Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems (IUPAC Technical Report)*

Kipton J. Powell[1], Paul L. Brown[2], Robert H. Byrne[3], Tamas Gajda[4], Glenn Hefter[5], Ann-Kathrin Leuz[6], Staffan Sjöberg[7,‡], and Hans Wanner[6]

[1]*Department of Chemistry, University of Canterbury, Christchurch, New Zealand;* [2]*Rio Tinto Technology and Innovation, 1 Research Avenue, Bundoora VIC 3083, Australia;* [3]*College of Marine Science, University of South Florida, 140 Seventh Avenue South, St. Petersburg, FL 33701-5016, USA;* [4]*Department of Inorganic and Analytical Chemistry, A. József University, P.O. Box 440, Szeged 6701, Hungary;* [5]*School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia;* [6]*Swiss Federal Nuclear Safety Inspectorate, CH-5232 Villigen, Switzerland;* [7]*Department of Chemistry, Umeå University, S-901 87 Umeå, Sweden*

Abstract: Complex formation between Pb^{II} and the common environmental inorganic ligands, Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}, can be significant in natural waters with low concentrations of organic matter. Numerical modeling of the speciation of Pb^{II} amongst these inorganic ligands requires reliable values for the relevant stability (formation) constants. This paper provides a critical review of such constants and related thermodynamic data. It recommends values of $\log_{10} \beta_{p,q,r}°$ valid at $I_m = 0$ mol kg^{-1} and 25 °C (298.15 K), along with the equations and empirical coefficients required to calculate $\log_{10} \beta_{p,q,r}$ values at higher ionic strengths using the Brønsted–Guggenheim–Scatchard specific ion interaction theory (SIT). Some values for reaction enthalpies, $\Delta_r H$, are also reported.

In weakly acidic fresh water systems ($-\log_{10} \{[H^+]/c°\} < 6$), the speciation of Pb^{II} is similar to that of Cu^{II}. In the absence of organic ligands, Pb^{II} speciation is dominated by Pb^{2+}(aq), with $PbSO_4$(aq) as a minor species. In weakly alkaline solutions, $8.0 < -\log_{10} \{[H^+]/c°\} < 9.0$, the speciation is dominated by the carbonato species $PbCO_3$(aq) and $Pb(CO_3)_2^{2-}$. In weakly acidic saline systems ($-\log_{10} \{[H^+]/c°\} < 6$), the speciation is dominated by $PbCl_n^{(2-n)+}$ complexes, ($n = 0–3$), with Pb^{2+}(aq) as a minor species. In this medium (and in seawater), the speciation contrasts with that of Cu^{II} because of the higher stability of the Pb^{2+}-chlorido- complexes. In seawater at $-\log_{10} \{[H^+]/c°\} = 8.2$, the calculated speciation is less well defined, although it is clearly dominated by the uncharged species $PbCO_3$(aq) (41 % of $[Pb]_T$) with a significant contribution (16 %) from $Pb(CO_3)Cl^-$ and minor contributions (5–10 %) from $PbCl_n^{(2-n)+}$, ($n = 0–3$) and $Pb(CO_3)_2^{2-}$. The uncertainty in calculations of Pb^{II} speciation in seawater arises from (a) the large uncertainty in the stability constant for the apparently dominant species $PbCO_3$(aq), (b) the reliance on statistical predictions for stability constants of the ternary species $Pb(CO_3)Cl^-$ and $Pb(CO_3)OH^-$, and (c) the uncertainty in the stability constant for $PbCl_4^{2-}$, the available value being considered

---

"indicative" only. There is scope for additional detailed high-quality measurements in the $Pb^{2+} + CO_3^{2-} + Cl^-$ system.

Keywords: chemical speciation; environmental; lead; ligands; stability constants.

CONTENTS

10. QUANTITIES, SYMBOLS, AND UNITS USED IN THIS TECHNICAL REPORT

1. INTRODUCTION

This review is the third in a series relevant to the speciation of heavy metal ions in environmental waters of low to moderate ionic strength. It provides access to the best available equilibrium data for use in chemical speciation modeling of reactions of Pb^{2+} with the major inorganic ligands present in environmental systems: Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. The previous reviews in this series were on the Hg^{2+} [2005PBa] and Cu^{2+} [2007PBa] complexation reactions with these ligands. Note: reference citations are based on those adopted in the IUPAC Stability Constants Database (*SC-Database*) [2009PET]; see further note in the Reference section. The protonation* reactions of CO_3^{2-} and PO_4^{3-} were also reviewed [2005PBa]. Subsequent reviews will focus on the equilibrium reactions of the same ligands with Cd^{2+} and Zn^{2+}.

The first review [2005PBa] noted the need for reliable equilibrium constants, valid at ionic strengths and temperatures relevant to chemical speciation modeling of labile equilibrium reactions in natural aquatic systems. The reader is referred to [2005PBa] for (i) the nomenclature used to express stability constants $\beta_{p,q,r}$, $*\beta_{p,q,r}°$, K_n, and $*K_n$ (Appendix 1A in [2005PBa]; see also Section 10), (ii) the criteria by which published data ($\beta_{p,q,r}$ and $\Delta_r H$) are "accepted" for inclusion in the critical evaluations, or "rejected", (iii) the principles of the Brønsted–Guggenheim–Scatchard specific ion interaction theory (SIT) [97GRE], and (iv) the application of SIT functions [97GRE] to effect regression of "accepted" values at finite ionic strengths to obtain values at $I_m = 0$ mol kg^{-1} (infinite dilution).

The first two reviews [2005PBa, 2007PBa] in this series outlined the procedure for converting stability constants published on the amount concentration scale (mol solute/dm^3 solution; expressed as [species *i*]) to values on the molality (mol kg^{-1}) scale, to permit the application of SIT and the regression of stability constant values to obtain the standard (state) equilibrium constants valid at $I_m = 0$ mol kg^{-1}. The primary source of data is the *SC-Database* [2009PET].

For each Pb^{2+}+ ligand combination, this review will, where possible:

•   identify the most reliable publications and stability constants;
•   identify (and reject) unreliable stability constants;
•   establish correlations between the accepted data on the basis of ionic strength dependence, using the SIT functions;
•   establish Recommended values of $\beta_{p,q,r}°$ and $K_{s0}°$ at 25 °C (298.15 K) and $I_m = 0$ mol kg^{-1};
•   identify the most reliable reaction enthalpy values $\Delta_r H$ for each equilibrium reaction;

---

*By common usage, the terms "proton" and "protonation" refer to the natural isotopic mixture of hydrogen, not isotopically pure $^1H^+$. Strictly speaking, the reaction is hydronation.

- provide the user with the numerical relationships required to interpolate values of $\beta_{p,q,r}$ at $I_m > 0$ mol kg^{-1};
- provide examples of SIT plots for $\beta_{p,q,r}$ extrapolations;
- provide examples of distribution diagrams for binary and multicomponent systems; and
- provide values of $\beta_{p,q,r}$ applicable to calculations in fresh and saline water systems.

All reactions described in this document refer to aqueous solution, e.g.,

$$Pb^{2+}(aq) + 2H_2O \rightleftharpoons Pb(OH)_2(aq) + 2H^+(aq)$$

For simplicity, suffixes such as (aq) are not used unless a species has zero net charge, in which case the phase is specified, e.g., $Pb(OH)_2(aq)$, $Pb(OH)_2(s)$, and $PbO(s)$. In this document, "amount concentration" is abbreviated to "concentration", the units being mol dm^{-3} (= mol L^{-1}, or M).

2. SUMMARY OF RECOMMENDED VALUES

Tables 1–5 provide a summary of the standard equilibrium constants ($I_m = 0$ mol kg^{-1}), SIT reaction ion interaction coefficients ($\Delta\varepsilon$) and, where available, reaction enthalpies for the formation of Pb^{2+} complexes with the selected inorganic anions. These were derived from a critical evaluation of the available literature, followed by regression analyses of the accepted data using SIT functions. The reader is referred to [2005PBa] for definition of the terms "Recommended" (R) and "Provisional" (P) used in these Tables. The $\log_{10} \beta_{p,q,r}°$, $\log_{10} K_n°$, and $\log_{10} *\beta_{p,q,r}°$ values are for 298.15 K, 1 bar (10^5 Pa), and infinite dilution ($I_m = 0$ mol kg^{-1}).

Table 1 Recommended (R) values for the $Pb^{2+} + OH^-$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. $\Delta\varepsilon$ values for $NaClO_4$ medium[1].

Reaction	Constant		Evaluation
$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$	$\log_{10} *K_1°$	$= -7.46 \pm 0.06$	R
	$\Delta\varepsilon$	$= -(0.06 \pm 0.04)$ kg mol^{-1}	
$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2(aq) + 2H^+$	$\log_{10} *\beta_2°$	$= -16.94 \pm 0.09$	R
	$\Delta\varepsilon$	$= -(0.13 \pm 0.04)$ kg mol^{-1}	
$Pb^{2+} + 3H_2O \rightleftharpoons Pb(OH)_3^- + 3H^+$	$\log_{10} *\beta_3°$	$= -28.03 \pm 0.06$	R
	$\Delta\varepsilon$	$= (0.26 \pm 0.05)$ kg mol^{-1}	
$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+$	$\log_{10} *\beta_{3,4}°$	$= -23.01 \pm 0.07$	R
	$\Delta\varepsilon$	$= -(0.39 \pm 0.03)$ kg mol^{-1}	
$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$	$\log_{10} *\beta_{4,4}°$	$= -20.57 \pm 0.06$	R
	$\Delta\varepsilon$	$= -(0.19 \pm 0.02)$ kg mol^{-1}	
$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+$	$\log_{10} *\beta_{6,8}°$	$= -42.89 \pm 0.07$	R
	$\Delta\varepsilon$	$= -(0.41 \pm 0.03)$ kg mol^{-1}	
$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+$	$\log_{10} *\beta_{2,1}°$	$= -7.28 \pm 0.09$	P[2]
	$\Delta\varepsilon$	$= (0.11 \pm 0.10)$ kg mol^{-1}	
$PbO(s)(red) + 2H^+ \rightleftharpoons Pb^{2+} + H_2O$	$\log_{10} *K_{s0}°$	$= 12.62 \pm 0.07$	R
$PbO(s)(yellow) + 2H^+ \rightleftharpoons Pb^{2+} + H_2O$	$\log_{10} *K_{s0}°$	$= 12.90 \pm 0.08$	R

[1]The uncertainties represent 95 % confidence limits of the regression intercept ($\log_{10} K°$) and of the slope ($-\Delta\varepsilon$).
[2]$\log_{10} *\beta_{2,1}°$ and $\Delta\varepsilon$ derived from data for nitrate media.

Table 2 Recommended values (R) for the $Pb^{2+} + Cl^-$ system at 298.15 K and $I_m = 0$ mol kg^{-1}. $\Delta\varepsilon$ values for $NaClO_4$ medium.

Reaction	Constant[1]		Evaluation
$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$	$\log_{10} K_1°$	$= 1.50 \pm 0.03$	R
	$\Delta\varepsilon$	$= -(0.14 \pm 0.01)$ kg mol^{-1}	
	$\Delta_r H°$	$= (10.3 \pm 1.5)$ kJ mol^{-1}	P
$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(aq)$	$\log_{10} \beta_2°$	$= 2.10 \pm 0.05$	R
	$\Delta\varepsilon$	$= -(0.26 \pm 0.02)$ kg mol^{-1}	
	$\Delta_r H°$	$= (17.0 \pm 0.6)$ kJ mol^{-1}	P
$Pb^{2+} + 3Cl^- \rightleftharpoons PbCl_3^-$	$\log_{10} \beta_3°$	$= 2.00 \pm 0.10$	R
	$\Delta\varepsilon$	$= -(0.32 \pm 0.03)$ kg mol^{-1}	
	$\Delta_r H°$	$= (14.7 \pm 1.0)$ kJ mol^{-1}	P

[1]The uncertainties represent 95 % confidence limits of the regression intercept ($\log_{10} K°$) and of the slope ($-\Delta\varepsilon$).

Table 3 Recommended (R), Provisional (P), and Indicative (I) values for the $Pb^{2+} + CO_3^{2-}$ system at 298.15 K, 1 bar, and $I_m = 0$ mol kg^{-1}. $\Delta\varepsilon$ values for $NaClO_4$ medium.

Reaction	Constant[1]		Evaluation
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3(aq)$	$\log_{10} K_1°$	$= 6.45 \pm 0.72$	I
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	$\log_{10} \beta_2°$	$= 10.13 \pm 0.24$	P
	$\Delta\varepsilon$	$= -(0.19 \pm 0.10)$ kg mol^{-1}	
$Pb^{2+} + HCO_3^- \rightleftharpoons PbHCO_3^+$	$\log_{10} K$	$= 1.86 \pm 0.1$[2]	P
$PbCO_3(s) \rightleftharpoons Pb^{2+} + CO_3^{2-}$	$\log_{10} K_{s0}°$	$= -13.18 \pm 0.07$	R
	$\Delta\varepsilon$	$= (0.62 \pm 0.70)$ kg mol^{-1}	
$Pb_2(CO_3)Cl_2(s) \rightleftharpoons 2Pb^{2+} + CO_3^{2-} + 2Cl^-$	$\log_{10} K_{s0}°$	$= -9.93 \pm 0.08$	R

[1]The uncertainties represent 95 % confidence limits of the regression intercept ($\log_{10} K°$) and of the slope ($-\Delta\varepsilon$).
[2]Value for $I_m = 3.5$ mol kg^{-1} $NaClO_4$.

Table 4 Recommended (R) values for the $Pb^{2+} + SO_4^{2-}$ system at 298.15 K and $I_m = 0$ mol kg^{-1}. $\Delta\varepsilon$ values for ClO_4^- medium.

Reaction	Constant[1]		Evaluation
$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4(aq)$	$\log_{10} K_1°$	$= 2.72 \pm 0.05$	R
	$\Delta\varepsilon$	$= (0.02 \pm 0.03)$ kg mol^{-1}	
$PbSO_4(s) \rightleftharpoons Pb^{2+} + SO_4^{2-}$	$\log_{10} K_{s0}°$	$= -7.80 \pm 0.05$	R

[1]The uncertainties represent 95 % confidence limits of the regression intercept ($\log_{10} K°$) and of the slope ($-\Delta\varepsilon$).

Table 5 Provisional (P) values for the $Pb^{2+} + H^+ + PO_4^{3-}$ system at 298.15 K and $I_m = 0$ mol kg^{-1}.

Reaction	Constant[1]		Evaluation
$Pb^{2+} + HPO_4^{2-} \rightleftharpoons PbHPO_4(aq)$	$\log_{10} K$	$= 3.3 \pm 0.2$	P[2]
$PbHPO_4(s) \rightleftharpoons Pb^{2+} + HPO_4^{2-}$	$\log_{10} K_{s0}°$	$= -11.4 \pm 0.3$	P
$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+} + 2PO_4^{2-}$	$\log_{10} K_{s0}°$	$= -44.4 \pm 1.0$	P

[1]The uncertainties represent 95 % confidence limits of the regression intercept ($\log_{10} K°$) and of the slope ($-\Delta\varepsilon$).
[2]Medium: 0.10 mol kg^{-1} NaClO$_4$.

3. Pb^{II} SOLUTION CHEMISTRY

In aqueous solution, lead occurs in two oxidation states: Pb^{II}, the dominant form under most conditions, and Pb^{IV}. Diagrams of pH-potential boundaries indicate that Pb^{IV} is stable in aqueous solution only as the mixed Pb^{II}/Pb^{IV} oxide mineral minium, Pb_3O_4(s), and as plattnerite, PbO_2(s); these exist to appreciable extents only over narrow pH domains in strongly alkaline solutions [2001BRO]. Analogous to Cu^{2+}, but in contrast to Hg^{2+} [2005PBa], the onset of the Pb^{2+} hydrolysis reactions occurs at about pH 5 in dilute ($< 1 \times 10^{-3}$ mol dm^{-3}) solution. At total (subscript $_T$) Pb^{II} concentrations $[Pb^{II}]_T < 5 \times 10^{-6}$ mol dm^{-3} ($<$1 mg dm^{-3}), the dominant hydrolysis species that form in aqueous solution are monomeric $PbOH^+$, $Pb(OH)_2$(aq), and $Pb(OH)_3^-$. Higher-order monomeric species $Pb(OH)_4^{2-}$ and $Pb(OH)_6^{4-}$ have been postulated at pH > 13 [89FSb] but remain controversial [2001PHa].

At $[Pb^{II}]_T > 5 \times 10^{-6}$ mol dm^{-3} ($>$1 mg dm^{-3}, a condition atypical of environmental systems) a number of polymeric species form. With increasing $[Pb^{II}]_T$, the dominant species are $Pb_3(OH)_4^{2+}$ (at 50×10^{-6} mol dm^{-3}), $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$ (at 1×10^{-3} mol dm^{-3}). At very high Pb^{II} concentrations ($>$0.5 mol dm^{-3}), $Pb_2(OH)^{3+}$ is reported [80SBa]. Note that none of these species will play a significant role at the submicromol/dm^3 concentrations of Pb^{II} typical of environmental fresh and saline waters. Other species such as $Pb_3(OH)_3^{3+}$ [80KIa] and $Pb_3(OH)_5^+$ [80SBa, 93CWa] have been postulated under various conditions but lack supporting evidence.

Heterogeneous solubility equilibria are unlikely to have a significant impact on the chemical speciation of Pb^{II}, except possibly in heavily polluted natural water systems (which are not under consideration in this document). Low $[Pb^{2+}]$ values may arise from other "mixed ligand" compounds, but none of these phases (and corresponding solubility) has been sufficiently well characterized, especially under typical environmental conditions, to justify their consideration in the present speciation calculations. Where relevant, they are mentioned in the appropriate parts of Section 7.

