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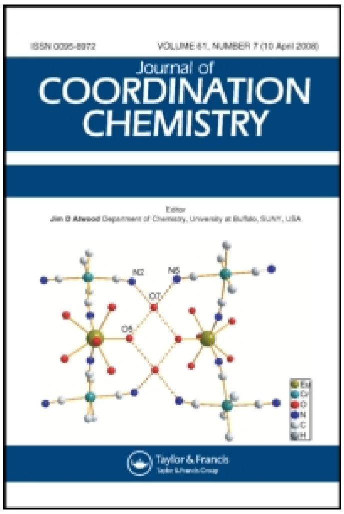

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# COMPLEX FORMATION BETWEEN LEAD(II) AND BROMIDE IONS

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Activity coefficient effects represent the main source of uncertainty in the interpretation of equilibrium data in the Pb(II)–$Br^-$ system. This is presumably the reason for a number of contrasting reports on the stoichiometry and formation constants of $PbBr_n^{2-n}$ complexes. Specific Interaction Theory is employed in the present paper to select experimental conditions under which minimal activity coefficient variations are produced as well as to interpret the data. Emf measurements (lead amalgam electrode) based on junctionless cell (sodium ion-sensitive glass electrode, internal reference) show that in the range of bromide concentration 0.03–5.0 *m* all species $PbBr_n^{2-n}$ ($1 \leqslant n \leqslant 6$) are formed. The corresponding formation constants, expressed on the 5.0 *m* ( = 4.1 M) $NaClO_4$ activity scale, are reported.

Keywords: lead(II), bromide, complexes, stability constants, activity coefficients

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## INTRODUCTION

Nearly any combination of the seven possible complexes $PbBr_n^{2-n}$ ($1 \leqslant n \leqslant 7$) has been assumed by different investigators[1] from time to time to explain equilibrium data in the Pb(II)–$Br^-$ system, derived from potentiometric, spectrophotometric or solubility measurements. For example Nilsson and Haight[2] have interpreted solubility measurements of $PbSO_4$(s) and $(CH_3)NPbBr_3$(s) by assuming the presence of $PbBr^+$, $PbBr_2$, $PbBr_4^{2-}$ and $PbBr_6^{4-}$. On the other hand, Vierling[3] reports the sequence $PbBr_n^{2-n}$ ($n = 1$ to 5), but not $PbBr_6^{4-}$, on the basis of extensive potentiometric, spectrophotometric and solubility ($PbBr_2$(s)) measurements, despite the fact that the same bromide concentration range (~0–4 M) as in ref. 2 was investigated. The sequence $PbBr^+$, $PbBr_3^-$, $PbBr_5^{3-}$, $PbBr_7^{5-}$ is proposed in reference 4 (spectrophotometry).

Careful examination of the literature shows that the fundamental reason for this state of affairs is that the ionic environment of the complex formation reaction (*1*)

$$Pb^{2+} + nBr^- \rightleftharpoons PbBr_n^{2-n} \qquad (1)$$

cannot be kept invariant as usual in equilibrium analysis (ionic medium method) because of the large concentrations of bromide ( $\gg$ 1 M) to be employed in order to form appreciable amounts of the higher $PbBr_n^{2-n}$ species. An obvious corollary is that activity coefficient variations will unavoidably occur (regardless of the method used) as the ligand concentration is increased, and these have to be accounted for before an accurate complex formation mechanism can be deduced.

By want of an exact account of activity coefficients in electrolyte mixtures, varied

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approaches have been taken by different authors. In order to minimize activity coefficient variations, solutions, whose molar ionic strength was made up to a selected high value (3–4 M) by addition of a background electrolyte, have generally been investigated. Nevertheless, it seems to have been overlooked[2] that the activity coefficient variations in such conditions depend on the nature of the background electrolyte and can become devastatingly large (despite the constant ionic strength) if an inappropriate choice is made. This is doubtless the case when the anion of the background electrolyte itself forms complexes with lead(II); mixed species formation will produce unaccountably large activity coefficient variations of all species at equilibrium as the concentration of the background anion varies. This possibility cannot be excluded in ref. 2 ($H_2SO_4$ was the background electrolyte).

Mean activity coefficients of $Pb(ClO_4)_2$[5,6] exhibit (up to 5 M) the pattern expected (on the basis of Specific Interaction Theory (SIT)[7–11] and other treatments of electrolyte solutions) for a non-associating salt. Alkali metal perchlorates are consequently suitable ionic media (and presumably the only correct choice) in the investigation of this and other analogous systems. $LiClO_4$ and $NaClO_4$ have been used in a number of cases.[3,12,13] However, residual activity coefficient effects still persist and interpretation of data with the assumption of constant values for activity coefficients can hardly be justified.

