}$, the relevant reactions and equilibrium constants being



Preliminary values for β_{01r} were determined by means of Leden's extrapolation method.⁷

When the function

$$F_1 = (B - b)/bc = \sum_1^r \beta_{01r} c^{r-1} = \beta_{011} + \beta_{012} c + \sum_3^r \beta_{01r} c^{r-1} \quad (8)$$

with the experimental data B , b , and C ($\approx c$) from series I, was plotted against C , a straight line was obtained (cf. Fig. 2). From the intercept and the slope of the line $\beta_{011} = 12.2 \text{ M}^{-1}$ and $\beta_{012} = 83.5 \text{ M}^{-1}$. The function

$$F_2 = (F_1 - \beta_{011})/C = \beta_{012} + \sum_3^r \beta_{01r} C^{r-2} \quad (9)$$

was calculated from the β_{011} value obtained and plotted against C . A straight line with a slope ≈ 0 (Fig. 2) was obtained, which indicates the absence of complexes $\text{Pb}(\text{HC})_r^{2-2r}$ with $r > 2$.

Furthermore, a strong mononuclear pH-dependent complexing between Pb^{2+} and HC^{2-} at pH > 5, is indicated by Fig. 1a–b. As HC^{2-} is a bidentate ligand and the two donor groups ($-\text{COOH}$ and $-\text{OH}$) are in a favourable position (*ortho*-position) for chelation of Pb^{2+} , the most likely chelate complexes are PbC^- and PbC_2^{4-} . A similar extrapolation method

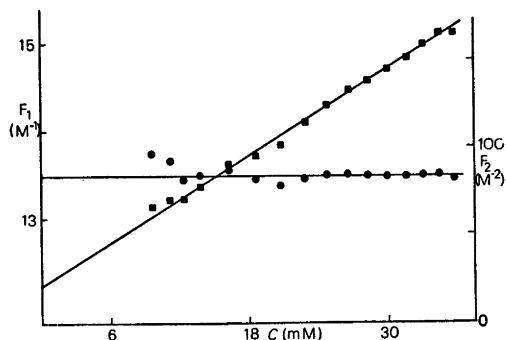


Fig. 2. Determination of β_{011} and β_{012} from eqn. (8). Line 1 (■) gives $\beta_{011} = 12.2 \text{ M}^{-1}$, $\beta_{012} = 83.5 \text{ M}^{-2}$. $B = 0.25 \text{ mM}$. Determination of β_{012} from eqn. (9). The intercept of line 2 (●) gives $\beta_{012} = 84 \text{ M}^{-2}$. $B = 0.25 \text{ mM}$.

was applied to determine β . Using the mass balance condition and the definitions for the equilibrium constants β_{pqr} (eqn. 4), the experimental quantity B may be expressed in the following form

$$B = b + \beta_{011}bc + \beta_{012}bc^2 + \beta_{-111}bch^{-1} + \beta_{-212}bc^2h^{-2} \quad (10)$$

Rearrangement of (10) gives

$$F_c = B/b - 1 - \beta_{011}c - \beta_{012}c^2 = \beta_{-111}ch^{-1} + \beta_{-212}c^2h^{-2} \quad (11)$$

As C is constant in titration series II and if $C \gg B$, then $C \approx c$, and the variable F_c is a function of h only. Thus, a set of experimental data from titration series II No. 1 ($B = 0.5 \text{ mM}$,

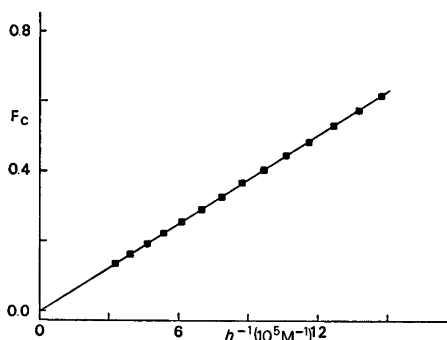


Fig. 3. Determination of β_{-111} from eqn. (11). The value of β_{-111} ($= 1.37 \times 10^{-5}$) was calculated according to $\beta_{-111} = \text{slope}/C$. $C = 29.95 \text{ mM}$, $B = 0.5 \text{ mM}$.

$C = 30 \text{ mM}$) was chosen for plotting F_c as a function of h^{-1} . In the calculation of F_c , the refined values of β_{011} and β_{012} were used. A straight line with no curvature for high values of h^{-1} was obtained (c.f. Fig. 3). This suggests that no complex higher than PbC^- is present in the solution at $C/B = 60$ and $\text{pH} < 6$. However, the complex PbC_2^{4-} ought to be present in the solutions at a higher pH and C/B ratio (cf. titration Nos. 6 and 7). The LETAGROP method was used subsequently to investigate the formation of PbC_2^{4-} .