4. DATA SELECTION AND EVALUATION

The data that meet our selection criteria for use in the SIT regression analyses are recorded in Tables A2-1 through A2-16 in Appendix 2. The criteria used for the acceptance of literature data as reliable (designated "reported" in these Tables, and included in the regression analysis) and those for the rejection of data (indicated by a reference superscript in the Table footnotes) are summarized in Appendix 1A. The values for $\log_{10} K_n$ (reported) are given on the molality (mol kg^{-1}) or amount concentration (mol dm^{-3}) scales, as published. In most cases, the uncertainties assigned to $\log_{10} K_n$ (reported) by the original authors reflect analytical and numerical precision but not systematic errors. Some $\log_{10} K_n$ (reported) values have much stronger experimental bases than others, being derived from a large amount of experimental data and/or from more than one experimental method. In determining the value of $\log_{10} K_n$ (accepted) for inclusion in the regression analysis, we therefore assign an addi-

tional uncertainty to each value of $\log_{10} K_n$ (reported) that reflects our estimation of accuracy and reliability of the experimental methods, according to [92GRE, Appendix C], and consistent with a 95 % confidence limit. The $\log_{10} K_n$ (accepted) values are listed in the Tables on the molality scale (to facilitate SIT analysis); our assigned uncertainty is used to weight each constant in the SIT regression analysis [2005PBa].

The abbreviations used in these Tables to describe the experimental methods are: **emf**: measurement of galvanic cell potentials (emf) using a redox electrode; **sol**: solubility determination; **gl**: pH measurement by glass electrode; **con**: conductivity; **ise**: measurement of cell potentials using an ion-selective electrode; **cal**: calorimetry; **vlt**: voltammetry; **pol**: polarography; **sp**: (UV–vis) spectrometry.

5. METHODS FOR NUMERICAL EXTRAPOLATION OF DATA TO I_m = 0 mol kg^{-1}

To obtain the most reliable values for $\beta_{p,q,r}°$, the accepted data for a wide range of ionic strengths were extrapolated to I_m = 0 mol kg^{-1} by application of the Brønsted–Guggenheim–Scatchard SIT model. This model accounts for the ionic strength-dependent short-range, weak, non-electrostatic interactions that occur between the reactant species and the electrolyte anions or cations.

For the general reaction (omitting charges except for that of H$^+$)

$$p\text{M} + q\text{L} + r\text{H}_2\text{O} \rightleftharpoons \text{M}_p\text{L}_q(\text{OH})_r + r\text{H}^+$$
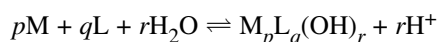
the formation constant $\beta_{p,q,r}$ determined in an ionic medium (typically containing a noncomplexing 1:1 electrolyte NX of ionic strength I_m at concentrations well in excess of the interacting ionic species) is related to the corresponding value at zero ionic strength, $\beta_{p,q,r}°$, by

$$\log_{10} \beta_{p,q,r} = \log_{10} \beta_{p,q,r}° + p\log_{10} \gamma_m(\text{M}) + q\log_{10} \gamma_m(\text{L}) + r\log_{10} a(\text{H}_2\text{O}) - \log_{10} \gamma_m(p,q,r) - r\log_{10} \gamma_m(\text{H}^+) \tag{1}$$

where $\gamma_m(p,q,r)$ and $\gamma_m(i)$ refer respectively to the activity coefficient on the molality scale for the species $\text{M}_p\text{L}_q(\text{OH})_r$ and for the interacting species i. According to the SIT, the latter is given [97GRE] by

$$\log_{10} \gamma_m(i) = -z_i^2 A \sqrt{I_m} (1 + a_j B \sqrt{I_m})^{-1} + \Sigma_k \, \varepsilon(i,k) \, m_k = -z_i^2 D + \Sigma_k \, \varepsilon(i,k) \, m_k \tag{2}$$

where $k = \text{N}^+$ or X^- and $\varepsilon(i,k)$ is the aqueous species interaction (SIT) coefficient for short-range interactions between ions i and k.

Substitution of (2) into (1), and for conditions such that $I_m \approx m_k$, gives

$$\log_{10} \beta_{p,q,r} - \Delta z^2 D - r\log_{10} a(\text{H}_2\text{O}) = \log_{10} \beta_{p,q,r}° - \Delta\varepsilon I_m \tag{3}$$

where $\Delta z^2 = (pz_\text{M} + qz_\text{L} - r)^2 + r - p(z_\text{M})^2 - q(z_\text{L})^2$ and $\Delta\varepsilon = \varepsilon$ (complex, N^+ or X^-) + $r\varepsilon$ (H^+,X^-) – $p\varepsilon$ (M^{n+},X^-) – $q\varepsilon$ (L^{m-},N^+) is the reaction-specific ion interaction coefficient.

Wherever possible in this review, to maintain thermodynamic consistency among the various constants, the term $a_j B$ is set at 1.5 kg$^{1/2}$ mol$^{-1/2}$, the value found by Scatchard to minimize the ionic strength dependence of derived $\varepsilon(i,k)$ values [76SCA]. For a 1:1 electrolyte, the term $\log_{10} a(\text{H}_2\text{O})$ can be calculated from the solution osmotic coefficient, Φ_m [59ROB]. For NaClO$_4$ media, the relationship $\log_{10} a(\text{H}_2\text{O}) = -(0.01484 \pm 0.00018) (I_m/\text{mol kg}^{-1})$ pertains at 25 °C and $0 \leq I_m/\text{mol kg}^{-1} \leq 3.5$ where the uncertainty pertains to the 95 % confidence limits; it is noted that this relationship is a correction from that reported in [2005PBa, 2007PBa].

The application of SIT to the accepted literature values (Tables A2-1 to A2-14) involves extrapolation of $\log_{10} \beta_{p,q,r} - \Delta z^2 D - r\log_{10} a(\text{H}_2\text{O})$ to m_k (or I_m) = 0 mol kg^{-1} for a system with a large excess of 1:1 electrolyte, using eq. 3. In the SIT regression analyses, the weighting of each datum point was $1/u^2$ where u is the assigned uncertainty for each value (Tables A2-1 to A2-14). The regression analyses (shown in Appendix 3) yield $\log_{10} \beta_{p,q,r}°$ ($\log_{10} K_n°$) as the intercept at I_m = 0 mol kg^{-1} and the reaction-specific ion interaction coefficient, $-\Delta\varepsilon(i,k)$, as the slope. The uncertainties reported for

$\log_{10} \beta_{p,q,r}°$ ($\log_{10} K_n°$) and $\Delta\varepsilon$ represent 95 % confidence limits of the regression intercept and slope, respectively. Where appropriate, an initial SIT analysis was used to identify (and reject) outliers based on their deviation from the calculated confidence limits. The data used in the regression analyses to obtain values for $\log_{10} \beta_{p,q,r}°$ ($\log_{10} K_n°$) are for perchlorate media [predominantly $NaClO_4$ but also for $LiClO_4$ and $(Li,Na,Mg,Ba)ClO_4$], except for Pb_2OH for which accepted values are available only in nitrate media. For $PbOH^+$ and $Pb_4(OH)_4^{4+}$, there are also a significant number of values for nitrate media, and for $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$, there are two values that meet our selection criteria. SIT analyses for nitrate media are discussed separately in Section 6.1.4.

6. EVALUATION OF EQUILIBRIUM CONSTANTS (HOMOGENEOUS REACTIONS)

6.1 The Pb^{2+} + OH^- system

Speciation diagrams for the Pb^{2+}+ OH^- system, based on our Recommended values recorded in Table 1 for stability constants at $I_m = 0$ mol kg^{-1}, are shown in Figs. 1a and 1b for $[Pb^{II}]_T = 4.8 \times 10^{-4}$ mol dm^{-3}
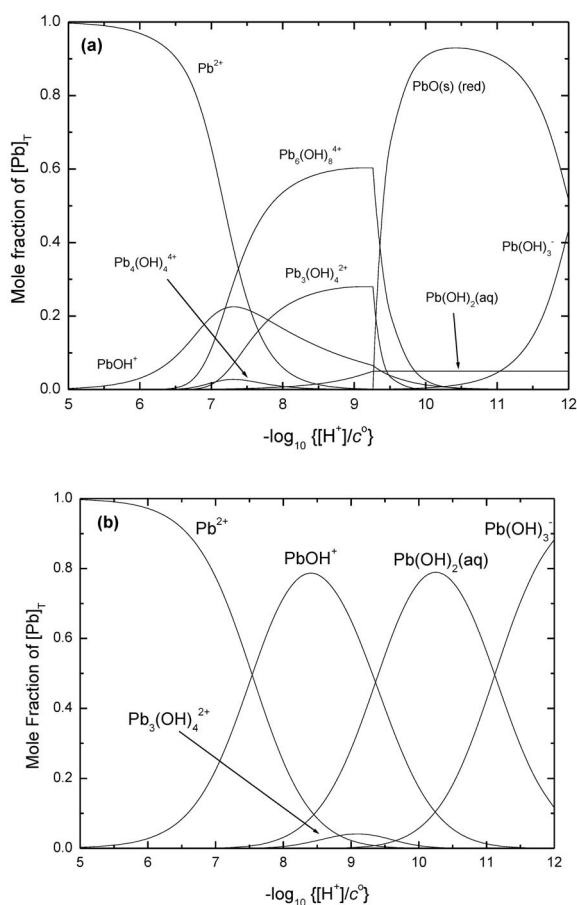
Fig. 1 Speciation diagram for the binary Pb^{2+} + hydroxide system as obtained from the Recommended stability constants at $I_m = 0$ mol kg^{-1} (Table 1). Results outside the $-\log_{10} \{[H^+]/c°\}$ range of 2–12 should be viewed with caution as activity coefficients deviate from 1.0. (No corrections were made for ionic strength-dependent changes in formation constants at high pH.) (a) $[Pb^{II}]_T = 4.8 \times 10^{-4}$ mol dm^{-3} (100 mg Pb dm^{-3}); (b) $[Pb^{II}]_T = 4.8 \times 10^{-6}$ mol dm^{-3} (1 mg Pb dm^{-3}).

(100 mg Pb dm^{-3}) and $[Pb^{II}]_T = 4.8 \times 10^{-6}$ mol dm^{-3} ($[Pb^{II}]_T = 1$ mg dm^{-3}), respectively. Results outside the range $2 \leq -\log_{10}\{[H^+]/c^\circ\} \leq 12$ should be viewed with caution as activity coefficients may deviate significantly from 1.0. The *SC-Database* [2009PET] reports results from 62 investigations for the hydrolysis of Pb^{2+}.

6.1.1 Formation of PbOH$^+$

Formation of the first monomeric hydrolysis species can be described by eq. 4

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \tag{4}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction interaction coefficient, $\Delta\varepsilon(4)$, were for perchlorate media at 25 °C and are listed in Table A2-1, along with references and our assigned uncertainties. The weighted regression of these data (Fig. A3-1) used the expression

$$\log_{10} {}^*K_1 + 2D - \log_{10} a(H_2O) = \log_{10} {}^*K_1^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 4 ($\Delta z^2 = -2$). The regression yields the Recommended value

$$\log_{10} {}^*K_1^\circ(\text{eq. 4, 298.15 K}) = -7.46 \pm 0.06$$

The value for $\Delta\varepsilon(4)$ in NaClO$_4$ medium is $-(0.06 \pm 0.04)$ kg mol^{-1}.

6.1.2 Formation of Pb(OH)$_n^{(2-n)+}$, n = 2, 3, 4

Pb(OH)$_2$(aq)
The formation of Pb(OH)$_2$(aq) can be described by reaction 5

$$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2(aq) + 2H^+ \tag{5}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(5)$, are listed in Table A2-2, along with references and our assigned uncertainties. The selected values for perchlorate media at 25 °C make a rather limited data set. The weighted regression (Fig. A3-2) used the expression

$$\log_{10} {}^*\beta_2 + 2D - 2\log_{10} a(H_2O) = \log_{10} {}^*\beta_2^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 5 ($\Delta z^2 = -2$). The regression yields the Recommended value

$$\log_{10} {}^*\beta_2^\circ(\text{eq. 5, 298.15 K}) = -16.94 \pm 0.09$$

The calculated value for $\Delta\varepsilon(5)$ in NaClO$_4$ medium is $-(0.13 \pm 0.04)$ kg mol^{-1}.

Pb(OH)$_3^-$, Pb(OH)$_4^{2-}$, and Pb(OH)$_6^{4-}$
The formation of Pb(OH)$_3^-$ is most frequently reported in the literature in terms of reaction 6

$$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^- \tag{6}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(6)$, are listed in Table A2-3, along with references and our assigned uncertainties. The weighted regression (Fig. A3-3), using the selected values for NaClO$_4$ media at 25 °C and the expression

$$\log_{10} \beta_3 + 6D = \log_{10} \beta_3^\circ - \Delta\varepsilon I_m$$

indicates good consistency among the accepted data and gave the Recommended value

$$\log_{10} \beta_3^\circ(\text{eq. 6, 298.15 K}) = 13.97 \pm 0.06$$

The calculated value for the reaction ion interaction coefficient is $\Delta\varepsilon(6) = -(0.28 \pm 0.02)$ kg mol^{-1}.

The formation of $Pb(OH)_3^-$ can also be defined by reaction 7

$$Pb^{2+} + 3H_2O \rightleftharpoons Pb(OH)_3^- + 3H^+ \tag{7}$$

for which we derive the Recommended value

$$\log_{10} *\beta_3°(\text{eq. 7, 298.15 K}) = -(28.03 \pm 0.06)$$

and the reaction ion interaction coefficient $\Delta\varepsilon(7) = 0.26 \pm 0.05$ kg mol^{-1} in $NaClO_4$ media.

Stability constant data have been reported by [89FSb] for the formation of the species $Pb(OH)_4^{2-}$ ($\log_{10} \beta_4 = 13.26 \pm 0.06$, $I_m = 5.0$ mol kg^{-1}) and $Pb(OH)_6^{4-}$ ($\log_{10} \beta_6 = 12.18 \pm 0.06$, $I_m = 5.0$ mol kg^{-1}) at pH > 13. Perera and Hefter [2001PHa] noted the experimental and theoretical difficulties associated with these measurements at high pH in a cell without liquid junction, and also noted that there is no spectroscopic or polarographic evidence for the existence of $Pb(OH)_6^{4-}$. Thus, these stability constant values are considered as doubtful, and the formation of $Pb(OH)_6^{2-}$ extremely doubtful.

Perera et al. [2001PH] studied the hydrolysis equilibria of Pb^{2+} by the spectrophotometric method at 25 °C, using total lead concentrations under 10 µmol dm^{-3} in 1 and 5 mol dm^{-3} $NaClO_4$. At these low lead concentrations they found evidence for the monomeric species $PbOH^+$ to $Pb(OH)_4^{2-}$ but no evidence for polymeric species (Section 6.1.3). Unfortunately, their stability constants disagree with the values accepted in Tables A2-1 to A2-3, differing by about 0.6 log units per hydroxide ion in each respective species, and thus have not been included in the present review.

6.1.3 Formation of $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$

The formation of polymeric hydrolysis products in perchlorate media has been extensively studied by Olin et al. using very careful potentiometric [60OLb, 60OLc, 62POa], calorimetric [62COa], and X-ray diffraction studies [68JOH]. Their work indicated very small differences in the magnitude of the respective Pb^{II} hydrolysis constants in 3 mol dm^{-3} $NaClO_4$ [60OLb, 60OLc, 62POa] and 1.5 mol dm^{-3} magnesium or barium perchlorate media [62POa] (all 3 mol dm^{-3} in perchlorate). In each system, before the onset of precipitation, the hydrolysis reactions involve the formation of cationic or neutral species only. Therefore, within the confines of SIT, the interaction coefficients will involve only the cationic lead hydrolysis species and the medium anion (in this case, perchlorate).

X-ray diffraction [68JOH] studies confirm the existence of the species $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ in aqueous solution. The analysis indicates a tetrahedral core of lead atoms in $Pb_4(OH)_4^{4+}$, with each hydroxide ion bound to three lead atoms. The same core occurs in $Pb_6(OH)_8^{4+}$, with the two additional lead atoms bound to adjacent faces of the tetrahedron, each forming a tetragonal pyramid with three lead atoms of the core. This interpretation is supported by the solid-state analysis of lead perchlorate compounds [72OLI].

More recently, Japanese workers have studied the formation of polymeric Pb^{II} hydrolysis products [80KIa, 81KOa, 2000KAa]. The first two studies utilized 3 mol dm^{-3} $LiClO_4$ as the ionic medium, whereas the latter used 0.1 mol dm^{-3} $NaClO_4$. The resultant $\log_{10} *\beta_{p,r}$ values are in good agreement with those reported by Olin et al. However, [80KIa] also postulated the formation of $Pb_3(OH)_3^{3+}$; this species has not been reported in any other study and, as such, its formation is considered doubtful. Kogure et al. [81KOa] examined the hydrolysis reactions at relatively high Pb^{II} concentrations in both water and deuterated water and found that the same polymeric species occur in both media.

$Pb_3(OH)_4^{2+}$
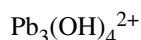
Formation of the trimeric hydrolysis species can be described by reaction 8

$$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+ \tag{8}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(8)$, refer to perchlorate media ($NaClO_4$ and $LiClO_4$) at 25 °C and

are listed in Table A2-4, along with references and our assigned uncertainties. A weighted regression for these data (Fig. A3-4) used the expression

$$\log_{10} {}^*\beta_{3,4} + 4D - 4 \log_{10} a(H_2O) = \log_{10} {}^*\beta_{3,4}{}^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 8 ($\Delta z^2 = -4$). The intercept yields the Recommended value

$$\log_{10} {}^*\beta_{3,4}{}^\circ(\text{eq. 8, 298.15 K}) = -23.01 \pm 0.07$$

Figure A3-4 indicates reasonable consistency among the stability constants measured in sodium and lithium perchlorate solutions. The value for $\Delta\varepsilon(8)$ in perchlorate media is $-(0.39 \pm 0.03)$ kg mol^{-1}.

Figure 1b illustrates that the maximum concentration of the polymeric species $Pb_3(OH)_4{}^{2+}$ accounts for less than 5 % of total lead at 10 μmol dm^{-3} and $I = 0$ mol kg^{-1}. However, the percentage of total lead present as this species varies with ionic strength and is ca. 22 % at $I_c = 1.0$ mol dm^{-3} and $[Pb^{II}]_T = 10$ μmol dm^{-3}.