In one paper (ref. 3) data referring to solutions (whose ionic strength was kept constant at the 4 M level by addition of $NaClO_4$) with bromide concentrations varying virtually between 0 and 4 M, were interpreted by introducing "apparent formation constants" $\chi_n^0$, postulated to depend on the bromide concentration, $\log\chi_n^0 = \log\chi_n + \alpha_n[\mathrm{Br}^-]$; $\chi_n$ is the equilibrium constant for reaction (*1*) in 4 M $NaClO_4$ and $\alpha_n$ is a freely varying parameter which was determined simultaneously with $\chi_n$. However, the potentiometric experimental data presented do not allow for the evaluation of both the set of parameters, $\chi_n$ and $\alpha_n$, because the data are only related to $\Sigma_n(1 + \chi_n^0[\mathrm{Br}^-]^n)$. Now, for small values of $\alpha_n[\mathrm{Br}^-]$ (as in the present case), the postulated dependence of the apparent formation constants above (on the bromide concentration) is equivalent to $\chi_n^0 = \chi_n + 2.3\chi_n\alpha_n[\mathrm{Br}^-]$. By substituting this expression in the above summation it is found that the data are related to $\Sigma_n(1 + (\chi_n + 2.3\chi_{n-1}\alpha_{n-1})[\mathrm{Br}^-]^n)$. It is apparent that when the parameters $\chi_n$ and $\alpha_n$ are independently varied in the calculation procedure an increase in $\alpha_{n-1}$ will produce the same qualitative effect as an increase in $\chi_n$ (and *vice versa*). Species $PbBr_n^{2-n}$ may give rise to a somewhat high $\alpha_{n-1}$ value and escape detection (this is very likely indeed if $\chi_n \ll \chi_{n-1}$). This possibly explains the failure to detect $PbBr_6^{4-}$ in ref. 3.

Activity coefficient variations are minimal and better evaluated if the molal (rather than the molar) ionic stength $I$ (Mol/kg) is kept constant. In the present investigation of lead(II) bromide complexes, test solutions, TS, had the following general analytical composition,

$$\mathrm{TS} = B\ m\ \mathrm{Pb(II)},\ A\ m\ \mathrm{Br}^-,\ (5.000 + 2B - A)\ m\ \mathrm{ClO}_4^-,\ 5.000\ m\ \mathrm{Na}^+$$

in which $B$, the analytical concentration of lead(II) ranged between $2.99 \times 10.^{-4}\ m$ and $1.27 \times 10^{-3}\ m$, and $A$, the analytical bromide concentration, between 0.03 $m$ and 5.0 $m$. The test solution contained about $10^{-4}\ m$ $HClO_4$, to suppress hydrolysis.

According to the SIT method, the molal activity coefficient of an ion j, $\gamma_j^0$ (infinite dilution reference state), of arithmetic charge $z_j$ can be expressed by (*2*).

$$\log\gamma_j^0 = -z_j^2 D(I) + \Sigma_k \varepsilon(j,k) m_k \qquad (2)$$

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$D(I) = 0.5107I^{0.5}/(1 + 1.5I^{0.5})$, at 25°C, is the Debye term and $\varepsilon(j,k)$ is the interaction coefficient between ions j and k, present in the solution at molality $m_k$. The summation extends over all ions k bearing charges of opposite sign to j, since interaction coeffecients between ions of the same charge sign are postulated to be equal to zero. If kj is a non associating electrolyte, $\varepsilon(j,k)$ is readily obtained from mean activity coefficients referring to solutions of kj.[11]

By applying (*2*) to solution TS it is found that activity coefficients of negatively charged species are constant throughout and equal unity if the reference state is so chosen that activities approach concentrations when the composition of the solution approaches 5.000 *m* $NaClO_4$. This reference state is adopted in this paper for all species and the molal activity coefficient of j on this scale is indicated by $\gamma_j$. Activity coefficients of positively charged species are expressed by (*3*)–(*5*).

$$\log \gamma_{Na^+} = [\varepsilon(Na^+,Br^-) - \varepsilon(Na^+, ClO_4^-)]A = A.\ \Delta\varepsilon_{Na^+} \qquad (3)$$

$$\log \gamma_{Pb^{2+}} = [\varepsilon(Pb^{2+},Br^-) - \varepsilon(Pb^{2+},ClO_4^-)]A = A\cdot\Delta\varepsilon_0 \qquad (4)$$

$$\log \gamma_{PbBr^+} = [\varepsilon(PbBr^+,Br^-) - \varepsilon(PbBr^+,ClO_4^-)]A = A\cdot\Delta\varepsilon_1 \qquad (5)$$

For the activity coefficient of the uncharged $PbBr_2$ species (*6*) holds to a very good approximation.[6,10,11]

$$\log \gamma_{PbBr_2} = (\varphi^{NaBr} - \varphi^{NaClO_4})A = A\cdot\Delta\varphi \qquad (6)$$

The terms $\varphi^{NaBr}$ and $\varphi^{NaClO_4}$ are the salting coefficients of NaBr and $NaClO_4$, respectively, upon $PbBr_2$.