The value of β_{-111} obtained as $\beta_{-111} = \text{gradient}/C$ was $1.37 \cdot 10^{-5}$.

LETAGROP method. In this method the β_{pqr} were sought as the values which gave a minimum for the error squares sum $U = \sum (E_{\text{calc}} - E_{\text{exp}})^2$, where E_{calc} represents a value for the emf of cell with lead amalgam, calculated by assuming a given β_{pqr} set and auxiliary data such as $B, C, E_{0\text{am}}, E_{0g}, E_{\text{am}}$ and E_g .

Refinement of β_{011} , β_{012} and β_{-111} , and test of the existence of the complexes PbC_2^{4-} and PbOHC^{2-} . In these calculations, the values of β_{101} , β_{102} , β_{202} , and β_{-101} , together with the equilibrium constants for the hydrolysis of Pb(II) obtained from this work, were given as input information and kept constant. $E_{0\text{am}}$ was the main systematic error to be adjusted. For the sake of convenience the data were used in the following three steps:

1. All the experimental data from series I (115 points) were used. Only β_{011} and β_{012} were varied.

2. Part of the data with $\text{pH} > 5$ from series II (185 points) were used. β_{-111} and β_{-212} were varied.

3. All the experimental data from series II (343 points) were used. First, β_{011} , β_{012} , β_{-111} , and β_{-212} obtained from calculation 1 and 2 were used as the input information, and the systematic errors $E_{0\text{am}}$, and then H , were adjusted. All the four constants β_{011} , β_{012} , β_{-111} , and β_{-212} were then varied without adjusting the systematic errors.

The main results from the above calculations are given in Table 3.*

In the investigation of the presence of PbOHC^{2-} only the experimental data for

* The output from the LETAGROP calculations can be obtained on request.

Table 3. Equilibrium constants β_{pqr} calculated by LETAGROP 25 °C, 3 M Na(ClO₄).

| Calculation No. | U_E | $\sigma(E)$ mV | $\log(\beta_{pqr} + 3\sigma)$ | | | |
|-----------------|-------|-------------------|-------------------------------|-------------------|--------------------|---------------------|
| | | | 011 | 012 | -111 | -212 |
| 1 (115 points) | 0.202 | 0.043 | 1.116 ± 0.006 | 1.930 ± 0.017 | | |
| 2 (185 points) | 1.592 | 0.0953 | 1.116 | 1.931 | -4.879 ± 0.003 | -11.187 ± 0.003 |
| 3 (343 points) | 5.635 | 0.1284 | 1.116 ± 0.006 | 1.931 ± 0.013 | -4.875 ± 0.004 | -11.187 ± 0.018 |

Table 4. The final equilibrium reactions and equilibrium constants in 3 M Na(ClO₄) at 25 °C.

| pqr | Reaction | $\log(\beta_{pqr} \pm 3\sigma)$ |
|-------|--|---------------------------------|
| 101 | $H^+ + HC^{2-} \rightleftharpoons H_2C^-$ | 2.028 ± 0.007^a |
| 102 | $H^+ + 2HC^{2-} \rightleftharpoons H_3C_2^{3-}$ | 2.537 ± 0.017^a |
| 202 | $2H^+ + 2HC^- \rightleftharpoons H_4C_2^{2-}$ | 4.739 ± 0.019^a |
| -101 | $HC^{2-} \rightleftharpoons C^{3-} + H^+$ | -10.467 ± 0.001^b |
| -110 | $Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$ | -7.962 ± 0.236 |
| -440 | $4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$ | -19.149 ± 0.010 |
| -430 | $3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+$ | -22.629 ± 0.042 |
| -860 | $6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+$ | -42.103 ± 0.046 |
| 011 | $Pb^{2+} + HC^{2-} \rightleftharpoons PbHC$ | 1.116 ± 0.006 |
| 012 | $Pb^{2+} + 2HC^{2-} \rightleftharpoons Pb(HC)_2^{2-}$ | 1.931 ± 0.013 |
| -111 | $Pb^{2+} + HC^{2-} \rightleftharpoons PbC^- + H^+$ | -4.875 ± 0.004 |
| -212 | $Pb^{2+} + 2HC^{2-} \rightleftharpoons PbC_2^{4-} + 2H^+$ | -11.187 ± 0.018 |

^a From Ref. 2. ^b From Ref. 3.

pH > 5 from titr. Nos. 4 and 5 in series II were used, since PbOHC²⁻ is most likely to be formed at a high pH value and a low C/B ratio.