$Pb_4(OH)_4{}^{4+}$
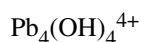
Formation of the tetrameric hydrolysis species can be described by reaction 9

$$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4{}^{4+} + 4H^+ \tag{9}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(9)$, refer to perchlorate media [NaClO$_4$, LiClO$_4$, and (Mg,Ca)(ClO$_4$)$_2$] at 25 °C and are listed in Table A2-4, along with references and our assigned uncertainties. A weighted regression for these data (Fig. A3-5) used the expression

$$\log_{10} {}^*\beta_{4,4} - 4D - 4 \log_{10} a(H_2O) = \log_{10} {}^*\beta_{4,4}{}^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 9 ($\Delta z^2 = 4$). The intercept yields the Recommended value

$$\log_{10} {}^*\beta_{4,4}{}^\circ(\text{eq. 9, 298.15 K}) = -20.57 \pm 0.06$$

As shown in Table A2-4, the effect of the medium cation (Na$^+$, Li$^+$, Mg^{2+}, or Ba^{2+}) on the magnitude of this stability constant in perchlorate media is minimal; this is not surprising given that all ions in reaction 9 are cations which, according to SIT, should have no effect on the equilibrium constant. The value derived for $\Delta\varepsilon(9)$ in perchlorate media is $-(0.19 \pm 0.02)$ kg mol^{-1}.

For the formation of $Pb_4(OH)_4{}^{4+}$, a significant number of data in nitrate media also meet our criteria for selection; these data are discussed in Section 6.1.4.

$Pb_6(OH)_8{}^{2+}$
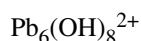
Formation of the hexameric hydrolysis species is described by reaction 10

$$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8{}^{4+} + 8H^+ \tag{10}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(10)$, refer to perchlorate media (NaClO$_4$ and LiClO$_4$) at 25 °C and are listed in Table A2-4, along with references and our assigned uncertainties. A weighted regression for these data (Fig. A3-6) used the expression

$$\log_{10} {}^*\beta_{6,8} - 8 \log_{10} a(H_2O) = \log_{10} {}^*\beta_{6,8}{}^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 10 ($\Delta z^2 = 0$). The regression intercept yields the Recommended value

$$\log_{10} {}^*\beta_{6,8}{}^\circ(\text{eq. 10, 298.15 K}) = -42.89 \pm 0.07$$

The value derived for $\Delta\varepsilon(10)$ in perchlorate media is $-(0.41 \pm 0.03)$ kg mol^{-1}.

6.1.4 Formation in nitrate media

Pb_2OH^{3+}

Formation of the dimeric hydrolysis species is described by reaction 11

$$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+ \tag{11}$$

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient, $\Delta\varepsilon(11)$, are listed in Table A2-4, along with references and our assigned uncertainties. The selected data refer only to nitrate media at 25 °C. The weighted regression (Fig. A3-7) for the selected values used the expression
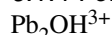
$$\log_{10} {}^*\beta_{2,1} - 2D - \log_{10} a(H_2O) = \log_{10} {}^*\beta_{2,1}{}^\circ - \Delta\varepsilon I_m$$

derived from eqs. 3 and 11 ($\Delta z^2 = 2$). The regression yields the Provisional value:

$$\log_{10} {}^*\beta_{2,1}{}^\circ(\text{eq. 11, 298.15 K}) = -7.28 \pm 0.09$$

The value derived for $\Delta\varepsilon(11)$ in nitrate media is (0.11 ± 0.10) kg mol^{-1}. This species only forms to a relatively small percentage at elevated Pb^{II} concentrations and is unlikely to be an important species in the environment.

$PbOH^+$

A weighted regression analysis based on the data for $(Na,K,Pb)NO_3$ media at 25 °C (Table A2-4) yielded a stability constant at zero ionic strength $\log_{10} {}^*K_1{}^\circ(\text{eq. 4, 298.15 K}) = -7.61 \pm 0.04$. This value contrasts with that derived from data for perchlorate media ($\log_{10} {}^*K_1{}^\circ = -7.46 \pm 0.06$). The data published for nitrate media were not corrected for nitrate complexation, although this should not impact significantly on the stability constant calculated for zero ionic strength, as the term for the effect of nitrate complexation tends to unity as $I_m \to 0$ (eq. B-7, Appendix 1B). The derived reaction ion interaction coefficient, $\Delta\varepsilon(4) = (0.50 \pm 0.07)$ kg mol^{-1} can be used to interpolate apparent stability constants applicable in nitrate media, but cannot be used to calculate individual species interaction coefficients in nitrate media because the contributing $\log_{10} {}^*K_1$ values have not been corrected for nitrate complexation.

 The discrepancies between the stability constants obtained at zero ionic strength from values in nitrate media and perchlorate media, for both this species and $Pb_4(OH)_4{}^{4+}$ (below), may be due to the large number of nitrate media data that are derived from use of the self-medium method. Comparison of these data with those obtained in either $NaNO_3$ or KNO_3 alone show statistical differences, with those obtained using the self-medium method being more negative when differences in ionic strength have been considered. These differences are consistent with the more negative stability constants obtained at zero ionic strength for both $PbOH^+$ and $Pb_4(OH)_4{}^{4+}$.
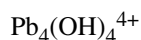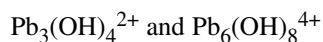
$Pb_4(OH)_4{}^{4+}$

A weighted regression analysis based on the data for $(Na,K,Pb)NO_3$ media at 25 °C (Table A2-4) yielded a stability constant at zero ionic strength $\log_{10} {}^*\beta_{4,4}{}^\circ(\text{eq. 9, 298.15 K}) = -20.79 \pm 0.04$. This value also contrasts with that derived from data for perchlorate media ($\log_{10} {}^*\beta_{4,4}{}^\circ = -20.57 \pm 0.06$). The value derived for $\Delta\varepsilon(9)$ in nitrate media is (0.90 ± 0.07) kg mol^{-1}.

$Pb_3(OH)_4{}^{2+}$ and $Pb_6(OH)_8{}^{4+}$

For $Pb_3(OH)_4{}^{2+}$, two values published for KNO_3 media at 25 °C meet our selection criteria. The values are $\log_{10} {}^*\beta_{3,4} = -23.91 \pm 0.02$ ($I_m = 0.101$ mol kg^{-1} [80SBa]) and $\log_{10} {}^*\beta_{3,4} = -24.3 \pm 0.02$ ($I_m = 1.045$ mol kg^{-1} [90CWa]). Similarly, for $Pb_6(OH)_8{}^{4+}$ two values published for KNO_3 media at 25 °C meet our selection criteria, viz. $\log_{10} {}^*\beta_{6,8} = -43.38 \pm 0.01$ ($I_m = 0.101$ mol kg^{-1} [80SBa]) and $\log_{10} {}^*\beta_{6,8} = -44.91$ ($I_m = 1.045$ mol kg^{-1} [90CWa]). In neither case is there sufficient data for a SIT regression analysis.

6.2 The Pb^{2+} + Cl$^-$ system

Pb^{II} appears to form up to four consecutive chlorido- complexes in aqueous solution, reactions 12–15

$$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+ \tag{12}$$

$$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(aq) \tag{13}$$

$$Pb^{2+} + 3Cl^- \rightleftharpoons PbCl_3^- \tag{14}$$

$$Pb^{2+} + 4Cl^- \rightleftharpoons PbCl_4^{2-} \tag{15}$$

These reactions have been widely studied, there being 112 entries in the *SC-Database* [2009PET]. Analogous to the Cu^{2+} + Cl$^-$ system, the complexes are all weak and are best studied in media of high [Cl$^-$]$_T$, high [Cl$^-$]$_T$: [Pb^{II}]$_T$ ratios, and high ionic strength. The stability constants have been investigated by voltammetry (vlt), ion-selective electrode (ise) and other types of potentiometry, and by UV–vis spectrometric measurements (sp). No polynuclear complexes have been reported in aqueous solution. The Recommended values for the stability constants at $I_m = 0$ mol kg^{-1} are given in Table 2.

6.2.1 Formation of PbCl$^+$

A substantial number of equilibrium constant values have been reported for the formation of PbCl$^+$, for different media (NaClO$_4$, LiClO$_4$, HClO$_4$, NaCl), ionic strengths and temperatures. Data selected for the SIT analysis, to determine the standard stability constant at zero ionic strength for reaction 12 and the reaction ion interaction coefficient $\Delta\varepsilon$, are listed in Table A2-5, along with our assigned uncertainties according to our estimate of the overall precision of the data. For this evaluation the selected data all refer to NaClO$_4$ media and 25 °C, but no significant differences can be observed for data determined in other perchlorate media.

The weighted linear regression (Fig. A3-8), which indicates reasonable consistency between the values, leads to the Recommended standard constant

$$\log_{10} K_1°(\text{eq. 12, 298.15 K}) = 1.50 \pm 0.03$$

The reaction ion interaction coefficient based on this regression is $\Delta\varepsilon(12) = -(0.14 \pm 0.01)$ kg mol^{-1}. The Recommended value of $\log_{10} K_1°$ is in good agreement with those of [2007LUO] [1.45 ± 0.02; from measurements in NaClO$_4$ ($I_m = 0.38$ to 5.89 mol kg^{-1}) and NaCl ($I_m = 0.08$ to 0.32 mol kg^{-1})], [84MBc] (1.48 ± 0.05; based on measurements of [84BMb] in NaCl/NaClO$_4$, $I_m = 0.38$ to 5.89 mol kg^{-1}) and [84SEa] (1.41 ± 0.05; from measurements in NaCl, $I_m = 0.001$ to 3.22 mol kg^{-1}).

Results from several studies in NaClO$_4$ at 25 °C were rejected, as indicated in the footnote to Table A2-5 with annotations on each reference. In the case of [73VIa], the $\log_{10} K_1$ values are given as a function of [Cl$^-$]$_T$; [74MId] reported constants calculated using a mathematical model, rather than based on experimental determinations; in [76FSa, 87KSd] the quality of the data could not be judged, because an English translation was not available; the values of [66VSa] were later corrected for liquid junction potentials and reported by [71VIa].

6.2.2 Formation of PbCl$_2$(aq)

Data selected for the SIT analysis, to determine the stability constant at zero ionic strength and the reaction ion interaction coefficient $\Delta\varepsilon(13)$, are listed in Table A2-6, along with our assigned uncertainties. The selected data all refer to NaClO$_4$ media and 25 °C. The uncertainties assigned to $\log_{10} \beta_2$ in this review are slightly larger than those assigned to $\log_{10} K_1$ to reflect the weakness of the 1:2 complex. The weighted linear regression (Fig. A3-9) indicates reasonable consistency between the values and yields the Recommended standard constant

$$\log_{10} \beta_2°(\text{eq. 13, 298.15 K}) = 2.10 \pm 0.05$$

The reaction ion interaction coefficient $\Delta\varepsilon(13) = -(0.26 \pm 0.02)$ kg mol^{-1} for NaClO$_4$ media. The Recommended value of log$_{10}$ $\beta_2°$ is in reasonable agreement with those of [2007LUO] (1.98 ± 0.06), [84MBc] (2.03 ± 0.05; from the measurements of [84BMb]), and [84SEa] (1.97 ± 0.04), all based on measurements in NaClO$_4$, NaCl/NaClO$_4$, or NaCl media, as indicated above (Section 6.2.1).

6.2.3 Formation of PbCl$_3^-$ and PbCl$_4^{2-}$

The stability constant for PbCl$_3^-$ (and PbCl$_4^{2-}$) in aqueous solution can be determined only at high chloride concentrations, and therefore at high ionic strengths. Some studies reported a stepwise stability constant for the 1:3 complex larger than that for the 1:2 complex [55KIa, 57KLa, 73BHb, 90HEa] mainly because they did not include the 1:4 complex in the speciation model. In contrast, other studies reported the common sequence of decreasing values for the stepwise stability constants from log$_{10}$ K_1 to log$_{10}$ K_4 [63MKc, 71VIa, 82BMc, 88FSb] in which cases they did include the 1:4 complex (but see below). Because of their consistency (Table A2-7), the log$_{10}$ β_3 values from all of these studies were included in the linear regression to evaluate log$_{10}$ $\beta_3°$ (Fig. A3-10). The uncertainties assigned to the constants (Table A2-7) are slightly larger than those for the 1:2 complex due to the weakness of the 1:3 complex and the possible formation of PbCl$_4^{2-}$.

The weighted linear regression of the selected values for log$_{10}$ β_3 (Fig. A3-10) yields the Recommended standard constant

$$\log_{10} \beta_3°(\text{eq. 14, 298.15 K}) = 2.00 \pm 0.10$$

and the reaction ion interaction coefficient $\Delta\varepsilon(14) = -(0.32 \pm 0.03)$ kg mol^{-1}. This Recommended value is in reasonable agreement with those of [2007LUO] (1.83 ± 0.03), [84MBc] (2.03 ± 0.05; from measurements of [84BMb]), and [84SEa] (1.66 ± 0.08), all based on measurements in NaClO$_4$, NaCl/NaClO$_4$, or NaCl media, as cited above (Section 6.2.1).

On the basis of UV-spectrometric and emf measurements [63MKc, 71VIa, 88FSb] there is some evidence for the existence of PbCl$_4^{2-}$ in NaClO$_4$ media (eq. 15), but the reported stability constants for its formation are limited in number, differ in magnitude, and mostly refer to very high ionic strengths (3.5 and 5.0 mol kg^{-1}) [63MKc, 71VIa, 88FSb]. Therefore, a meaningful regression analysis is not possible and we cannot recommend a formation constant for PbCl$_4^{2-}$ in NaClO$_4$ media. Detailed UV-spectrometric analysis of the Pb^{2+}+ Cl$^-$ system in NaCl media ([Cl$^-$]$_T$ = 0.001 to 3.22 mol kg^{-1}) and at temperatures from 25 to 300 °C [84SEa] suggested the existence of PbCl$_4^{2-}$ between 25 and 150 °C at high [Cl$^-$]$_T$, but the value reported, log$_{10}$ $\beta_4°$(eq. 15, 298.15 K) = 1.46 ± 0.05, was considered only a rough estimate by the author. In contrast, (a) [2007LUO] found no evidence (spectrometric measurements; 15–45 °C) for the formation of PbCl$_4^{2-}$ in NaCl/NaClO$_4$ mixtures within the ionic strength interval 0–6 mol kg^{-1} and [Cl$^-$]$_T$ = 0.001–1.99 mol kg^{-1}, and (b) [90HEa] could not detect PbCl$_4^{2-}$ in NaCl/NaClO$_4$ mixtures using Pb(Hg) potentiometry even at [Cl$^-$]/[Pb^{2+}] ratios up to 70 000. These conflicting results imply that at present not even an indicative value for the formation of PbCl$_4^{2-}$ is possible; further high-quality measurements are needed to resolve this uncertainty.

6.3 The Pb^{2+} + CO$_3^{2-}$ system

Figure 2 shows a speciation diagram for the Pb^{2+} + H$^+$ + CO$_3^{2-}$ system, based on the stability constants recorded in Tables 1 and 3. The calculations, which assume I_m = 0 mol kg^{-1}, t = 25 °C, and f(CO$_2$) = 10$^{-3.5}$ bar (1 bar = 10^5 Pa), indicate a similar result to that for Cu^{II} [2007PBa], namely, that carbonato-complexes dominate over hydroxo- complexes for a wide range of solution conditions unless f(CO$_2$) is significantly lower than atmospheric levels. This contrasts with the situation for Hg^{II} where hydroxo-complexes dominate up to pH 10.5 [2005PBa]. Figure 2 shows that for f(CO$_2$) = 10$^{-3.5}$ bar, PbCO$_3$(aq) is the dominant species of Pb^{II} in weakly alkaline solutions (7.6 < $-$log$_{10}$ {[H$^+$]/$c°$} < 8.9). Pb(CO$_3$)$_2^{2-}$ becomes dominant above $-$log$_{10}$ {[H$^+$]/$c°$} = 8.9. The maximum concentration of PbCO$_3$(aq) corresponds to 74 % of [Pb^{II}]$_T$ at $-$log$_{10}$ {[H$^+$]/$c°$} = 8.35 for the specified conditions; for Cu^{II} the analo-
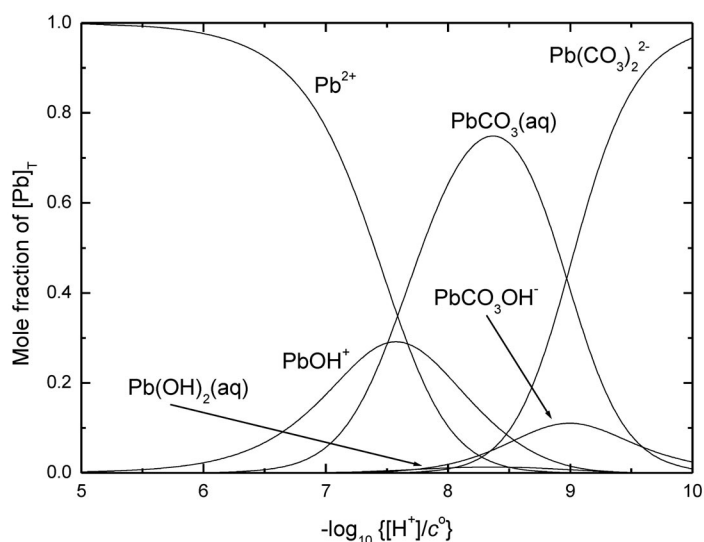
Fig. 2 Speciation diagram for the ternary Pb^{2+} + H^+ + carbonate system as obtained from the stability constants at I_m = 0 mol kg^{-1} (reported in Tables 1 and 3) and calculated for $[Pb]_T$ = 10^{-9} mol dm^{-3} and $f(CO_2)$ = $10^{-3.5}$ bar. The upper limit of $-\log_{10} \{[H^+]/c°\}$ is set at 10 to limit the equilibrium carbonate concentration determined by $f(CO_2)$.

gous values are 82 % and $-\log_{10} \{[H^+]/c°\}$ = 8.1. However, it should be noted that the calculations for Pb^{II} are based on somewhat poorly quantified stability constants (see below).