It will be shown that the form of (*3*)–(*6*) is eminently suitable to be used in the interpretation of emf measurements. Uncertainties which arise in the interpretation of emf data based on cells with a junction (because of variations of the liquid junction potential) have been avoided in the present investigation by employing a sodium ion-sensitive glass electrode as internal reference.

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## EXPERIMENTAL

### *Method*

Complex formation equilibria between lead(II) and bromide ions have been investigated at 25°C by emf measurements based on the cell (*H*).

$$-\mathrm{Pb(Hg)|TS|GE{-}Na} + \qquad (H)$$

The lead amalgam electrode was about 0.1% Pb by weight. GE–Na represents a sodium ion sensitive glass electrode and TS, the test solution, had the general analytical composition given above. *In situ* generation of lead(II), employing a constant current coulometric technique, allowed the analytical concentration of Pb(II) in TS, *B*, to take any value over the range investigated. Accurate variations of the analytical bromide concentration, *A*, were generated by addition of weighted amounts of titrating solution T.

$$T = A_T\,m\,Br^-,\ (5.000{-}A_T)\,m\,ClO_4^-,\ 5.000\,m\,Na^+$$

The emf $E_H$(mv) of cell ($H$) can be written as in (7),

$$E_H = E_H^0 + 59.16 \log \gamma_{Na^+} - 29.58 \log b - 29.58 \log \gamma_{Pb^{2+}} \qquad (7)$$

in which $b$ represents the equilibrium concentration of $Pb^{2+}$ and $E_H^0$ (including the $Na^+$ concentration term) is a constant which can be determined from measurements on solutions with $A = 0$ (when $\gamma_{Na^+} = 1$, $\gamma_{Pb^{2+}} = 1$ and $b = B$).

Data $E_H$–$E_H^0$(log $A$, log $B$) presented in Table I are the basis for the evaluation of the prevailing $PbBr_n^{2-n}$ complexes and of the corresponding formation constants, $\beta_n(m^{-n})$ on the 5.0 $m$ (= 4.06 M) $NaClO_4$ activity scale.

## *Measurements*

All experiments were performed at constant temperature in a thermostatted oil bath (25.00 ± 0.05°C). Emf measurements were carried out with a precision of 0.01 mV by using a computerized data acquisition apparatus based on Hewlett-Packard components.

Metrohm $Na^+$-selective glass electrodes have been employed. Lead amalgams were prepared by dissolving lead metal in mercury under an inert atmosphere. In each experiment, carried out in the form of a titration, the test solution, TS, was prepared from a starting 5.000 $m$ $NaClO_4$ solution by the following procedure. A weighed amount of 5.000 $m$ $NaClO_4$ was introduced into the titration vessel and completely freed of oxygen by passing a nitrogen stream; lead amalgam was poured into two separated cavities at the bottom of the titration vessel (the amalgam in one of the cavities served as the measuring electrode for cell ($H$) and the other as the working anode in the coulometric circuit below). Lead(II) was then generated stepwise in the solution by passing an accurately known electrolysis current through the circuit shown below.

$$-|\,0.1\,m\,Hg_2(ClO_4)_2,\ 4.8\,m\,NaClO_4|5.000\,m\,NaClO_4|TS|Pb(Hg)\ +$$

constant current source

After each electrolysis step the emf, $E_H$, was recorded. The data served to assess $E_H^0$ in (7). $E_H^0$ values constant within 0.1 mV were obtained. After a selected $B$ value had been attained the experiment was continued by stepwise addition of solution T. Bromide concentrations close to 5 $m$ cannot obviously be arrived at by this procedure. For this reason a few experiments were carried out by starting with a 5 $m$ NaBr solution in the cell and titrating with 5 $m$ $NaClO_4$. In such cases $E_H^0$ was determined at the end of the titration by the same procedure described above after transferring the amalgam and sodium electrodes to a second cell containing 5.000 $m$ $NaClO_4$. Care must be taken to avoid amalgam oxidation by atmospheric oxygen.

## *Materials and Analysis*

Sodium perchlorate stock solutions were prepared and analyzed as described elsewhere.[14] Sodium bromide stock solutions were prepared by dissolving NaBr(s) (Baker *p.a.*) and were analyzed by standard methods. Lead and mercury, Fluka 99.999%, were used for amalgam preparation without further purification. The nitrogen stream passed through the test and titrating solutions in order to exclude

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oxygen was freed from oxidizing impurities by passing through a chromium(II) solution and saturated with water vapour using 5 $m$ $NaClO_4$ or 5 $m$ NaBr.