RESULTS AND DISCUSSION

It is apparent from Table 3 that the low values of $\sigma(E)$ in calculations 1, 2, and 3 (< 0.13 mV) and the good agreement between these calculations indicate the reliability of the results.

The LETAGROP calculations yielded a negative value for β_{-211} , which means that the complex PbOHC²⁻ is not present in the solutions studied. This is probably due to the fact that precipitation occurred at pH \approx 6–7. The available pH range is thus too restricted to permit formation of PbOHC²⁻. Only four complexes, namely PbHC, Pb(HC)₂²⁻, PbC⁻, and PbC₂⁴⁻, are formed between Pb²⁺ and HC²⁻ ions. The data are best explained by the equilibria and the corresponding formation constants given in Table 4.

Fig. 4a–b show the distribution of Pb(II) in different species at various pH values. It

can be seen from Fig. 4a–b that the main species in the solutions at pH < 4.5 are PbHC and Pb(HC)₂²⁻ (the latter one only when C \gg B). The concentration of PbC⁻ increases rapidly after pH > 5.7–6, while both PbC₂⁴⁻ and PbOH⁺ exist in minor amounts. The other Pb(II) hydrolysis products at the high C/B ratios are present only in negligible amounts.

It was expected that PbC⁻ and PbC₂⁴⁻ would be much more stable than PbHC and Pb(HC)₂²⁻, due to the formation of chelate rings involving the donor groups –COOH and –OH from the same ligand. This chelate effect can be explained in terms of the contribution from the entropy of formation accompanying the metal chelate ring formation.⁸

No direct comparison with β_{pqr} values obtained by others can be made. Nevertheless, it is still of interest to compare the orders of magnitude of β_{pqr} with β_{pqr} for complexes which contain similar ligands with the same donor groups –COOH and –OH, e.g. 5-sulfosalicylate ion. As a general rule, Co(II) complexes usually have stabilities comparable with

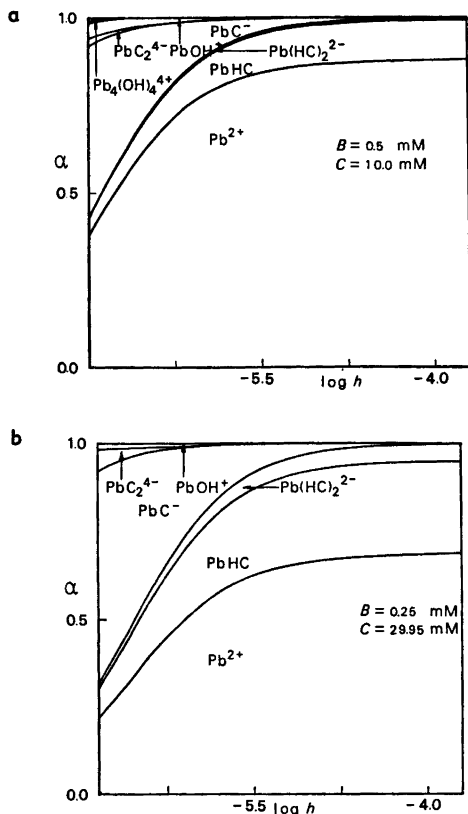


Fig. 4. The distribution of Pb(II) in different species plotted versus $\log h$. The calculations were performed with HALTAFALL¹⁰ using the β_{pq} obtained in this paper (cf. Table 4). At a given $\log h$ the fraction of Pb²⁺ present in each species is represented by the segment of a vertical line falling within the corresponding area.

those of the corresponding Pb(II) complexes. The stability constants K_1 and K_2 for the chelate reactions $M + L \rightleftharpoons ML$ and $ML + L \rightleftharpoons ML_2$ (where M is metal ion and L is ligand), are related to the value of β_{-111} , β_{-212} , and β_{-101} by the following equations:

$$K_1 = \beta_{-111} / \beta_{-101} \quad \text{and} \quad K_1 K_2 = \beta_{-212} / 2\beta_{-101}$$

A comparison of the values of $\log K_1$ and $\log K_2$ for Co(II)-5-sulfosalicylate complexes,⁹ namely 6.13 and 3.69, respectively, with those obtained in this paper, namely 5.590 and 4.161, respectively, shows that the constants are of the same order of magnitude.

As mentioned earlier the titrations were interrupted when a white precipitate was formed at $\text{pH} \approx 6-7$.

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