6.3.1 Formation of PbCO₃(aq)

An accurate estimate of the value for $\log_{10} K_1°$ for reaction 16

$$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3(aq) \tag{16}$$

is not possible on the basis of the available data, since each of the "accepted" values for $\log_{10} K_1$ (Table A2-8) is poorly defined. The formation constants of [82BSa] at I_m = 0.305 mol kg^{-1} were based on relatively few data and were regarded by the original authors as approximate. The values for $\log_{10} K_1$ reported by [80SVb] for I_m = 0.725 mol kg^{-1} are based on two sources of carbonate protonation constants. The "accepted" values of [80SVb] shown in Table A2-8 are an average of results obtained using total lead concentrations of 4 μM and 6 nM, and the carbonate protonation constants of [72DHa]. The rejected results of [80SVb], which are also summarized in [80SRa], were obtained by using the carbonate protonation constants of [74PHc], which are inconsistent with the selected protonation constants in a previous IUPAC report in this series [2005PBa]. The results of [82BSa] and [80SVb] do not form an adequate basis for extrapolation of $\log_{10} K_1$ to zero ionic strength. A SIT regression (not shown) leads to the following approximate values: $\log_{10} K_1°$(eq. 16, 298.15 K) = 6.45 ± 0.72 (I_m = 0 mol kg^{-1}) and $\Delta\varepsilon(16)$ = –(0.58 ± 1.19) kg mol^{-1}. For comparison, the corresponding values reported for $CuCO_3(aq)$ formation are $\log_{10} K_1°$ = 6.75 ± 0.03 and $\Delta\varepsilon$ = –(0.19 ± 0.04) kg mol^{-1} [2007PBa].

Comparisons of the stability constants for $PbCO_3(aq)$ and $CuCO_3(aq)$ measured under comparable conditions at finite I suggest that their $\log_{10} K_1°$ values should be similar. For example, the $\log_{10} K_1$ values at I_m = 0.725 mol kg^{-1} reported for lead and copper are 5.36 ± 0.04 [80SVb] and 5.36 ± 0.05 [85BMb], respectively. In 0.1 mol dm^{-3} KNO_3 medium, the $\log_{10} K_1$ values reported for lead by anodic stripping voltammetry (ASV) and differential pulse polarography (DPP) were 6.4 and 6.1, respectively, while the corresponding results obtained for copper were 6.0 and 6.1 [76BHa]. Again in 0.1 mol dm^{-3} KNO_3 medium, the reported $\log_{10} K_1$ results obtained by ASV and DPP were 6.3 and 6.2 for

PbCO$_3$(aq) and 6.1 and 5.7 for CuCO$_3$(aq) [75EAa]. The absence of corrections for complexation of Pb^{2+} and Cu^{2+} by NO$_3^-$ creates some ambiguity in both comparisons.

Although nitrate complex stability is low, nitrate binds Pb^{2+}(aq) more strongly than Cu^{2+}(aq) [2009PET]. Therefore, the above data [76BHa, 80SVb, 85BMb] suggest that $\log_{10} K_1$[PbCO$_3$(aq)] ≳ $\log_{10} K_1$[CuCO$_3$(aq)], viz. ≳ 6.75. The value of $\log_{10} K_1^\circ = 6.4_5 \pm 0.7$ is therefore considered by the present reviewers to be an underestimate (see Section 9.2), and is taken to be "Indicative" only.

6.3.2 Formation of Pb(CO$_3$)$_2^{2-}$

The accepted values for $\log_{10} \beta_2$, reaction 17

$$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-} \tag{17}$$

in NaClO$_4$ media are given in Table A2-8. A SIT regression (Fig. A3-11) yields the Provisional values $\log_{10} \beta_2^\circ = 10.13 \pm 0.24$ and $\Delta\varepsilon(17) = -(0.19 \pm 0.10)$ kg mol^{-1}. The $\log_{10} \beta_2^\circ$ value for Pb(CO$_3$)$_2^{2-}$ is similar to that Recommended [2007PBa] for Cu(CO$_3$)$_2^{2-}$ formation, $\log_{10} \beta_2^\circ = 10.3 \pm 0.1$.

Using the $\log_{10} K_1$ and $\log_{10} \beta_2$ results of [82BSa] and [80SVb] in Table A2-8, the equilibrium constant calculated for reaction 18

$$PbCO_3(aq) + CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-} \tag{18}$$

is $\log_{10} K_2 = 3.45$ (at $I_m = 0.305$ mol kg^{-1}) and 3.22 (at $I_m = 0.725$ mol kg^{-1}), respectively. Results obtained by [76BHa] for this reaction in 0.10 mol dm^{-3} KNO$_3$, a reaction which should be little influenced by nitrate complexation, are 3.4 by ASV and 3.0 by DPP, values which are broadly comparable. The $\log_{10} K_1^\circ$ and $\log_{10} \beta_2^\circ$ results obtained from regressions of the data in Table A2-8 provide the indicative value $\log_{10} K_2^\circ = 3.7 \pm 0.7$. To the extent that $\log_{10} K_1^\circ$ may be underestimated (Section 6.3.1), this result can be considered as an upper bound.

6.3.3 Formation of PbHCO$_3^+$

The stability constant obtained by [92NEa] for reaction 19 in 3.5 mol kg^{-1} NaClO$_4$ (Table A2-8)

$$Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons PbHCO_3^+ + H^+ \tag{19}$$

can be combined with data for the reaction H$^+$ + HCO$_3^-$ ⇌ CO$_2$(g) + H$_2$O ($\log_{10} K = 7.88$ at $I_m = 3.5$ mol kg^{-1} NaClO$_4$; [58FNa]) to calculate a Provisional value of $\log_{10} K(20) = 1.86 \pm 0.1$ for reaction 20 in $I_m = 3.5$ mol kg^{-1} NaClO$_4$

$$Pb^{2+} + HCO_3^- \rightleftharpoons PbHCO_3^+ \tag{20}$$

This value is similar to that reported at $I_m = 0$ for Cu^{2+} + HCO$_3^-$ ⇌ CuHCO$_3^+$: $\log_{10} K^\circ = 1.84 \pm 0.1$ [2007PBa]. It is also compatible with the formation constant for the 1:1 Pb^{II}–ethanoate complex [2009PET].

The value for $\log_{10} K(20)$ indicates that the formation of PbHCO$_3^+$ should be considered in any experimental examination of PbCO$_3$(aq) and Pb(CO$_3$)$_2^{2-}$ equilibria that is conducted at high concentrations of HCO$_3^-$. However, apart from [92NEa], formation of PbHCO$_3^+$ has been neglected in essentially all investigations of PbCO$_3$(aq) and Pb(CO$_3$)$_2^{2-}$ formation.

6.3.4 Formation of Pb(CO$_3$)OH$^-$ and Pb(CO$_3$)Cl$^-$

Evaluations of stability constants for ternary (mixed ligand) complexes are especially challenging because such species attain significant concentrations only in media of somewhat complicated composition.

The one reported stability constant for the formation of Pb(CO$_3$)OH$^-$, reaction 21

$$Pb^{2+} + CO_3^{2-} + OH^- \rightleftharpoons Pb(CO_3)OH^- \tag{21}$$

is $\log_{10} K(21) = 10.77 \pm 0.4$ ($I_m = 3.503$ mol kg^{-1}) [87FGb]. This value can be compared with that from a statistical prediction based on the value $\log_{10} \beta_2(17) = 8.77 \pm 0.20$ [87FGb], the Pb^{2+} hydrolysis con-

stant $\log_{10} {}^*\beta_2(5) = -17.09 \pm 0.1$ [60COa] and $\log_{10} K_w = -14.22$ [57ILa], all values being for $I_m = 3.503$ mol kg^{-1} NaClO$_4$. The calculated value is $\log_{10} K(21) = 10.35 \pm 0.3 = (0.3 + 0.5\{8.77 + 11.35\})$. Based on the values of $\log_{10} {}^*\beta_2°$ and $\log_{10} \beta_2°(17)$ (Tables 1 and 3), the statistically predicted value at $I_m = 0$ mol kg^{-1} is $\log_{10} K°(21) = 10.9 \pm 0.2$, which can be compared with the value for the analogous reaction of Cu^{II}, $\log_{10} K°(21) = 11.2 \pm 0.3$ [2007PBa]. Although Pb(CO$_3$)OH$^-$ is a minor species in saline waters (Section 9.2) it is important to have a reliable value for $\log_{10} K(21)$ at $I_m = 0.70$ mol dm^{-3} to calculate Pb^{II} speciation in such systems. To facilitate this, a value for $\Delta\varepsilon(21)$ has been calculated from the statistically predicted values for $\log_{10} K(21)$ at $I_m = 0$ and 3.50 mol kg^{-1}, $\Delta\varepsilon(21) = 0.18 \pm 0.04$ mol kg^{-1}.

There are no reported stability constants for Pb(CO$_3$)Cl$^-$. This species is expected to be an important component in saline waters in the pH range in which both PbCl$_2$(aq) and Pb(CO$_3$)$_2^{2-}$ are present in significant concentrations. Based on the values of $\log_{10} \beta_2°(13)$ and $\log_{10} \beta_2°(17)$ (Tables 2 and 3), the statistically derived value for reaction 22 at $I_m = 0$ mol kg^{-1} is $\log_{10} K°(22) = 6.41 \pm 0.25$.

$$Pb^{2+} + CO_3^{2-} + Cl^- \rightleftharpoons Pb(CO_3)Cl^- \tag{22}$$

From the regression analyses in Figs. A3-9 and A3-11, the statistically derived values for $\log_{10} K(22)$ are 5.21 ± 0.27 ($I_m = 1.05$ mol kg^{-1}) and 5.46 ± 0.33 ($I_m = 3.50$ mol kg^{-1}). From these values, we derive $\log_{10} K°(22) = 6.47 \pm 0.16$ and $\Delta\varepsilon(22) = -(0.29 \pm 0.08)$ mol kg^{-1}.

The formation of Pb(CO$_3$)Cl$^-$ can also be considered in terms of the isocoulombic equilibrium, 23.

$$PbCO_3(aq) + Cl^- \rightleftharpoons Pb(CO_3)Cl^- \tag{23}$$

Based on $\log_{10} K_1° = 6.45$ for the formation of PbCO$_3$(aq), we derive $\log_{10} K°(23) = 6.47 - 6.45 = -0.02$. The K values for reactions 22 and 23 both imply that Pb(CO$_3$)Cl$^-$ will be a significant species in seawater relative to PbCO$_3$(aq).

6.3.5 Formation of polynuclear carbonato species

The stability constants reported in Table A2-8 for formation of polynuclear species, reactions 24 and 25

$$2Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons Pb_2CO_3^{2+} + 2H^+ \tag{24}$$

$$3Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons Pb_3CO_3^{4+} + 2H^+ \tag{25}$$

indicate that these are unlikely to be important species in the natural environment. The results of [92NEa] for formation of Pb$_2$CO$_3^{2+}$, [87FGb] for formation of Pb(CO$_3$)$_2^{2-}$, and [58FNa] for the equilibrium between CO$_2$(g) and CO$_3^{2-}$, can be combined to show that the ratio [Pb$_2$CO$_3^{2+}$]/[Pb(CO$_3$)$_2^{2-}$] = $10^{-1.77}$ [Pb^{2+}]/[CO$_3^{2-}$]. Since the equilibrium constant ($10^{-1.77}$) describes an isocoulombic reaction, Pb$_2$CO$_3^{2+}$ + CO$_3^{2-}$ $\rightleftharpoons$ Pb(CO$_3$)$_2^{2-}$ + Pb^{2+}, the [Pb$_2$CO$_3^{2+}$]/[Pb(CO$_3$)$_2^{2-}$] concentration ratio should be very small over a wide range of reactant stoichiometries unless the [Pb^{2+}]/[CO$_3^{2-}$] concentration ratio is greater than one. Using the approximate upper-bound formation constant appropriate to the isocoulombic reaction, PbCO$_3$(aq) + CO$_3^{2-}$ $\rightleftharpoons$ Pb(CO$_3$)$_2^{2-}$ ($\log_{10} K_2° = 3.7$, Section 6.3.2), it follows that [Pb$_2$CO$_3^{2+}$]/[PbCO$_3$(aq)] $\leq 10^{1.91}$ [Pb^{2+}]. Accordingly, the dinuclear species is significant relative to PbCO$_3$(aq) only at very high [Pb^{2+}]. The stability constants for Pb$_3$CO$_3^{4+}$ and Pb$_2$CO$_3^{2+}$ can be combined to show that [Pb$_3$CO$_3^{4+}$]/[Pb$_2$CO$_3^{2+}$] = $10^{1.44}$[Pb^{2+}]/($c°$) at $I_m = 3.5$ mol dm^{-3}. The Pb$_3$CO$_3^{4+}$ species is significant relative to Pb$_2$CO$_3^{2+}$ only at very high [Pb^{2+}]; thus, neither polynuclear species is likely to be significant for environmentally relevant concentrations of lead even if their importance is substantially underestimated via the above analysis.

6.4 The Pb^{2+} + SO$_4^{2-}$ system

Characterization of the chemical speciation of higher-charged systems such as Pb^{2+}+ SO$_4^{2-}$ is complicated by a number of factors such as activity coefficient variation in mixed ClO$_4^-$/SO$_4^{2-}$ media and the

formation of solvent-separated (outer sphere) complexes. These problems have been discussed in detail in earlier parts of this series [2005PBa, 2007PBa] to which the reader is referred.

The stability constants for $Pb^{2+} + SO_4^{2-}$ equilibria in homogenous solution are rather poorly characterized, except at very low ionic strengths. This is in large part because the speciation is dominated by the sparing solubility of $PbSO_4(s)$. Although this means that solubility measurements can be used to quantify the homogeneous equilibria in this system, it also restricts the range of other techniques that can be usefully employed.

6.4.1 Formation of PbSO₄(aq)

The available data for equilibrium 26 are summarized in Table A2-9.

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4(aq) \tag{26}$$

At low concentrations and ambient temperatures, three experimental studies based on solubility, conductivity (mostly on supersaturated solutions), and ise potentiometric measurements provide results corrected to infinite dilution that are in good agreement. The three values at 25 °C give a weighted average of log $K_1°$(eq. 26, 298.15 K) = 2.73 ± 0.04 (with weightings based on the inverse of the uncertainties for the "accepted" values). This value is Recommended. The approximate value of Korenman [61KOa] is rejected, being inconsistent with the other studies.

At finite I, no direct comparisons are possible for the $\log_{10} K_1$ values reported, as no two studies were made under identical conditions (Table A2-9). However, it is notable that the two values at I_c = 3.0 mol dm⁻³, one obtained by solubility measurements in $LiClO_4$ and the other by polarography in $NaClO_4$, agree within the assigned error limits.

The SIT regression of the accepted data for $NaClO_4$ media (Fig. A3-12) yields $\log_{10} K_1°$ = 2.72 ± 0.05, consistent with the value discussed above, and $\Delta\varepsilon(26)$ = 0.02 ± 0.03 kg mol⁻¹ (Fig. A3-12).

6.4.2 Formation of Pb(SO₄)₂²⁻ and other complexes

While some M^{2+}/SO_4^{2-} systems form higher-order complexes [2005CHE, 2006ARa], others such as Cu^{2+}/SO_4^{2-} appear not to [2007PBa]. The existence of $Pb(SO_4)_2^{2-}$ is controversial: some papers have presented evidence for its formation (Table A2-10), whereas others [2004LIE, 85SBa], have argued the opposite. The most reliable data for the calculation of the $Pb(SO_4)_2^{2-}$ stability constant would be expected from those measurements in media at high ionic strengths, where high $[SO_4^{2-}]_T$ and high $[SO_4^{2-}]_T:[Pb^{2+}]_T$ ratios are possible.

The available stability constants for equilibrium 27 are shown in Table A2-10.

$$Pb^{2+} + 2SO_4^{2-} \rightleftharpoons Pb(SO_4)_2^{2-} \tag{27}$$

A SIT analysis did not show consistency among these reported results, thus no value is Recommended for reaction 27. The value $K_2 > K_1$ reported in [72BHb] differs from the "normal" complexation sequence. Further, the value of K_2 in [60RKa] is reported with low precision and is stated to be a "maximum". Analogous to the Cu^{2+}/SO_4^{2-} system [2007PBa], the apparent "observation" of $Pb(SO_4)_2^{2-}$ could relate to changes in activity coefficients when there is significant replacement of the medium anion (ClO_4^-) by SO_4^{2-}. More detailed studies are required to resolve this issue, and the data in Table A2-10 must be regarded as indicative only.

A number of other equilibria have been proposed for the $Pb^{2+} + SO_4^{2-}$ system, particularly in acidic solutions, e.g., [60RKa]. However no convincing evidence has been given for the existence of such species, nor have they been confirmed by independent studies. They are therefore not considered further.

6.5 The Pb²⁺ + PO₄³⁻ system

Difficulties in quantifying the speciation and stability constants in $M^{2+} + H^+ + PO_4^{3-}$ systems have been discussed in the earlier parts of this series [2005PBa, 2007PBa]. In this context, it is not surprising that

only three papers report equilibrium data for the water-soluble phosphate complexes of Pb^{II} (Table A2-11).

The formation of the protonated complexes $PbH_2PO_4^+$, $PbHPO_4(aq)$, and $Pb(HPO_4)_2^{2-}$ in acidic solution has been proposed. The value $\log_{10} K = 3.3 \pm 0.2$ reported by [74RMa] for reaction 28 ($I_m = 0.101$ mol kg^{-1} NaClO$_4$)

$$Pb^{2+} + HPO_4^{2-} \rightleftharpoons PbHPO_4(aq) \tag{28}$$
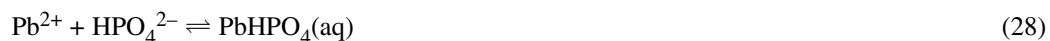
is in acceptable agreement with that determined by Nriagu [72NRc] ($I_m \to 0$, Table A2-11) and with that calculated using a recently published free energy relationship for Pb^{II} complexes formed with phosphomonoesters ($\log_{10} K = 3.2$) [99CS]. Consequently, for $I_m = 0.10$ mol kg^{-1} we assign $\log_{10} K$(eq. 28, 298.15 K) $= 3.3 \pm 0.2$ as a Provisional value. The stability constant values for the formation of the other two phosphate complexes can only be considered as indicative.