## RESULTS AND DISCUSSION

### *Mathematical Development of (7)*

The analytical lead(II) concentration in TS, B, can be expressed by (*8*)

$$B = b + \Sigma_n \beta_n b a^n \gamma_{Pb^{2+}} \gamma^n_{Br^-} \gamma_n^{-1} \qquad (8)$$

in which $a$ is the equilibrium concentration of bromide and $\gamma_n$ represents the molal activity coefficient of $PbBr_n^{2-n}$. Equation (*9*) is readily obtained by substituting (*8*) into (*7*) and noticing that under the experimental conditions prevailing in this study activity coefficients of negatively charged species equal unity

$$E_H - E_H^0 + 29.58 \log B - 59.16 \log \gamma_{Na^+} = Y =$$

$$= 29.58 \log(\gamma^{-1}_{Pb^{2+}} + \beta_1 a \gamma_1^{-1} + \beta_2 a^2 \gamma_2^{-1} + \Sigma_{n=3}\, \beta_n a^n) \qquad (9)$$

SIT expressions for activity coefficients (*3*)–(*6*)) allow (*9*) to be written in the abridged form shown in (*10*).

$$E_H - E_H^0 + 29.58 \log B - 59.16\, A\, \Delta\varepsilon_{Na^+} = Y =$$

$$= 29.58 \log(10^{-A\Delta\varepsilon_0} + \beta_1 a \cdot 10^{-A\,\Delta\varepsilon_1} + \beta_2 a^2 \cdot 10^{-A\Delta\varphi} + \Sigma_{n=3}\, \beta_n a^n) \qquad (10)$$

Experimental values of the $Y$ function, $Y_{exp}$, are readily obtained from the data in Table I since $\Delta\varepsilon_{Na^+} = 0.04$ kg/mol (evaluated from activity data referring to NaBr and $NaClO_4$ solutions[5,11]). On the other side, $\Delta\varepsilon_0$, $\Delta\varepsilon_1$, and $\Delta\varphi$ are not directly evaluable. Estimates of their values can be obtained as follows. $\Delta\varepsilon_0$ is not expected to be far from 0.01 kg/mol, because $\varepsilon(Pb^{2+}, ClO_4^-) = 0.15$ kg/mol (obtained from activity coefficients of $Pb(ClO_4)_2$)[11] and $\varepsilon(Pb^{2+}, Br^-)$ is very likely close to $\varepsilon(Ba^{2+}, Br^-) = 0.15$ kg/mol (it is usually found that ions of the same charge and similar sizes have comparable interaction coefficients;[10,11] note that $\varepsilon(Ba^{2+}, ClO_4^-) = \varepsilon(Pb^{2+}, ClO_4^-) = 0.15$ kg/mol). One also finds that complex ion interaction coefficients are not dramatically different from those of the parent metal ion as long as the charge keeps off the same sign and consequently $\Delta\varepsilon_1 \simeq \Delta\varepsilon_0$. On the basis of the presumed similarity in size and structure of $PbBr_2$ and $Pb(OH)_2$ it is plausible to assume that $\varphi^{NaClO_4} \simeq -0.08$ kg/mol (this is in fact the value of the salting coefficient of $NaClO_4$ upon $Pb(OH)_2$ evaluated from the dependence of its formation constant on the concentration of the $NaClO_4$ ionic medium[10,11,15]). We have not however been able to make an unambiguous estimate of $\varphi^{NaBr}$ by want of activity data for neutral molecules in NaBr, but for our purposes it is sufficient to state that $|\Delta\varphi|$ is of the order of 0.1 kg/mol. In the light of these estimates it is apparent that the following approximations can be introduced in (*10*): $10^{-A\Delta\varepsilon_0} \simeq 1 - 2.3a\Delta\varepsilon_0$; $10^{-A\Delta\varepsilon_1} \simeq 1 - 2.3a\Delta\varepsilon_1$;$10^{-A\Delta\varphi} \simeq 1 - 2.3a\Delta\varphi$; this is reasonable since $A\Delta\varepsilon_i \ll 1$ and $A\Delta\varphi \ll 1$. Furthermore because of the large $A/B$ ratios in TS, no appreciable error will be

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introduced at this point by using $a$ in place of $A$. The final expression of the $Y$ function to be used is given in (*11*).

$$Y = 29.58\log[1 + (\beta_1 - 2.3\Delta\varepsilon_0)a + (\beta_2 - 2.3\beta_1\Delta\varepsilon_1)a^2 +$$

$$+ (\beta_3 - 2.3\beta_2\Delta\varphi)a^3 + \Sigma_{n=4} \quad \beta_n a^n] \qquad (11)$$

It can easily be shown that the derivative of $Y$ with respect to $\log a$, yields to a very good approximation $29.58\bar{n}$, $\bar{n}$ being the average number of bromide ions bonded per lead(II). This allows a closer approximation to $a$ (than $a = A$) to be obtained from the data in Table I by an iteration procedure. Starting with $\bar{n} = \Delta Y_{exp}/(29.58\Delta\log A)$, the bromide equilibrium concentration is calculated from (*12*) and $\bar{n}$ from (*13*).

$$a = A - \bar{n}B \qquad (12)$$

$$\bar{n} = \Delta Y_{exp}/(29.58\Delta\log a) \qquad (13)$$

Final values of $\bar{n}$ and $a$ are deduced from data in Table I after three iterations. In Fig. 1 a plot of $Y_{exp}$ as a function of $\log a$ is shown.