7. EVALUATION OF EQUILIBRIUM CONSTANTS (HETEROGENEOUS SYSTEMS)

Available data refer to reactions of pure crystalline phases used in the laboratory. Amorphous phases, which may form more rapidly, will do so at different pH or pL and have different (generally higher) solubility.

7.1 The $Pb^{2+} + OH^-$ system and the solubility of PbO(red), PbO(yellow), and "Pb(OH)$_2$"(s)

Solubility product data have been reported for the dissolution reactions of red (litharge, tetragonal) and yellow (massicot, orthorhombic) lead oxide, PbO(s), in water to produce cationic, neutral, and anionic solution species (Table A2-12). The majority of these data were determined in dilute solutions and were corrected by the original authors to $I_m = 0$ mol kg^{-1}. From these data, the standard equilibrium constant for reaction 29, $*K_{s0}°$, can be calculated

$$PbO(s) \text{ (red or yellow)} + 2H^+ \rightleftharpoons Pb^{2+} + H_2O \tag{29}$$

For red PbO(s), for which $\Delta_f G° = -219.0$ kJ mol^{-1} [82WAG], the solubility constant is $\log_{10} *K_{s0}°(29) = 12.69 \pm 0.12$, 12.57 ± 0.13, and 12.61 ± 0.12 (calculated, respectively, from the equilibrium data for reactions 30–32):

$$PbO(s) \text{ (red)} + H_2O \rightleftharpoons PbOH^+ + OH^- \tag{30}$$

$$PbO(s) \text{ (red)} + H_2O \rightleftharpoons Pb(OH)_2(aq) \tag{31}$$

$$PbO(s) \text{ (red)} + 2H_2O \rightleftharpoons Pb(OH)_3^- + H^+ \tag{32}$$

For calculation of the latter two values, the appropriate standard equilibrium constants in Table A2-12 have been averaged. The good agreement between the three calculated values of $\log_{10} *K_{s0}°$ indicates consistency between the Recommended stability constants for the formation of the monomeric lead hydrolysis species, reactions 4, 5, and 7. The Recommended solubility constant for reaction 29 is the average of the three values

$$\log_{10} *K_{s0}°\text{[eq. 29 (red), 298.15 K]} = 12.62 \pm 0.07$$

For yellow PbO(s) ($\Delta_f G° = -217.3$ kJ mol^{-1}; [82WAG]), the solubility constant is $\log_{10} *K_{s0}°(29) = 12.96 \pm 0.13$ (calculated from the equilibrium data for formation of $Pb(OH)_2(aq)$) and 12.84 ± 0.12 from the formation of $Pb(OH)_3^-$ (using the average solubility constant from Table A2-12). The value for $\log_{10} *K_{s0}°$ calculated from data for formation of $PbOH^+$ ($\log_{10} K_{s1}° = -7.59$ [29TOa]) is at variance with these results; it is inferred that this value of $\log_{10} K_{s1}°$ is incorrect, and it is there-

fore rejected. The Recommended solubility constant for reaction 29 with respect to yellow PbO(s) is the average of the two accepted values: $\log_{10} {}^*K_{s0}^\circ$ [eq. 29 (yellow), 298.15 K] = 12.90 ± 0.08.

The difference between these calculated values of $\log_{10} {}^*K_{s0}^\circ$ for the red and yellow forms of PbO(s) is consistent with that derived from their respective Gibbs free energy of formation ($\Delta\log_{10} {}^*K_{s0}^\circ$ = 0.30).

Based on published values of $\log_{10} K_{s0}^\circ$ = –19.3 to –19.96 at 20–22 °C [51DCa, 52KFa, 73PPb], it appears that hydrated lead oxide, Pb(OH)$_2$(s), is less soluble than either red or yellow PbO(s). This is unexpected as hydrated salts are normally more soluble than the analogous anhydrous ones. Further, there is a large degree of scatter in the $\log_{10} K_{s0}^\circ$ data for Pb(OH)$_2$(s). However, it should be noted that the preparation of "lead hydroxide" by the addition of NaOH to a solution of PbX$_2$ (X$^-$ = Cl$^-$, NO$_3^-$, ClO$_4^-$, …) produces "basic" salts such as Pb(OH)$_2 \cdot x$PbX$_2$ or Pb(OH)$_2 \cdot x$PbCO$_3$ or PbO$\cdot x$ Pb(OH)$_2$ [73BAI, 92EGW]. Thus, it is probable that the solid phase used in these solubility studies [51DCa, 52KFa, 73PPb] was not pure "Pb(OH)$_2$(s)", which does not appear to exist. For this reason, no solubility constant for Pb(OH)$_2$(s) is provided here.

7.2 The Pb^{2+} + Cl$^-$ system

The solubility of PbCl$_2$(s) is comparatively high ($\log_{10} K_{s0}^\circ$ = ca. –4.75 [2009PET]), and therefore PbCl$_2$(s) would not influence the speciation of Pb^{II} in natural fresh or saline waters. However, the solubility of laurionite, PbClOH(s) is much lower: $\log_{10} K_{s0}^\circ \approx$ –13.27 [74DZc], and this phase *might* affect the speciation of Pb^{II} in heavily polluted saline water systems. A number of other "mixed" solids have been reported in the Pb^{2+} + Cl$^-$ + OH$^-$ system [92EDW]. However, as they have not been well characterized they are not included in this evaluation.

7.3 The Pb^{2+} + CO$_3^{2-}$ + Cl$^-$ system

7.3.1 Solubility of PbCO$_3$(s) (cerussite)

The average of the solubility constants reported by [61NMc] and [59UGa] for reaction 33

$$PbCO_3(s) \rightleftharpoons Pb^{2+} + CO_3^{2-} \tag{33}$$

(Table A2-13) leads to the Recommended value $\log_{10} K_{s0}^\circ$(eq. 33, 298.15 K) = –13.18 ± 0.07. In conjunction with the result of [82BSa] at I_m = 0.305 mol kg^{-1} ($\log_{10} K_{s0}$ = –12.15 ± 0.15), the ionic strength dependence of the solubility constant, based on eq. 3, can be expressed as $\log_{10} K_{s0}$(33) = –(13.18 ± 0.07) + 8D – (0.62 ± 0.70)I_m. This result indicates that cerrusite is unlikely to exist in equilibrium with natural unpolluted fresh waters at typical environmental total concentrations of Pb^{2+} (10^{-8}–10^{-10} mol dm^{-3}) and CO$_3^{2-}$ (10^{-10}–10^{-6} mol dm^{-3}).

For the solubility reaction 34

$$PbCO_3(s) \rightleftharpoons PbCO_3(aq) \tag{34}$$

at zero ionic strength, we calculate $\log_{10} K^\circ$(eq. 34, 298.15 K) = –6.73 ± 0.72, based on $\log_{10} K_1^\circ$ [PbCO$_3$(aq)] = 6.45 ± 0.72, and the cerussite solubility constant at zero ionic strength, $\log_{10} K_{s0}^\circ$ = –13.18 ± 0.07. For I_m = 0.305 mol kg^{-1}, the direct observations of [82BSa] produce the estimate $\log_{10} K^\circ$(34) = –6.40 ± 0.1. However, it should be noted that this estimate is based on very few observations within the range of conditions where PbCO$_3$(aq) is a significant species.

7.3.2 Solubility of Pb$_2$(CO$_3$)Cl$_2$(s) (phosgenite)

The average of the values reported by [63NMd] and [62NMf] leads to the Recommended value $\log_{10} K_{s0}^\circ$ = –9.93 ± 0.08 for the solubility constant of phosgenite written in the form K_{s0} = [Pb^{2+}][CO$_3^{2-}$]$^{0.5}$[Cl$^-$]/$(c^\circ)^{2.5}$, reaction 35

$$0.5\ Pb_2(CO_3)Cl_2(s) \rightleftharpoons Pb^{2+} + 0.5\ CO_3^{2-} + Cl^- \tag{35}$$
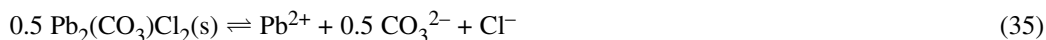
This result indicates that phosgenite is unlikely to exist in equilibrium with natural fresh waters at typical environmental concentrations of Pb^{2+} (10^{-8}–10^{-10} mol dm^{-3}), Cl$^-$ (0.23 mmol dm^{-3}), and CO_3^{2-} (10^{-10}–10^{-6} mol dm^{-3}).

7.4 The Pb^{2+} + SO_4^{2-} system

The speciation of Pb^{2+} in the presence of SO_4^{2-} is unlikely to be influenced by the sparing solubility of anglesite, PbSO$_4$(s), under normal environmental conditions. Selected data from the *SC-Database* [2009PET] for equilibrium 36

$$PbSO_4(s) \rightleftharpoons Pb^{2+} + SO_4^{2-} \tag{36}$$

are listed in Table A2-14. The older studies [03BOb, 07PLa, 08KOa], while in reasonable agreement with more recent values, are of historical interest only and have, therefore, not been included in the present analysis.

At infinite dilution, most of the available data, all obtained by direct solubility measurements, are in excellent agreement, although most lack error estimates from the original authors (Table A2-14). The unweighted average of all six experimental studies at 25 °C gives $\log_{10} K_{s0}°$(eq. 36, 298.15 K) = –7.80 ± 0.05, which is Recommended. The most recent computational modeling, employing the Pitzer formalism, of the extensive solubility database that exists for PbSO$_4$(s) in neutral and acidic solutions [92PKa] gave $\log_{10} K_{s0}°$(eq. 36, 298.15 K) = –7.76 ± 0.01, which is in excellent agreement with the Recommended value.

At finite I only the value of Ramette and Stewart [61RSa] at I_c = 1.0 mol dm^{-3} NaClO$_4$ appears to be reliable, so no SIT analysis could be performed. Clearly, there is a need for further experimental investigation in this area.

A number of "basic lead sulfates" have been reported [56CHa, 70BIL], but their solubilities and stoichiometry in contact with saturated aqueous solutions have not been well characterized nor confirmed by independent studies. They have, therefore, been excluded from this review.

7.5 The Pb^{2+} + PO_4^{3-} system

The least soluble Pb^{II} minerals in aerobic soils are the lead phosphates, especially the pyromorphites (Pb$_5$(PO$_4$)$_3$X, with X = F$^-$, Cl$^-$, Br$^-$, or OH$^-$) [73NRa]. Thus, the concentration of phosphate in soil solutions may control the solubility and bioavailability of lead. As a consequence, in situ immobilization of lead in contaminated soils by phosphate addition has been proposed as a cost-effective remediation strategy [2007XIE]. Despite this significance, few studies report the determination of solubility constants for lead phosphate salts (Table A2-15). The only comprehensive dataset was determined by Nriagu [72NRc, 73NRa, 73NRb].

The solubility constants reported in [72NRc] for PbHPO$_4$(s) and Pb$_3$(PO$_4$)$_2$(s) at 25 °C, reactions 37 and 38

$$PbHPO_4(s) \rightleftharpoons Pb^{2+} + HPO_4^{2-} \tag{37}$$

$$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+} + 2PO_4^{3-} \tag{38}$$

are, for an endothermic reaction, qualitatively consistent with the higher values reported for 37 °C [32JPa]. The values at I_m = 0 mol kg^{-1}, $\log_{10} K_{s0}°$(eq. 37, 298.15 K) = –11.4 ± 0.3 and $\log_{10} K_{s0}°$(eq. 38, 298.15 K) = –44.4 ± 1.0, are accepted as Provisional.

Chloropyromorphite, Pb$_5$(PO$_4$)$_3$Cl(s), has fundamental importance among the lead phosphate solids because the phosphate-induced immobilization strategies for lead are based on its low solubility.

The two available K_{s0} values for chloropyromorphite [32JPa, 73NRa], show only moderate agreement (Table A2-15). Although Nriagu's value is widely accepted in the literature, several investigations have reported equilibrium concentrations of dissolved Pb^{II} that are 1 to 2 orders of magnitude higher than predicted from this solubility constant. Possibly this is due to a nonequilibrium situation or to incomplete crystallization (the formation of amorphous phases) of chloropyromorphite and/or the presence of higher-solubility Pb^{II} minerals in small amounts [2007XIE]. This latter situation could arise in many soils and sediments, where pure metal-phosphate minerals are unlikely to form under the environmental conditions.

8. EVALUATION OF ENTHALPY DATA (HOMOGENEOUS AND HETEROGENEOUS REACTIONS)

When enthalpy data are available for an appropriate electrolyte and they cover an adequate range of ionic strength, an extrapolation to $I_m = 0$ mol kg^{-1} is possible by use of the SIT procedure for enthalpy data [97GRE]. The relevant equation, including the term for water, at sufficiently high concentrations of added swamping electrolyte I_m, is

$$\Delta_r H - 0.75\Delta(z^2)A_L \sqrt{I_m} (1 + 1.5\sqrt{I_m})^{-1} - rL_1 = \Delta_r H° - RT^2 I_m \Delta\varepsilon_L \qquad (39)$$

For a more detailed discussion and definition of terms, see [2005PBa]. A linear regression of ($\Delta_r H - \Psi(I_m) - rL_1$) against I_m yields $\Delta_r H°$ as the intercept and ($-RT^2\Delta\varepsilon_L$) as the slope.

8.1 The Pb^{2+} + OH^- system

There are few reported reaction enthalpies for the hydrolysis reactions of Pb^{II}. Those for the formation of the polymeric species $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$ were reported by Carell and Olin [62COa], Ishiguro and Ohtaki [81IOa], and Cruwagen and van de Water [93CWa] for 3 mol dm^{-3} NaClO$_4$, 3 mol dm^{-3} LiClO$_4$, and 1 mol dm^{-3} NaClO$_4$, respectively (Table A2-16). Enthalpy data for the formation of $PbOH^+$ and $Pb_3(OH)_5^+$ were also reported in [93CWa]. Except for the reaction enthalpy for the tetrameric species, there is poor agreement between the values measured in 3 mol dm^{-3} perchlorate media. The values reported by [93CWa] are more consistent with those of [62COa] than with [81IOa]. There are insufficient data to derive reaction enthalpies at zero ionic strength. Tugarenov et al. [75TUG] have presented enthalpy data for a wide range of Pb^{II} hydrolysis reactions but it is not apparent how these values were determined, so they are not accepted in this review.

8.2 The Pb^{2+} + Cl^- system

No calorimetric studies on the formation of Pb^{II}-chlorido- complexes have been reported. However, two extensive investigations examined the temperature dependence of the stability constants [84SEa, 2007LUO]. In [84SEa], the formation of Pb^{II}-chlorido- complexes was measured in the temperature range 25–300 °C with chloride concentrations increasing from 0.0012 to 3.223 mol kg^{-1}. No inert electrolyte was used, and the reported enthalpy data cannot be used in a SIT analysis. In the second study [2007LUO], the temperature dependence of the stability constants was examined in NaClO$_4$ media between 15 and 50 °C at ionic strengths varying from 0.5 to 5.89 mol kg^{-1}. These data were analyzed [2007LUO] using Pitzer equations to extrapolate the stability constants to $I_m = 0$. The corresponding standard enthalpy changes for the formation of the Pb^{II}-chlorido complexes (eqs. 12–14) were calculated [2007LUO] from the observed temperature dependence of the standard equilibrium constants

$$\Delta_r H° (\beta_1) = (10.3 \pm 1.5) \text{ kJ mol}^{-1}$$

$$\Delta_r H° (\beta_2) = (17.0 \pm 0.6) \text{ kJ mol}^{-1}$$

$\Delta_r H^\circ (\beta_3) = (14.7 \pm 1.0)$ kJ mol^{-1}

Although a SIT analysis was not performed and therefore the specific ion interaction coefficients for the reaction enthalpies cannot be given, these enthalpy data can be accepted as Provisional values, because the stability constants determined in [2007LUO] are in fair (but only fair) agreement with those Recommended in this review (Section 6.2).

8.3 The Pb^{2+} + SO$_4^{2-}$ system

No direct calorimetric studies have been reported for either the homogeneous equilibrium reactions 26 and 27, or the heterogeneous equilibrium reaction 36 in the Pb^{2+}-SO$_4^{2-}$ system. On the other hand, the solubility of PbSO$_4$(s) as a function of temperature is moderately well known [90CSa, 92PKa]. The most recent analysis of these data gives $\Delta_r H^\circ(36) = 13 \pm 1$ kJ mol^{-1} at 25 °C [92PKa]. Estimated reaction enthalpy values for the homogeneous equilibria are $\Delta_r H_1^\circ(26) = 9.2 \pm 0.5$ kJ mol^{-1} and $\Delta_r H_2^\circ(27) = 18.4 \pm 1.0$ kJ mol^{-1} from solubility measurements in 3 mol dm^{-3} LiClO$_4$ at 25 °C [90CSa]. The corresponding entropy values are $\Delta_r S_1^\circ = 27 \pm 2$ J K^{-1} mol^{-1} and $\Delta_r S_2^\circ = 59 \pm 4$ J K^{-1} mol^{-1} [90CSa]. In the absence of independent confirmatory studies little can be said about the reliability of these values or their likely uncertainties; the numbers quoted should be regarded as indicative only.

9. SPECIATION IN MULTICOMPONENT SYSTEMS: Pb^{2+} + H$^+$ + Cl$^-$ + CO$_3^{2-}$ + PO$_4^{3-}$ + SO$_4^{2-}$

This section presents results from speciation calculations for model aquatic systems. The required stability constants were calculated from the standard equilibrium constants in Tables 1–5, or from the published critical evaluation for the protonation reactions of the ligands [2005PBa]. These standard equilibrium constants were corrected, as required, for ionic strength effects and water activity, $a(H_2O)$, according to eq. 3 and as described in Section 5

$$\log_{10} \beta_{p,q,r} = \log_{10} \beta_{p,q,r}^\circ + \Delta z^2 D + r\log_{10} a(H_2O) - \Delta \varepsilon I_m$$

The calculation of $\log_{10} \beta_{p,q,r}$ at the required ionic strength (molality scale) and its correction to the amount concentration (molarity) scale are conveniently achieved by using the program SIT which is included in *SC-Database* [2009PET], in the *Sol-Eq* tutorials [98PET], and is also available in the suite of programs *Aq Solutions* from <www.iupac.org/publications/epub/index.html>. However, in the present work the program WinSGW, a version of SOLGASWATER [79ERI], was used. This program <http://www.dagger.mine.nu/MAJO/winsgw.htm>, incorporates the SIT functions (eq. 3) and generates the ionic strength-corrected values of $\log_{10} \beta_{p,q,r}$ for each datum in the calculation. In the calculations presented here, the changes in I and therefore in $\log_{10} \beta_{p,q,r}$ are minimal within the prescribed pH ranges.