TABLE I

Summary of the experimental data $E_{II}$–$E^0_{II}$($\log A$, $\log B$), $E_{II}$–$E^0_{II}$ in mV. Data are listed in the form $E_{II}$–$E^0_{II}$($\log A$, $\log B$).

| | | |
|---|---|---|
| 100.26(−1.520, −3.165) | 106.07(−1.228, −3.173) | 111.57(−1.060, −3.181) |
| 116.55(−0.944, −3.189) | 121.03(−0.855, −3.196) | 124.80(−0.784, −3.204) |
| 128.40(−0.725, −3.211) | 133.39(−0.652, −3.221) | 137.74(−0.593, −3.232) |
| 142.99(−0.528, −3.245) | 147.57(−0.475, −3.258) | 151.57(−0.431, −3.270) |
| 156.95(−0.376, −3.288) | 161.58(−0.331, −3.305) | 165.58(−0.294, −3.321) |
| 170.72(−0.243, −3.327) | 179.65(−0.160, −3.338) | 187.20(−0.093, −3.348) |
| 196.72(−0.014, −3.363) | 204.60( 0.048, −3.378) | 211.31( 0.098, −3.392) |
| 217.17( 0.141, −3.405) | 223.90( 0.188, −3.422) | 229.77( 0.227, −3.438) |
| 229.58( 0.245, −3.345) | 235.93( 0.268, −3.458) | 232.01( 0.268, −3.322) |
| 234.29( 0.289, −3.301) | 241.26( 0.301, −3.476) | 236.03( 0.305, −3.286) |
| 237.88( 0.322, −3.269) | 245.96( 0.330, −3.493) | 239.98( 0.339, −3.252) |
| 249.95( 0.354, −3.510) | 241.95( 0.357, −3.235) | 244.09( 0.375, −3.216) |
| 253.47( 0.376, −3.525) | 246.26( 0.395, −3.197) | 248.48( 0.415, −3.177) |
| 251.08( 0.436, −3.156) | 253.28( 0.454, −3.138) | 255.60( 0.473, −3.120) |
| 258.01( 0.492, −3.100) | 260.64( 0.513, −3.080) | 263.48( 0.534, −3.059) |
| 264.95( 0.545, −3.048) | 266.48( 0.557, −3.037) | 267.67( 0.565, −3.028) |
| 268.90( 0.574, −3.019) | 269.73( 0.580, −3.013) | 270.59( 0.586, −3.007) |
| 271.52( 0.593, −3.001) | 272.38( 0.599, −2.995) | 273.29( 0.605, −2.988) |
| 274.24( 0.612, −2.982) | 275.18( 0.618, −2.975) | 276.19( 0.625, −2.968) |
| 277.19( 0.632, −2.962) | 278.25( 0.639, −2.955) | 279.27( 0.646, −2.948) |
| 280.34( 0.653, −2.941) | 281.40( 0.660, −2.933) | 282.55( 0.668, −2.926) |
| 283.73( 0.675, −2.919) | 284.93( 0.683, −2.911) | 286.14( 0.691, −2.903) |
| 287.41( 0.698, −2.895) | | |

In the above discussion it has been implicitly assumed that only mononuclear complexes are formed; that this is correct can be deduced from Fig. 1, which shows that points are on the same curve regardless of $B$.

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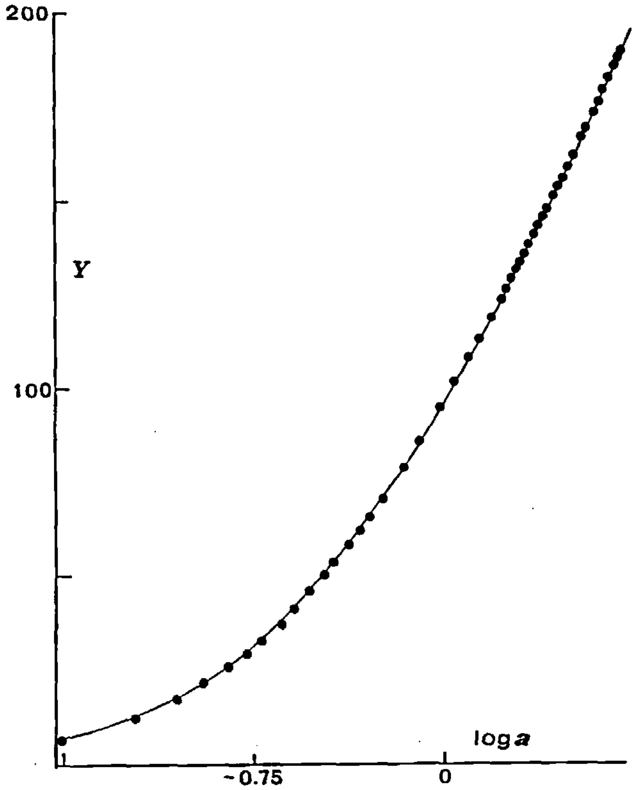