9.1 Fresh water in equilibrium with CO$_2$(g)

To illustrate the speciation of Pb^{II} in typical fresh water in equilibrium with CO$_2$(g), the total concentration of Pb^{II} was set to 1 nmol dm^{-3} and it was assumed that the system was in equilibrium with air having a CO$_2$ fugacity of $10^{-3.5}$ bar. Total concentrations of inorganic anions were those typically found in fresh water [93MOR]: [Cl$^-$]$_T$ = 0.23 mmol dm^{-3}, [SO$_4^{2-}$]$_T$ = 0.42 mmol dm^{-3}, and [HPO$_4^{2-}$]$_T$ = 0.7 μmol dm^{-3}. Furthermore, $-\log_{10}\{[H^+]/c^\circ\}$ was allowed to vary between 4.98 and 8.96 (ca. pH 5.0 to 9.0); in this range, the ionic strength is approximately constant, ca. I_c = 0.0015 mol dm^{-3} up to $-\log_{10}\{[H^+]/c^\circ\}$ = 7, and 0.008 mol dm^{-3} at $-\log_{10}\{[H^+]/c^\circ\}$ = 9, an increase due to the increase in [HCO$_3^-$] and [CO$_3^{2-}$] at constant $f(CO_2)$.

The stability constants applicable at I_c = 0.0015 mol dm^{-3} for the critical species are shown in Table 6. Note that although the calculations included all of the species critically evaluated in this review, Table 6 includes only those species that make a significant contribution to the speciation of Pb^{II} in the two media considered. The constants are shown for the equilibrium reactions as defined in this review and also in the format used in the speciation calculations, i.e., in terms of the component species $H_2CO_3(aq)$ with $[H_2CO_3(aq)]_T = [CO_2(aq)] + [H_2CO_3(aq)]$. The reported $\Delta\varepsilon$ values apply to NaClO$_4$ media. For calculations in fresh water media of low ionic strength, (i) the use of $\Delta\varepsilon$ (NaClO$_4$) values has minimal effect, and (ii) the activity of water can be set equal to one.

**Table 6** Stability constants for species critical to the speciation of Pb^{II} in fresh water and seawater at 25 °C. $Log_{10} K_1°$ values for Mg^{2+} and Ca^{2+} complexes taken from [2009PET].

Reaction	Medium ionic strength I_c/mol dm^{-3}		
	$Log_{10} K°$ (I_c = 0)	$Log_{10} K$ (I_c = 0.0015)	$Log_{10} K$ (I_c = 0.67)
$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$	–7.46	–7.50	–7.79
$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2(aq) + 2H^+$	–16.94	–16.98	–17.23
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3(aq)$	6.45	6.30	5.37
$Pb^{2+} + H_2CO_3 \rightleftharpoons PbCO_3(aq) + 2H^+$	–10.24	–10.28	–10.15
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	10.13	9.98	8.77
$Pb^{2+} + 2H_2CO_3 \rightleftharpoons Pb(CO_3)_2^{2-} + 4H^+$	–23.25	–23.18	–22.27
[1]$Pb^{2+} + H_2O + CO_3^{2-} \rightleftharpoons Pb(CO_3)OH^- + H^+$	–3.10	–3.21	–4.44
[1]$Pb^{2+} + H_2CO_3 \rightleftharpoons Pb(CO_3)OH^- + 3H^+$	–19.79	–19.79	–19.96
[1]$Pb^{2+} + CO_3^{2-} + Cl^- \rightleftharpoons Pb(CO_3)Cl^-$	6.47	5.19	
[1]$Pb^{2+} + H_2CO_3 + Cl^- \rightleftharpoons Pb(CO_3)Cl^- + 2H^+$	–10.22		–10.33
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	–6.355	–6.317	–5.983
$H_2CO_3 \rightleftharpoons CO_3^{2-} + 2H^+$	–16.691	–16.58	–15.52
$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4(aq)$	2.72	2.58	1.04
$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$	1.50	1.40	0.85
$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(aq)$	2.10	1.99	1.17
$Pb^{2+} + 3Cl^- \rightleftharpoons PbCl_3^-$	2.00	1.89	1.12
$Mg^{2+} + H_2CO_3 \rightleftharpoons MgHCO_3^+ + H^+$	–5.67		–6.21
$Mg^{2+} + H_2CO_3 \rightleftharpoons MgCO_3(aq) + 2H^+$	–13.81		–14.15
$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3(aq)$	2.88		1.37
$Mg^{2+} + CO_3^{2-} + H^+ \rightleftharpoons MgHCO_3^+$	11.02		9.31
$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4(aq)$	2.23		0.87
$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(aq)$	2.31		0.91
$Ca^{2+} + H_2CO_3 \rightleftharpoons CaHCO_3^+ + H^+$	–5.36		–5.94
$Ca^{2+} + H_2CO_3 \rightleftharpoons CaCO_3(aq) + 2H^+$	–13.54		–13.92
$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(aq)$	3.15		1.60

[1]Reactions for which the constants have been predicted from statistical considerations.

The results from this calculation are presented in a distribution diagram in Fig. 3. The speciation is not significantly different from that for the Pb^{2+}-H$^+$-CO$_3^{2-}$ system (Fig. 2), except for the formation of a small amount of PbSO$_4$(aq) at $-log_{10}$ {[H$^+$]/$c°$} < 8. Thus, SO$_4^{2-}$ plays a minor role, and Cl$^-$ and PO$_4^{3-}$ a negligible role, in Pb^{II} speciation with inorganic ligands in weakly acidic or weakly alkaline fresh waters in equilibrium with CO$_2$. None of the possible Pb^{II}-containing solid phases forms under the specified conditions. At $-log_{10}$ {[H$^+$]/$c°$} = 6.4, the dominant species is Pb^{2+}(aq) (80.2 % of [Pb^{2+}]$_T$): the minor species are PbSO$_4$(aq) (12.8 %), PbOH$^+$ (6.1 %), and PbCl$^+$ (0.5 %). The speciation is also similar to that for the Cu^{2+} + H$^+$ + CO$_3^{2-}$ system under the same conditions [2007PBa], the
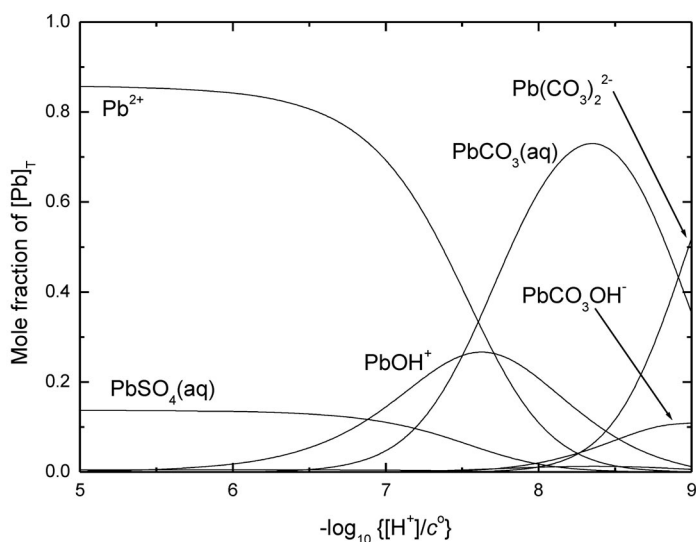
Fig. 3 Speciation diagram for the $Pb^{2+} + H^+ + Cl^- + CO_2 + HPO_4^{2-} + SO_4^{2-}$ system with total concentrations $[Cl^-]_T = 0.23$ mmol dm^{-3}, $[SO_4^{2-}]_T = 0.42$ mmol dm^{-3}, and $[HPO_4^{2-}]_T = 0.7$ µmol dm^{-3} (fresh water medium). The total concentration of Pb^{II} was set at 1 nmol dm^{-3}, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of 370 µbar. Log $K_{10}[CO_2(g) = CO_2(aq)] = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.0015$ mol dm^{-3}). The minor species shown at $-log_{10}\{[H^+]/c^\circ\}$ ca. 8, but not labeled, is $Pb(OH)_2(aq)$, analogous to Fig. 2.

most significant difference being the higher percentage of $[Pb^{II}]_T$ complexed by sulfate (for Cu^{II}: 6.0 %).

9.2 Seawater and saline systems

Distinctive features of natural saline systems are: the higher pH (seawater); the much higher concentrations of Cl^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}; and the significant concentrations of Mg^{2+} and Ca^{2+}, both of which form moderately stable complexes with CO_3^{2-} and SO_4^{2-} [2009PET]. Although the pH of surface seawater is in a narrow band, $-log_{10}\{[H^+]/c^\circ\}$ ca. 8.2 ± 0.2, it is informative to effect a calculation for a more generic saline system over a range of pH but approximating to seawater composition. The calculations presented here included all of the inorganic components of seawater with the exception of trace metals, fluoride, bromide, silicate, and borate. Thus, they included the competing reactions of Ca^{2+} and Mg^{2+} with the inorganic anions. Weaker interactions, such as those between Na^+ and CO_3^{2-} and SO_4^{2-}, are considered as an implicit aspect of the SIT theory when applied to measurements in $NaClO_4$ medium and so do not require inclusion as ion-pairing interactions in the speciation calculations. For saline media, a larger approximation arises in using SIT parameters, $\Delta\varepsilon$, that were derived for $NaClO_4$ media rather than NaCl, although the overall uncertainty may be small (because of the relative importance of the terms $\Delta z^2 D$ and $\Delta\varepsilon I_m$ in eq. 3).

The increase in ionic strength in the range $-log_{10}\{[H^+]/c^\circ\} = 7$ to 9 due to increasing $[HCO_3^-]$ and $[CO_3^{2-}]$ at constant $f(CO_2)$ was negligible in this medium and therefore had minimal effect on the stability constants. The stability constants calculated by WinSGW applicable at $I_c = 0.67$ mol dm^{-3} for the critical species are shown in Table 6.

As described in Section 6.3.4, significant approximations were required to establish stability constants for the formation of $Pb(CO_3)OH^-$ and $Pb(CO_3)Cl^-$. Specifically, the constants used in these calculations were based on statistically predicted values at $I_m = 0$ and at higher ionic strengths of $NaClO_4$.

Further, there are significant uncertainties associated with the best available stability constant values for $PbCl_4^{2-}$ and $PbCO_3(aq)$ (see Sections 6.2.3 and 6.3.1, and below.)

The speciation diagram (Fig. 4) indicates that at $-\log_{10}\{[H^+]/c°\} < 6.5$, the composition (mole fraction) is ca. 33.2 % $PbCl^+$, 37.8 % $PbCl_2(aq)$, 8.4 % $Pb^{2+}(aq)$, 18.5 % $PbCl_3^-$, and 1.8 % $PbSO_4(aq)$. In contrast, at $-\log_{10}\{[H^+]/c°\} = 8.2$ (taken to approximate the pH of surface seawater in equilibrium with the atmosphere at 25 °C) the strongly basic carbonate ion dominates complex formation and the composition is 41.2 % $PbCO_3(aq)$, 16.1 % $Pb(CO_3)Cl^-$, 9.0 % $Pb(CO_3)_2^{2-}$, 8.8 % $PbCl^+$, 10.1 % $PbCl_2(aq)$, 4.9 % $PbCl_3^-$, 5.8 % $PbOH^+$, 2.2 % Pb^{2+}, 1.1 % $Pb(CO_3)OH^-$, 0.4 % $Pb(OH)_2(aq)$, and 0.5 % $PbSO_4(aq)$. The species $Pb(CO_3)Cl^-$ thus seems to form to a significant extent. Given that there is no direct experimental proof of the existence of this species (Section 6.3.4), the foregoing distributions must be regarded as approximate only. There is clearly a need for further experimental investigation to positively identify and quantify the existence (or otherwise) of these species.
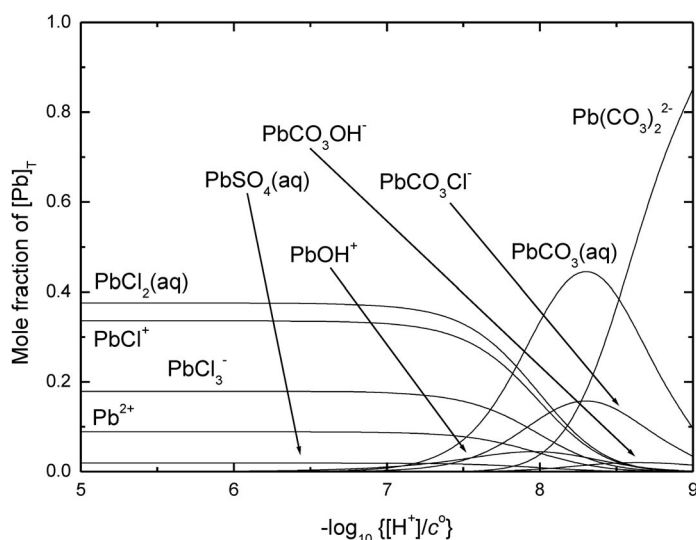
Fig. 4 Speciation diagram for the $Pb^{2+} + H^+ + Cl^- + CO_2 + HPO_4^{2-} + SO_4^{2-}$ system in a simulated seawater medium, $I_c = 0.67$ mol dm^{-3} including carbonato- and sulfato- complexes of Mg^{2+} and Ca^{2+}. The total concentration of Pb^{II} was set at 1 nmol dm^{-3}, and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar. Log $K_{10}[CO_2(g) = CO_2(aq)] = -1.5$ [93MOR]. All other formation constants are according to Table 6 ($I_c = 0.67$ mol dm^{-3}).

In a recent publication, Soli et al. [2008SOL] reported on the formation of $PbCO_3(aq)$ in seawater, a study based on the use of UV spectrometry to measure the partitioning of Pb^{II} between "free lead" (Pb^{2+}, $PbOH^+$, and $PbCl_n^{(2-n)+}$) and lead bound in different carbonato- species. This analysis indicated that some 74 % of lead is bound to carbonate at $-\log_{10}\{[H^+]/c°\} = 8.2$, which contrasts with ca. 67 and 61 % calculated in the presence or absence of $Pb(CO_3)Cl^-$ in the present evaluation. This comparison provides a further indication that the "best available value" derived in the current work for the formation of $PbCO_3(aq)$, $\log_{10} K_1°(16) = 6.45$, is an underestimate. However, it is also noted that the values of $\log_{10} K°$ and $\Delta\varepsilon I_m$ from which values of $\log_{10} K$ ($I_c = 0.67$ mol dm^{-3}) were derived are applicable to $NaClO_4$, a medium that contrasts markedly with seawater, salinity 35.4 g kg^{-1} (where salinity, S_T, is the mass of total salt (in all forms) divided by the mass of saline solution).

The most significant difference between the speciation of Cu^{II} [2007PBa] and Pb^{II} in natural brines arises from the higher stability of the chlorido- complexes of Pb^{2+}. As a consequence, at

$-\log_{10}\{[H^+]/c^\circ\} < 7$ there is a significantly higher contribution to the speciation of Cu^{II} from the free metal ion [Cu^{2+}(aq), 52.5 %, Pb^{2+}(aq) 7.8 %], and a lower contribution from chlorido- complexes (41.4 % $CuCl^+$, 89.5 % $PbCl_n^{(2-n)+}$). Another effect of Pb^{2+}-chlorido- complex formation in saline waters is to displace the $PbCO_3$(aq), distribution curve to higher values of $-\log_{10}\{[H^+]/c^\circ\}$ such that it dominates Pb^{II} speciation at $-\log_{10}\{[H^+]/c^\circ\} > 7.8$ (c.f. Cu^{II}, > 7.5) and has its maximum concentration at $-\log_{10}\{[H^+]/c^\circ\} = 8.4$ (Cu^{II}, 8.1).

As reported for Cu^{II} speciation in the same medium ([2007PBa]; Fig. 5b) the exclusion of carbonato- complexes of Ca^{2+} and Mg^{2+} from the model did not affect the calculated concentrations of Pb^{II}-hydroxo or carbonato- species because at a given pH the concentration of free CO_3^{2-} is constant in an open system in equilibrium with CO_2.

9.3 Summary

The speciation calculations indicate that, in fresh water systems in equilibrium with atmospheric CO_2, Pb^{2+}(aq) is the dominant Pb^{II} species in weakly acidic solutions in the absence of organic ligands. In humic-free fresh water, a small percentage of Pb^{II} will be present as the species $PbSO_4$(aq). In weakly alkaline solutions, $8.0 < -\log_{10}\{[H^+]/c^\circ\} < 8.8$, the speciation is dominated by the carbonato species $PbCO_3$(aq) and $Pb(CO_3)_2^{2-}$. In slightly acidic saline systems, the $PbCl_n^{(2-n)+}$ species ($n = 0$ to 3, or possibly 4) prevail. At salinities and pH values typical of seawater, the carbonato- complexes $PbCO_3$(aq), $Pb(CO_3)_2^{2-}$, and $Pb(CO_3)Cl^-$ are important in addition to the chlorido- complexes $PbCl^+$, $PbCl_2$, and $PbCl_3^-$. However, it is noted that there is no direct experimental evidence for the existence of $Pb(CO_3)Cl^-$, whose stability constant was estimated from statistical considerations. Table 6 provides the user with values for the critical constants in media at $I_c = 0.0015$ mol dm^{-3} (simulating fresh water) and $I_c = 0.67$ mol dm^{-3} (simulating seawater).

For reliable speciation calculations of Pb^{II} in environmental systems, the accuracy of the equilibrium data ($I_m = 0$ mol kg^{-1}) for formation of Pb^{2+}–CO_3^{2-} and related complexes (reactions 16, 17, 22), $PbOH^+$ (reaction 4), $PbSO_4$(aq) (reaction 26), and $PbCl_n^{(2-n)+}$ (reactions 12–15) is crucial. This document provides critically evaluated, IUPAC-Recommended (or Provisional) standard equilibrium constant values for the formation of each of these species, with the exception of $PbCO_3$(aq), $Pb(CO_3)Cl^-$, and $PbCl_4^{2-}$.

For $PbCO_3$(aq), the SIT regression was based on only two published values (Section 6.3.1), and thus the standard stability constant is of low precision. Because of the significant contribution of $PbCO_3$(aq) to the speciation of Pb^{II} in fresh water at pH > 7 and in saline water at pH > 7.5, the poor precision of its standard stability constant represents a serious limitation on the present reliability of speciation calculations for Pb^{II} in natural waters. The stability constants used for $Pb(CO_3)Cl^-$ and $Pb(CO_3)OH^-$ are based on statistical predictions, and have yet to be corroborated by high-quality experimental data. Accordingly, there is scope for additional careful measurements of stability constants in the $Pb^{2+} + CO_3^{2-} + Cl^-$ system. The possible formation of $PbCl_4^{2-}$ has been inferred from studies using very high $[Cl^-]_T$. However, other results conflict strongly, so if $PbCl_4^{2-}$ does form it must be in minor concentrations in saline systems like seawater. Again, further high-quality measurements are required.

10. QUANTITIES, SYMBOLS, AND UNITS USED IN THIS TECHNICAL REPORT

10.1 Quantities, symbols, and units

Name	Symbol	Definition	SI unit
amount of substance	n	(SI base unit)	mol
molar mass	M	$M_A = m_A/n_A$ (= mass/amount)	kg mol^{-1}
molality	m, b	$m_B = n_B/M_A(n - \sum_B n_B)$	mol kg^{-1}
amount concentration	c, [species]	$c_B = $ [species B] $= n_B/V$	mol m^{-3} (mol dm^{-3})^1
ionic strength, molality basis	I_m	$I_m = \frac{1}{2} \sum m_i z_i^2$	mol kg^{-1}
ionic strength, amount concentration basis	I_c	$I_c = \frac{1}{2} \sum c_i z_i^2$	mol m^{-3} (mol dm^{-3})^1
stepwise formation constant (equilibrium concentration product)	K_n	$K_n = [ML_n](c°)/[ML_{n-1}][L]$ for the reaction: $ML_{n-1} + L \rightleftharpoons ML_n$	1
cumulative (overall) formation constant	β_n	$\beta_n = [ML_n](c°)^n/[M][L]^n$ for the reaction: $M + nL \rightleftharpoons ML_n$	1
stepwise (metal ion) hydrolysis constant	$*K_n$	$*K_n = [M(H_2O)_{6-n}(OH)_n][H^+]/[M(H_2O)_{6-n+1}(OH)_{n-1}](c°)$ for the reaction: $M(H_2O)_{6-n+1}(OH)_{n-1} + H_2O \rightleftharpoons M(H_2O)_{6-n}(OH)_n + H^+$ or: $M(OH)_{n-1} + H_2O \rightleftharpoons M(OH)_n + H^+$	1
cumulative (metal ion) hydrolysis constant	$*\beta_n$	$*\beta_n = [M(H_2O)_{6-n}(OH)_n][H^+]^n/[M(H_2O)_6](c°)^n$ for: $M(H_2O)_6 + nH_2O \rightleftharpoons M(H_2O)_{6-n}(OH)_n + nH^+$	1
	$*\beta_{m,n}$	$*\beta_{m,n} = [M_m(OH)_n][H^+]^n/[M(H_2O)_6]^m(c°)^{n-m+1}$ for: $mM(H_2O)_6 + nH_2O \rightleftharpoons M_m(OH)_n + nH^+$	1
solubility constant	K_{s0}	$K_{s0} = [M][X]^p/(c°)^{p+1}$ for the reaction: $MX_p(s) \rightleftharpoons M + pX$	1
solubility constant	K_{sn}	$K_{sn} = [MX_{p+q}](c°)^{q-1}/[X]^q$ (where $n = p + q$) for the reaction: $MX_p(s) + qX \rightleftharpoons MX_{p+q}$	1

(*continues on next page*)

(*Continued*).

Name	Symbol	Definition	SI unit
solubility constant	$*K_{s0}$	$*K_{s0} = [M](c^o)^{p+1}/[H^+]^p$ for the reaction: $M(OH)_p(s) + pH^+ \rightleftharpoons M + pH_2O$	1
cumulative (overall) equilibrium concentration product	$\beta_{p,q,r}$	$\beta_{p,q,r} = [M_pL_q(OH)_r][H^+]^r/[M]^p[L]^q(c^o)^{r-p-q+1}$ for the reaction: $pM + qL + rH_2O \rightleftharpoons M_pL_q(OH)_r + rH^+$	1
(molar) enthalpy	H	H/n	J mol^{-1}
(molar) reaction enthalpy	$\Delta_r H$	$\Delta_r H = \Sigma H(\text{products}) - \Sigma H(\text{reactants})$	J mol^{-1}
activity coefficient, molality basis	γ_m	$RT \ln(\gamma_{m,B} m_B/m^\theta) = \mu_B - \mu_B^\theta =$ $\lim [\mu_B - RT \ln (m_B/m^\theta)]$ $m_B \rightarrow 0$	1
osmotic coefficient, molality basis	$\boldsymbol{\Phi}_m$	$\boldsymbol{\Phi}_m = (\mu_A^* - \mu_A)/RTM_A\Sigma m_B$	1
temperature (Celsius)	θ, t	$\theta/°C = T/K - 273.15$	°C
temperature, thermodynamic	T	(SI base unit)	K

[1]Common units used in this report.

10.2 Subscripts and superscripts

10.2.1 Subscripts
A, B general constituent
m quantity expressed on a molality basis
c quantity expressed on an amount concentration basis

10.2.2 Superscripts
o standard state for dissolved species ($I \rightarrow 0$)

MEMBERSHIP OF SPONSORING BODIES

Membership of the Analytical Chemistry Division Committee for the period 2008–2009 was as follows:

*President***:** A. Fajgelj (Slovenia); *Vice President***:** W. Lund (Norway); *Past President***:** R. Lobinski (France); *Secretary***:** B. Hibbert (Australia); *Titular Members***:** M Camões (Portugal); Z. Chai (China); P. De Bièvre (Belgium); J. Labuda (Slovakia); Z. Mester (Canada); S. Motomizu (Japan); *Associate Members***:** P. De Zorzi (Italy); A. Felinger (Hungary); M. Jarosz (Poland); P. Minkkinen (Finland); J. Pingarrón (Spain); *National Representatives***:** S. Aggarwal (India); R. Apak (Turkey); M. Iqbal

(Pakistan); H. Kim (Korea); T. Maryutina (Russia); R. Smith (UK); N. Trendafilova (Bulgaria); **Provisional Member:** N. Torto (Botswana).

Membership of the Analytical Chemistry Division Task Group on Chemical Speciation of Environmentally Significant Heavy Metals and Inorganic Ligands was as follows:

Chair: S. Sjöberg (Sweden); **Members:** P. Brown (Australia); R. H. Byrne (USA); T. Gajda (Hungary); G. Hefter (Australia); A. Leuz (Switzerland); K. Powell (New Zealand); H. Wanner (Switzerland).

REFERENCES

References with the format 15LIa (with the last letter in lower case) link the article to the IUPAC Stability Constant Database, *SC-Database* [2009PET], and the short reference 1915LIa therein. References with the format 39THO have no link to data in *SC-Database*.

03BOb	W. Böttger. *Z. Phys. Chem.* **46**, 521 (1903).
07PLa	M. Pleissner. *Arb. Kaiser Gesundh.* **26**, 384 (1907).
08KOa	F. Kohlrausch. *Z. Phys. Chem.* **64**, 129 (1908).
10WOa	J. K. Wood. *J. Chem. Soc.* 878 (1910).
13APa	F. Auerbach, H. Pick. *Arb. Kaiser Gesundh.* **45**, 113 (1913).
13KUa	C. Kullgren. *Z. Phys. Chem.* **85**, 466 (1913).
21GLa	S. Glasstone. *J. Chem. Soc.* 1689 (1921).
22ARa	M. P. Applebey, R. D. Reid. *J. Chem. Soc.* 2129 (1922).
23HEa	J. Heyrovský. *Trans. Faraday. Soc.* **19**, 692 (1923).
28RSa	M. Randall, H. M, Spencer. *J. Am. Chem. Soc.* **50**, 1572 (1928).
29MJa	H. Millet, M. Jowett. *J. Am. Chem. Soc.* **51**, 997 (1929).
29TOa	H. Töpelmann. *J. Prakt. Chem.* **121**, 320 (1929).
31CMa	I. Cowperthwaite, V. la Mer. *J. Am. Chem. Soc.* **53**, 4333 (1931).
32JPa	M. Jowett, H. Price. *Trans. Faraday Soc.* **28**, 668 (1932).
34LEa	A. Lebettre. *J. Chim. Phys.* **31**, 348 (1934).
35KAa	K. Kelley, C. Anderson. *Bur. Mines Bull.* 384 (1935).
37CBa	J. A. Cranston, H. F. Brown. *J. Royal Tech. Coll., Glasgow* **4**, 54 (1937).
39GVa	A. B. Garrett, S. Vellenga, C. M. Fontana. *J. Am. Chem. Soc.* **61**, 367 (1939).
42KPa	I. M. Kolthoff, R. Perlich, D. Weiblen. *J. Phys. Chem.* **46**, 561 (1942).
45PEa	K. J. Pedersen. *Kgl. Danske Vid. Sels. Medd.* **22**, 10; 12 (1945).
46TMa	I. Tananaev, I. Mizetskaya. *Zh. Anal. Khim.* **1**, 6 (1946).
51DCa	P. Deschamps, B. Charreton. *Compt. Rend.* **232**, 162 (1951).
52KFa	I. M. Korenman, F. S. Frum, V. G. Chebakova. *Zh. Obshch. Khim.* **22**, 1771 (1952).
55KIa	P. Kivalo. *Suomen Kem. B* **28**, 155 (1955).
54GOa	G. A. Goward. *A Polarographic Study of the Hydrolysis of Metal Ions*, Ph.D. dissertation, Princeton University (1954).
55AGa	A. Ågren. *Acta Chem. Scand.* **9**, 39; 49 (1955).
55SIa	D. Singh. *J. Sci. Res. Benares Hindu Univ.* **6**, 131 (1955).
55VLa	A. A. Vl ek. *Collect. Czech. Chem. Commun.* **20**, 400 (1955).
56CHa	B. Charreton. *Bull. Soc. Chim. Fr.* **337**, 347 (1956).
57ILa	N. Ingri, G. Lagerström, M. Frydman, L. G. Sillen. *Acta Chem. Scand.* **11**, 1034 (1957).
57KLa	P. Kivalo, R. Luoto. *Suomen Kem. B* **30**, 163 (1957).
58FNa	M. Frydman, G. Nilsson, T. Rengemo, L. Sillén. *Acta Chem. Scand.* **12**, 878 (1958).
58JAa	L. Jager. *Chem. Listy* **52**, 734 (1958).
59FBa	J. Faucherre, Y. Bonnaire. *Compt. Rend.* **248**, 3705 (1959).

59OHa	J. W. Olver, D. N. Hume. *Anal. Chim. Acta* **20**, 559 (1959).
59ROB	R. A. Robinson, R. H. Stokes. *Electrolyte Solutions*, 2nd ed., p. 483, Butterworths, London (1959).
59UGa	R. Uggla. *Ann. Acad. Sci. Fennicae* 97 (1959).
60COa	B. Carell, Å. Olin. *Acta Chem. Scand.* **14**, 1999 (1960).
60NMa	R. Näsänen, P. Merilainen. *Suomen Kem. B* **33**, 149 (1960).
60OLb	Å. Olin. *Acta Chem. Scand.* **14**, 126 (1960).
60OLc	Å. Olin. *Acta Chem. Scand.* **14**, 814 (1960).
60RKa	B. van't Riet, I. M. Kolthoff. *J. Phys. Chem.* **64**, 1045 (1960).
61KOa	I. Korenman. *Isvest. VUZ. Khim.* **4**, 554 (1961).
61NMc	R. Näsänen, P. Merilainen, K. Leppanen. *Acta Chem. Scand.* **15**, 913 (1961).
61RSa	R. Ramette, R. Stewart. *J. Phys. Chem.* **65**, 243 (1961).
61NRa	C. J. Nyman, D. K. Roe, R. A. Plane. *J. Am. Chem. Soc.* **83**, 323 (1961).
62COa	B. Carell, Å. Olin. *Acta Chem. Scand.* **16**, 2350 (1962).
62ETc	A. Egorov, Z. Titova. *Zh. Neorg. Khim.* **7**, 275 (1962).
62NMf	R. Näsänen, P. Merilainen, R. Havanka. *Acta Chem. Scand.* **16**, 1549 (1962).
62NMg	R. Näsänen, P. Merilainen, L. Oja. *Suomen Kem. B* **35**, 105 (1962).
62POa	L. Pajdowski, Å. Olin. *Acta Chem. Scand.* **16**, 983 (1962).
63MKc	V. Mironov, F. Kulba, V. Fedorov, O. Tikhomirov. *Zh. Neorg. Khim.* **8**, 2536 (1963).
63NMd	R. Näsänen, P. Merilainen, M. Hyle. *Suomen Kem. B* **36**, 73 (1963).
64FBa	R. Fischer, J. Byé. *Bull. Soc. Chim. Fr.* 2920 (1964).
64HUa	R. Hugel. *Bull. Soc. Chim. Fr.* 1462 (1964).
65HUa	(a) R. Hugel. *Bull. Soc. Chim. Fr.* 968 (1965); (b) R. Hugel. *Bull. Soc. Chim. Fr.* 971 (1965); (c) R. Hugel. *Bull. Soc. Chim. Fr.* 2017 (1965).
65LIc	K. Lieser. *Z. Anorg. Chem.* **339**, 208 (1965).
66NHb	L. Nilsson, G. Haight. *Acta Chem. Scand.* **20**, 486 (1966).
66VSa	F. Vierling, G. Schorsch, J. Bye. *Rev. Chim. Miner.* **3**, 875 (1966).
67SIa	G. Schorsch, N. Ingri. *Acta Chem. Scand.* **21**, 2727 (1967).
68BAb	N. Baranova. *Geochem. Intl.* **5**, 13 (1968).
68JOH	G. Johansson, Å. Olin. *Acta Chem. Scand.* **22**, 3197 (1968).
69AWA	S. A. Awad, Z. A. Elhady. *J. Electroanal. Chem.* **20**, 79 (1969).
69BAc	N. Baranova. *Zh. Neorg. Khim.* **14**, 3257 (1969).
69DIa	D. Dyrssen, E. Ivanova, K. Aren. *Vest. Moskov. Univ.* **24**, 41 (1969).
69FFa	F. Fromage, S. Fiorina. *Compt. Rend.* **268C**, 1511; 1764 (1969).
70BIL	H. W. Billhardt. *J. Electrochem. Soc.* **117**, 690 (1970).
70GNa	G. Gardner, G. Nancollas. *Anal. Chem.* **42**, 794 (1970).
71BHb	A. Bond, G. Hefter. *J. Electroanal. Chem.* **31**, 477 (1971).
71VIa	F. Vierling. *Bull. Soc. Chim. Fr.* 22 (1971).
71VIb	F. Vierling. *Bull. Soc. Chim. Fr.* 25 (1971).
72BHb	A. Bond, G. Hefter. *J. Electroanal. Chem.* **34**, 227 (1972).
72CBd	G. Carpeni, E. Boitard, R. Pilard, S. Poize, N. J. Sabiani. *J. Chim. Phys.* **69**, 1437 (1972).
72DHa	D. Dyrssen, I. Hansson. *Mar. Chem.* **1**, 137 (1972).
72NRc	J. O. Nriagu. *Inorg. Chem.* **11**, 2499 (1972).
72OLI	Å. Olin, R. Söderquist. *Acta Chem. Scand. A* **26**, 3505 (1972).
73BAI	J. C. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson. *Comprehensive Inorganic Chemistry*, Pergamon, Oxford (1973).
73BHb	A. Bond, G. Hefter. *J. Electroanal. Chem.* **42**, 1 (1973).
73HHb	M. Hutchinson, W. Higginson. *J. Chem. Soc., Dalton Trans.* 1247 (1973).
73NRa	J. O. Nriagu. *Geochim. Cosmochim. Acta* **37**, 367 (1973).