FIGURE 1 Plot of $Y(\mathrm{mV}) = E_{\mathrm{II}} - E^0_{\mathrm{II}} + 29.58\log B - 2.366A$ *vs* the free bromide concentration, *a* (mol/kg). Dots represent experimental values while the full curve has been calculated from (*11*) using parameters values in (*17*)–(*20*). Not all the points have been reported.

### *Graphical Evaluation of the Prevailing $PbBr_n^{2-n}$ Complexes*

The problem of the speciation of lead(II) in bromide solutions is reduced by (*11*) to the determination of the $n$ unknown parameters from the set of experimental data $Y_{\exp}(\log a)$. Most reasonably, the limiting lead(II) bromide complex is $PbBr_6^{4-}$. In fact $\bar{n}$ values significantly higher than 5 are estimated from the slope of the curve in Fig. 1 at the highest $\log a$ ($>0.6$) but $\bar{n}$ never exceeds 6. Since for any finite value of $a$, $\log\beta_6 < (Y_{\exp}/29.58 - 6\log a)$ the higher limit of $\beta_6$ compatible with our data is $\sim 170\,m^{-6}$.

The curve $(10^{Y_{\exp}} - 1)a^{-1}$ *vs* $a$ has beyond any reasonable doubt a non zero intercept at $a = 0$. The value $(\beta_1 - 2.3\Delta\varepsilon_0) = 17.7 \pm 1\,m^{-1}$ obtained by extrapolating the above function strongly supports the formation of $PbBr^+$.

Plots of the function $(10^{Y_{\exp}/29.58} - (\beta_1 - 2.3\Delta\varepsilon_0)a - 1)a^{-2}$ *vs* $a$ constructed by varying the parameter $(\beta_1 - 2.3\Delta\varepsilon_0)$ between the limits $16.7\,m^{-1}$ and $18.7\,m^{-1}$ also show a non zero intercept at $a = 0$. Extrapolation of the plots gives $(\beta_2 - 2.3\beta_1\Delta\varepsilon_1) = 110 \pm 10\,m^{-2}$. The value of $Y$ at $a = 1\,m$ is close to 96 mV (see Fig. 1). From (*11*) ($a = 1\,m$) we then derive (*14*).

$$1 + (\beta_1 - 2.3\Delta\varepsilon_0) + (\beta_2 - 2.3\beta_1\Delta\varepsilon_1) + (\beta_3 - 2.3\beta_2\Delta\varphi) + \Sigma_{n=4}\,\beta_n \simeq 1800 \qquad (14)$$

On the grounds of the above estimates and of (*14*) we deduce that $PbBr^+$, $PbBr_2$ and $PbBr_6^{4-}$ account only for a small fraction of the total lead in solution for $a$ in the vicinity of 1 *m*. Function *F*, (*15*), can then be accurately evaluated from the $Y_{exp}(\log a)$ values at $Br^-$ concentrations around 1 *m*; uncertainties in $(\beta_1 - 2.3\Delta\varepsilon_0)$ and $(\beta_2 - 2.3\beta_1\Delta\varepsilon_1)$ are not relevant as long as $PbBr^+$ and $PbBr_2$ are not prevailing.

$$F = \log[10^{Y_{exp}/29.58} - (\beta_1 - 2.3\Delta\varepsilon_0)a - (\beta_2 - 2.3\beta_1\Delta\varepsilon_1)a^2 - 1] - 4\log a =$$

$$\log[(\beta_3 - 2.3\beta_2\Delta\varphi)a^{-1} + \beta_4 + \beta_5 a + \beta_6 a^2] \qquad (15)$$

The plot of *F vs* log*a* (Fig. 2) shows a well defined minimum at $a \simeq 1\,m$. This is convincing evidence that $(\beta_3 - 2.3\beta_2\Delta\varphi) > 0$. Equation (*16*) expresses the condition for *F* having a minimum at $a = 1\,m$.

$$\beta_3 - 2.3\beta_2\Delta\varphi = \beta_5 + 2\beta_6 \qquad (16)$$

Uncertainty in the abscissa of the minimum in Fig. 2 makes (*16*) approximate but in a measure that would not modify the discussion below. According to (*15*), as *a* decreases *F* ultimately approaches a straight line of slope $-1$ and of intercept $\log(\beta_3 - 2.3\beta_2\Delta\varphi)$ at $\log a = 0$. This line should not be far from that drawn in Fig. 2, which allows the approximate value $(\beta_3 - 2.3\beta_2\Delta\varphi) \simeq 700\,m^{-3}$ to be determined. From (*16*) there is little doubt that $\beta_5 > 0$ (in fact since $0 < 2\beta_6 < 340\,m^{-6}$, $360 < \beta_5 < 700\,m^{-5}$). Finally, when the higher limits of the parameters so far estimated are substituted in (*14*) it becomes soon apparent that $\beta_4 > 0$. Six parameters substantially larger than zero are indicated by the above qualitative analysis to be necessary in (*11*) in order to explain the experimental data.

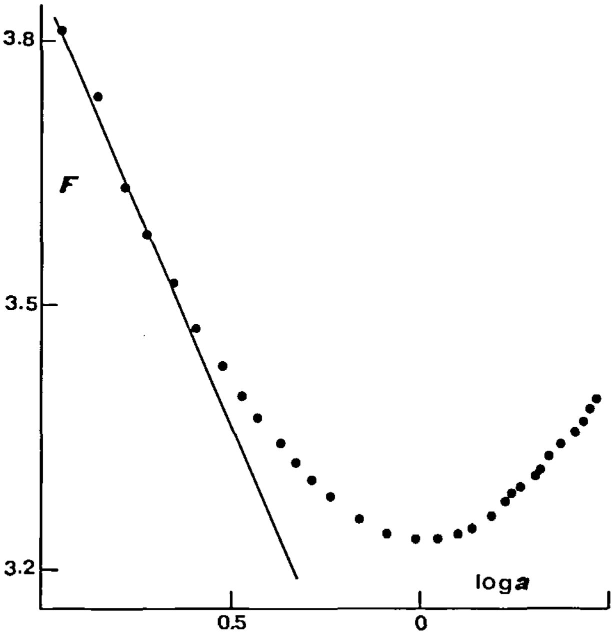

FIGURE 2 The function *F* (*15*) *vs* the free bromide concentration, *a* (mol/kg). When $a \to 0$, *F* approaches a straight line of slope $-1$.

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## *Numerical Treatment of the Data*

Calculated values of the $Y$ function, $Y_{\text{calc}}$, for each of the experimental $a$ values, are readily obtained from (*11*) for an assumed set of parameters. Starting with approximate values deduced from the graphical procedure, systematic variation of the parameters by a computer program rapidly converges to a minimum for the sum $\Sigma | Y_{\text{calc}} - Y_{\text{exp}} |$. An average minimal absolute deviation ($\Sigma | Y_{\text{calc}} - Y_{\text{exp}} | /$(*number of data points*)) of 0.27 mV is obtained with the following set of parameters.

$$\beta_1 - 2.3\Delta\varepsilon_0 = 17.7 \pm 1\, m^{-1} \tag{17}$$

$$\beta_2 - 2.3\beta_1\Delta\varepsilon_1 = 103 \pm 3\, m^{-2} \tag{18}$$

$$\beta_3 - 2.3\beta_2\Delta\varphi = 680 \pm 15\, m^{-3} \tag{19}$$

$$\beta_4 = 480 \pm 25\, m^{-4};\ \beta_5 = 500 \pm 10\, m^{-5};\ \beta_6 = 40 \pm 10\, m^{-6} \tag{20}$$

Errors are maximum deviations evaluated from the maximum variation of the parameters which still produce an acceptable fit for the data. The values $\beta_1$ and $\beta_2$ are immediately deduced from (*17*) and (*18*) since $2.3\Delta\varepsilon_0$ and $2.3\beta_1\Delta\varepsilon_1$ are negligible and at any rate lower than the errors given. On the other side, the term $2.3\beta_2\Delta\varphi$ is possibly of some relevance in (*19*) and makes a precise determination of $\beta_3$ impossible. However, $\Delta\varphi$ will hardly exceed $\pm 0.2$ kg/mol so that to a high degree of confidence $630 < \beta_3 < 730\, m^{-3}$. It is worth noting that if by chance $\beta_3$ had been smaller ($< \sim 100\, m^{-3}$), the actual formation of $PbBr_3^-$ would have been dubious. The full line in Fig. 1 has been drawn using values from (*17*)–(*20*). Results are summarized in Table II.

TABLE II

Summary of the results for $\beta_n$ formation constants in molal units ($m^{-n}$) and $\beta_n^M$ in molar units ($M^{-n}$) expressed on the $5\,m$ ($=4.06$ M) $NaClO_4$ activity scale.

| $n$ | $\log\beta_n$ | $\log\beta_n^M$ |
|---|---|---|
| 1 | 1.25 ± 0.02 | 1.34 ± 0.02 |
| 2 | 2.01 ± 0.02 | 2.19 ± 0.02 |
| 3 | 2.83 ± 0.03 | 3.10 ± 0.03 |
| 4 | 2.67 ± 0.03 | 3.03 ± 0.03 |
| 5 | 2.70 ± 0.02 | 3.15 ± 0.02 |
| 6 | 1.6 ± 0.1 | 2.14 ± 0.1 |

The ratio of the fourth to the third stepwise formation constant of lead(II) hydroxo complexes is not larger than $\sim 10^{-2.8}$. In fact Carell and Olin[15] in their study of the hydrolysis of Pb(II) in alkaline solutions state that $K_3 = 10^{2.76}\, M^{-1}$ in 3 M $NaClO_4$ ($K_r$ is the equilibrium constant for the reaction $PbL_{r-1} + L \rightleftharpoons PbL_r$) and that no evidence for $Pb(OH)_4^{2-}$ could be obtained. Since $OH^-$ concentrations as high as 0.5 M were reached in the above investigation it must be concluded that $K_4 < 1$. Consistent with this result we have shown[16] that no chloride is coordinated to $Pb(OH)_3^-$ even in solutions containing as much as 3 M $Cl^-$, while in acidic solutions $PbCl_4^-$ is readily obtained from $PbCl_3^-$ at chloride concentrations lower than 3 M ($K_4/K_3$ for chloride complexes is in fact 0.45; this figure is much larger than for hydroxo complexes and of the magnitude expected on a statistical basis).'

There is little doubt that the striking difference in the behaviour of $PbCl_3^-$ and $Pb(OH)_3^-$ toward the addition of the fourth ligand is the result of major differences in electronic and/or geometric structures. An $sp^3$ hybridization of lead(II) in $Pb(OH)_3^-$ (with the lone pair occupying one of the tetrahedron corners) and $sp^3d^x$ ($x = 1, 2$ or 3) in $PbCl_3^-$ would tentatively explain the above observations. If this is accepted the question concerning which of two possible electronic structures has to be attributed to lead(II) in the general $PbL_3$ species arises. Apparently this dilemma can be solved on the basis of the $K_4/K_3$ ratio. Nevertheless, when this argument is pursued, it becomes evident that not all cases are necessarily clear cut since the $K_4/K_3$ ratio is dependent on the free energy barrier of the conversion $PbL_3(sp^3) \rightarrow PbL_3(sp^3d^x)$. A very large and positive energy barrier will appear as a very low $K_4/K_3$ value, while a negative one will lead to the statistical ratio. As a corollary, cases may exist in which two structures of comparable energy give rise to intermediate $K_4/K_3$ ratios; this is possibly the case with lead(II) bromide complexes ($K_4/K_3 = 0.1$).

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## REFERENCES

1. L.G. Sillén and E.A. Martell, "Stability Constants of Metal Complexes," (The Chemical Society, Special Publications, **17**, 1964, and **25**, 1971, London).
2. L. Nilsson and G.P. Haight, Jr., *Acta Chem. Scand.*, **20**, 486 (1966).
3. F. Vierling, *Bull. Soc. Chim. (France)*, **7**, 2557, 2563 (1972).
4. V.G. Avramenko and M.V. Belyi, *Chem. Abstr.*, **61**, 269 (1964).
5. R.A. Robinson and R.H. Stokes. "Electrolyte Solutions", (Butterworths, London, 1955).
6. H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolyte Solutions, (Reinhold, New York, 1958).
7. J.N. Brønsted, *J. Am. Chem. Soc.*, **44**, 877 (1922) and **45**, 2898 (1923).
8. E.A. Guggenheim, "Applications of Statistical Mechanics," (Clarendon, Oxford, 1966).
9. G. Scatchard, in W.J. Hamer (Ed.,) "The Structure of Electrolyte Solutions", (John Wiley and Sons, New York, 1959).
10. G. Biedermann, "Dahlem Workshop on the Nature of Seawater", (Dahlem Konferenzen, Berlin, 1975).
11. L. Ciavatta, *Ann. Chim. (Rome)*, **70**, 551 (1980).
12. V.E. Mironov, *Zh. Neorg. Khim.*, **6**, 897 (1961).
13. F.Ya. Kulba, V.E. Mironov, G.S. Troitskaya and N.G. Maksimova, *Zh. Neorg. Khim.*, **6**, 1985 (1961).
14. G. Biedermann, *Arkiv Kemi*, **9**, 277 (1956).
15. B. Carell and Å. Olin, *Acta Chem. Scand.*, **14**, 1999 (1960).
16. D. Ferri and F. Salvatore *Ann. Chim. (Rome)*, in press.

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