73NRb   J. O. Nriagu. *Geochim. Cosmochim. Acta* **37**, 1735 (1973).
73PPb   B. Pokrić, Z. Puča. *J. Inorg. Nucl. Chem*. **35**, 1987 (1973).
73VIa   F. Vierling. *Ann. Chim. (France)* **8**, 53 (1973).
74DZc   V. V. Danilov, V. S. Zaitsev, A. A. Ravdel. *Zh. Prikl. Khim.* **47**, 1930 (1974).
74MId   M. Mihailov. *J. Inorg. Nucl. Chem.* **36**, 107 (1974).
74PHc   R. Pytkowicz, J. Hawley. *Limnol. Oceanogr.* **19**, 223 (1974).
74RMa   S. Ramamoorthy, P. G. Manning. *J. Inorg. Nucl. Chem.* **36**, 695 (1974).
74RMb   S. Ramamoorthy, P. G. Manning. *J. Inorg. Nucl. Chem.* **36**, 1671 (1974).
75EAa   P. Ernst, H. Allen, K. Mancy. *Water Res.* **9**, 969 (1975).
75TUG   I. A. Tugarinov, I. G. Ganeyev, I. L. Khodakovskiy. *Geochem. Intl.* **9**, 47 (1975).
76BHa   H. Bilinski, R. Huston, W. Stumm. *Anal. Chim. Acta* **84**, 157 (1976).
76FSa   V. Fedorov, L. Shishin. *Zh. Fiz. Khim.* **50**, 356 (1976).
76SCA   G. Scatchard. *Equilibrium in Solution: Surface and Colloid Chemistry*, Harvard University Press, Cambridge, MA (1976).
77BLc   C. Birraux, J.-C. Landry, W. Haerdi. *Anal. Chim. Acta* **90**, 51 (1977).
78LIN   C. J. Lind. *Environ. Sci. Technol.* **12**, 1406 (1978).
78PBa   S. Poddar, S. Bhattacharya, A. K. Das. *Indian J. Chem., Sect. A* **16**, 367 (1978).
79BKa   S. Brown, B. Kowalski. *Anal. Chem.* **51**, 2133 (1979).
80KIa   T. Kawai, S. Ishiguro, H. Ohtaki. *Bull. Chem. Soc. Jpn.* **53**, 2221 (1980).
80SBa   R. N. Sylva, P. L. Brown. *J. Chem. Soc., Dalton Trans.* 1577 (1980).
80SRa   L. Sipos, B. Raspor, H. Nurnberg, R. Pytkowicz. *Mar. Chem.* **9**, 37 (1980).
80SVb   L.Sipos, P. Valenta, H. W. Nurnberg, M. Branica. *Lead in the Marine Environment. Proceedings of International Experts Discussion*, 1977, p. 61, Pergamon Press, Oxford (1980).
81IOa   S. Ishiguro, H. Ohtaki. *Bull. Chem. Soc. Jpn.* **54**, 335 (1981).
81KOa   K. Kogure, M. Okamoto, H. Kakihana, M. Maeda. *J. Inorg. Nucl. Chem.* **43**, 1561 (1981).
82BMc   H. Bendiab, J. Meullemeestre, M. J. Schwing, F. Vierling. *J. Chem. Res. (M)* 2718 (1982).
82BSa   H. Bilinski, P. Schindler. *Geochim. Cosmochim. Acta* **46**, 921 (1982).
82ROa   R. Rohl. *Anal. Chim. Acta* **135**, 99 (1982).
82WAG   D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11**, (Suppl. 2) (1982).
83BPa   M. Barrera, J. Placeres, J. Sanchez. *Ann. Quim.* **79**, 145 (1983).
84BMb   R. Byrne, W. Miller. *Am. J. Sci.* **284**, 79 (1984).
84FCa   C. Fouillac, A. Criaud. *Geochem. J.* **18**, 297 (1984).
84MBc   F. Millero, R. Byrne. *Geochim. Cosmochim. Acta* **48**, 1145 (1984).
84SEa   T. M. Seward. *Geochim. Cosmochim. Acta* **48**, 121 (1984).
85BMb   R. Byrne, W. Miller. *Geochim. Cosmochim. Acta* **49**, 1837 (1985).
85MMa   F. Mulla, F. Marsicano, B. S. Nakani, R. D. Hancock. *Inorg. Chem.* **24**, 3076 (1985).
85SBa   S. Shi, Y. Bai, J. Wang. *Anal. Chem. (China)* 646 (1985).
86BAE   C. F. Baes, R. E. Mesmer. *The Hydrolysis of Cations*, R. E. Krieger, Malabar, FL (1986).
87AZa   H. A. Azab. *Bull. Soc. Chim. Fr.* 265 (1987).
87FGb   D. Ferri, I. Grenthe, S. Hietanen, F. Salvatore. *Acta Chem. Scand. A* **41**, 349 (1987).
87KSd   A. Khokhlova, L. Shishin, G. Chernikova, L. Rubchevskaya. *Koord. Khim.* **13**, 63 (1987).
88FSb   (a) D. Ferri, F. Salvatore. *Ann. Chim. (Rome)* **78**, 441 (1988); (b) D. Ferri, F. Salvatore. *Ann. Chim. (Rome)* **78**, 497 (1988); (c) D. Ferri, F. Salvatore. *Ann. Chim. (Rome)* **78**, 509 (1988).

88PBb	I. Pizeta, M. Branica. *J. Electroanal. Chem.* **250**, 293 (1988).
89FSb	D. Ferri, F. Salvatore, E. Vasca. *Ann. Chim. (Rome)* **79**, 1 (1989).
89HSa	A. Hannisdal, K. Schroder. *J. Electroanal. Chem.* **263**, 23 (1989).
89NWa	L. Nyholm, G. Wikmark. *Anal. Chim. Acta* **223**, 429 (1989).
90CSa	G. Chernikova, L. Shishin, A. Khokhlova. *Zh. Neorg. Khim.* **35**, 973 (1990).
90HEa	G. Hefter. *Polyhedron* **9**, 2429 (1990).
92EDW	R. Edwards, R. D. Gillard, P. A. Williams, A. M. Pollard. *Miner. Mag.* **56**, 53 (1992).
92NEa	E. Neher-Neumann. *Acta Chem. Scand.* **46**, 231 (1992).
92PKa	C. Paige, W. Kornicker, O. Hileman. *Geochim. Cosmochim. Acta* **56**, 1165 (1992).
93CWa	J. J. Cruywagen, R. F. van de Water. *Talanta* **40**, 1091 (1993).
93MOR	F. M. M. Morel, J. G. Hering. *Principles and Applications of Aquatic Chemistry*, John Wiley, New York (1993).
95CMa	I. Cukrowski, F. Marsicano, R. D. Hancock, P. T. Tshetlho, W. A. L. Otterlo. *Polyhedron* **14**, 1661 (1995).
96FOa	M. Fiore, S. Orecchio, V. Romano, G. Ruggirello, R. Zingales. *J. Chem. Soc., Dalton Trans.* 4597 (1996).
97GRE	I. Grenthe, A. V. Plyasunov, K. Spahiu. In *Modelling in Aqueous Chemistry*, I. Grenthe, I. Puigdomenech (Eds.), pp. 325–426, Organisation for Economic Co-operation and Development, Paris (1997).
99DSa	C. P. Da Costa, H. Sigel. *J. Biol. Inorg. Chem.* **4**, 508 (1999).
2000KAa	Y. Kanekiyo, S. Aizawa, N. Koshino, S. Funahashi. *Inorg. Chim. Acta* **298**, 154 (2000).
2001BRO	S. A. Brown. *The Aqueous Chemistry of Polonium and its Relationship to Mineral Processing Streams*, Ph.D. dissertation, University of Western Sydney (2001).
2001LEM	R. J. Lemire, J. Fuger, H. Nitsche, P. Potter, M. H. Rand, J. Rydberg, K. Spahiu, J. C. Sullivan, W. J. Ullman, P. Vitorge, H. Wanner. *Chemical Thermodynamics of Plutonium and Neptunium*, North Holland, Amsterdam (2001).
2001PHa	W. N. Perera, G. Hefter, P. M. Sipos. *Inorg. Chem.* **40**, 3974 (2001).
2004LIE	K. H. Lieser, G. Beyer, E. Lakatos. *Z. Anorg. Chem.* **339**, 208 (2004).
2005CHE	T. Chen, G. T. Hefter, R. Buchner. *J. Solution Chem.* **34**, 1059 (2005).
2005PBa	K. J. Powell, P. L. Brown, R. H. Byrne, T. Gajda, G. Hefter, S. Sjöberg, H. S. Wanner. *Pure Appl. Chem.* **77**, 739 (2005).
2006ARa	C. Akilan, N. Rohman, G. T. Hefter, R. Buchner. *Chem. Phys. Chem.* **7**, 2319 (2006).
2007LUO	Y. Luo, F. J. Millero. *Geochim. Cosmochim. Acta* **71**, 326 (2007).
2007PBa	K. J. Powell, P. L. Brown, R. H. Byrne, T. Gajda, G. Hefter, S. Sjöberg, H. Wanner. *Pure Appl. Chem.* **79**, 895 (2007).
2007XIE	L. Xie, D. E. Giammar. *Environ. Sci. Technol.* **41**, 8050 (2007).
2008SOL	A. L. Soli, Z. I. Stewart, R. H. Byrne. *Mar. Chem.* **110**, 1 (2008).
2008GAM	H. Gamsjäger, J. W. Lorimer, P. Scharlin, D. G. Shaw. *Pure Appl. Chem.* **80**, 233 (2008).
2009PET	L. D. Pettit, K. J. Powell. *SC-Database*, IUPAC Stability Constants Database. Release 5.8. IUPAC; Academic Software, Otley, UK (2009); for availability, see <www.iupac.org/publications/scdb> or <www.acadsoft.co.uk>.

APPENDIX 1A

Data evaluation criteria

Literature data have been accepted as reliable (designated "reported" in relevant Tables), and thus included in the regression analyses, when all, or in some cases most, of the following requirements have been met:

- full experimental details are reported (solution stoichiometry, electrode calibration method, temperature, ionic strength, error analysis);
- the equilibrium model is considered to be complete (including hydrolysis reactions), data are for a non-complexing medium; or
- the experimental method and numerical analysis are considered to have minimal systematic errors.

References that contain data rejected from our analyses are recorded in the footnotes to relevant Tables. Reasons for rejection of specific references (indicated by superscripts) include:

(a) data for temperature(s) other than 25 °C, cannot be corrected to 25 °C, or the temperature is not defined;
(b) data are for a different medium and are not readily comparable with other data;
(c) ionic strength has not been held constant, or the medium composition has changed excessively, or inadequate allowance has been made for activity coefficient changes;
(d) description of experimental method is inadequate or inappropriate;
(e) equilibrium model is incomplete or inappropriate;
(f) electrode calibration details are missing;
(g) experimental data is incomplete;
(h) numerical analysis of measurement data is inadequate;
(i) correction for competing equilibria is inadequate;
(j) value(s) appear to be in error when compared with results from more than one other reliable laboratory;
(k) values are inconsistent with other thermodynamic data;
(l) measurements of historical interest only: superseded by subsequent work;
(m) reference does not contain any original data;
(n) translation into English not available; and
(o) values are predicted.

APPENDIX 1B

Competitive complex formation by medium anions

For the general reaction

$$p\text{M} + q\text{L} + r\text{H}_2\text{O} \rightleftharpoons \text{M}_p\text{L}_q(\text{OH})_r + r\text{H}^+ \qquad \text{(B-1)}$$

the formation constant $\beta_{p,q,r}$ determined in an ionic medium (typically containing a 1:1 electrolyte NX of ionic strength I_m) is defined by

$$\beta_{p,q,r} = [\text{M}_p\text{L}_q(\text{OH})_r][\text{H}]^r/[\text{M}]^p(c^\circ)^{r-p+1} \qquad \text{(B-2)}$$

However, when the metal ion can also react with the anion of the medium to form aqueous species, and this complexation has not been specifically corrected for, the quotient determined experimentally is

$$\beta_{p,q,r}' = [\text{M}_p\text{L}_q(\text{OH})_r][\text{H}]^r/[\text{M}]_{\text{app}}{}^p(c^\circ)^{r-p+1} \qquad \text{(B-3)}$$

where the concentration of metal used in B-3 is given by

$$[\text{M}]_{\text{app}} = [\text{M}] + [\text{MX}] + [\text{MX}_2] + ... + [\text{MX}_n] \qquad \text{(B-4)}$$

The concentrations of the various MX_n species are, in turn, defined by

$$[\text{MX}] = K_n[\text{M}][\text{X}]^n/(c^\circ)^{n+1} \qquad \text{(B-5)}$$

where K_n is the stability constant of the MX_n species in the particular medium being investigated. Equation B-5 may be substituted in eq. B-4 to give

$$[\text{M}]_{\text{app}} = [\text{M}](1 + \Sigma\, K_n[\text{X}]^n) \qquad \text{(B-6)}$$

This latter equation may be substituted in equation B-3 which, with rearrangement, gives the thermodynamic constant $\beta_{p,q,r}$:

$$\beta_{p,q,r} = \beta_{p,q,r}'(1 + \Sigma\, K_n[\text{X}]^n)^p = [\text{M}_p\text{L}_q(\text{OH})_r][\text{H}]^r/[\text{M}]^p/(c^\circ)^{r-p+1} \qquad \text{(B-7)}$$

The value of $(1 + \Sigma\, K_n[\text{X}]^n)^p$ is a constant at each ionic strength and approaches 1.0 as $I_m \to 0$. Thus, the value of $\beta_{p,q,r}'$ is also dependent on I_m and consequently measured stability constants that have not been corrected for complexation with the medium can still be used to calculate stability constants for $\text{M}_p\text{L}_q(\text{OH})_r$ at zero ionic strength. They cannot, however, be used to determine the associated interaction coefficients.

APPENDIX 2

Selected equilibrium constants

Table A2-1 Selected equilibrium constants for the reaction: $Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$ in $NaClO_4$ and $(Na,K,Pb)NO_3$ media at 25 °C.

Method	Ionic strength		$t/°C$	$Log_{10} *K_1$ (reported)	$Log_{10} *K_1$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
$NaClO_4$						
vlt	0.01 $NaClO_4$	0.010	25	-7.34[3]	-7.34 ± 0.3	78LIN
gl	0.10 $NaClO_4$	0.101	25	-7.76 ± 0.02	-7.76 ± 0.10	2000KAa
gl	0.30 $NaClO_4$	0.305	25	-7.8 ± 0.1	-7.79 ± 0.10	60OLb
gl	1.0 $NaClO_4$	1.052	25	-7.80 ± 0.06	-7.78 ± 0.06	93CWa
gl	2.0 $NaClO_4$	2.212	25	-7.92 ± 0.02	-7.89 ± 0.20	64HUa
gl	3.0 $NaClO_4$	3.503	25	-7.9 ± 0.1	-7.84 ± 0.10	60OLb
$(Na,K,Pb)NO_3$						
gl	0.005 $Pb(NO_3)_2$	0.015	25	-7.89	-7.89 ± 0.2	45PEa
gl	0.01 $Pb(NO_3)_2$	0.03	25	-7.94	-7.94 ± 0.2	45PEa
gl	0.02 $Pb(NO_3)_2$	0.06	25	-7.98	-7.98 ± 0.2	45PEa
gl	0.10 KNO_3	0.101	25	-7.86 ± 0.006	-7.86 ± 0.04	80SBa
gl	0.10 $NaNO_3$	0.101	25	-7.67	-7.67 ± 0.1	95CMa
gl	0.05 $Pb(NO_3)_2$	0.151	25	-8.07	-8.07 ± 0.2	45PEa
gl	0.1 $Pb(NO_3)_2$	0.302	25	-8.18	-8.18 ± 0.2	45PEa
gl	0.2 $Pb(NO_3)_2$	0.607	25	-8.34	-8.34 ± 0.2	45PEa
gl	1.0 KNO_3	1.045	25	-8.72	-8.70 ± 0.06	93CWa
gl	0.4 $Pb(NO_3)_2$	1.227	25	-8.74	-8.73 ± 0.2	45PEa
gl	2.0 $NaNO_3$	2.138	25	-8.84 ± 0.02	-8.81 ± 0.20	65HUa

[1]Constant converted from molar (amount concentration) to molal units and including our assigned errors (see Section 4).
[2]References for rejected data: [10WOa]^{b,c}, [13KUa]^{a,j}, [37CBa]^a, [39GVa]^j, [45PEa]^a, [54GOa]^j, [76BHa]^{d,e,h}, [77BLb]^{e,h,i,j}, [85MMa]^j, [87AZa]^b, [96FOa]^a, [2001PHa]^j.
[3]Converted to the form of reaction 4 using a value of log $K_w = -13.91$.

Table A2-2 Selected equilibrium constants for the reaction $Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2(aq) + 2H^+$ in $NaClO_4$ media at 25 °C.

Method	Ionic medium		$Log_{10} *\beta_2$ (reported)	$Log_{10} *\beta_2$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}			
sol	var.	0 corr	-17.12	-17.12 ± 0.2	39GVa
pol	0.01 $NaClO_4$	0.010	-17.01	-17.01 ± 0.3	78LIN
emf	0.30 $NaClO_4$	0.305	-17.2 ± 0.1[3]	-17.19 ± 0.1	60COa
gl	3.0 $NaClO_4$	3.503	-17.22 ± 0.1[4]	-17.09 ± 0.1	60COa

[1]Constant converted from molar to molal units and including our assigned errors.
[2]References for rejected data: [54GOw]^j, [67SIa]^{b,j}, [76BHa]^{d,e,h}, [77BLb]^{e,h,i,j}, [87AZa]^b, [93CWa]^b, [2000KAa]^j, [2001PHa]^j.
[3]Converted to the form of reaction 5 using the stability constant and log K_w (-13.76) in 0.3 mol dm^{-3} $NaClO_4$ reported in [60COa].
[4]Converted to the form of reaction 5 using the stability constant reported in [60COa] and an average value for log K_w (-14.06) reported in [55AGa, 57ILa, 60NMa, 64FBa, 72CBd] for 3 mol dm^{-3} $NaClO_4$.

Table A2-3 Selected equilibrium constants for the formation of $Pb(OH)_3^-$ in $NaClO_4$ media at 25 °C.

Method	Ionic medium Reported[1]	Molality/ mol kg^{-1}	$t/°C$	$Log_{10}\,\beta_3$ (reported)	$Log_{10}\,\beta_3$ (accepted)[2]	Ref.
$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$						
sol	var.	0 corr	25	13.86	13.86 ± 0.2	39GVa[3]
vlt	var.	0 corr	25	13.95 ± 0.08	13.95 ± 0.2	55VLa
vlt	var.	0 corr	25	13.90	13.90 ± 0.2	61NRa
pol	0.01 M NaClO$_4$	0.010	25	13.63	13.63 ± 0.1	78LIN
gl	0.30 M NaClO$_4$	0.305	25	13.29 ± 0.05	13.27 ± 0.1	60COa
gl	3.0 M NaClO$_4$	3.503	25	13.66 ± 0.05	13.46 ± 0.1	60COa
ise	3.0 M NaClO$_4$	3.503	25	13.3 ± 0.3	13.1 ± 0.3	87FGb
emf	5.0 m NaClO$_4$	5.0	25	13.80 ± 0.05	13.80 ± 0.1	89FSb

[1]Ionic medium for reported values. The symbol M indicates the amount concentration (molar) scale, units mol dm^{-3}. The symbol m indicates the molal scale, units mol kg^{-1}.
[2]Constant converted from molar to molal units and including our assigned errors.
[3]References for rejected data: [23HEa][a], [54GOa][b], [59OHa][j], [67SIa][b,j], [87AZa][b], [95CMa][b], [2000KAa][j], [2001PHa][j].

Table A2-4 Selected equilibrium constants for the formation of $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, and Pb_2OH^{3+} in perchlorate and nitrate media at 25 °C.

Method	Ionic strength Amount concn./ mol dm^{-3}	Molality/ mol kg^{-1}	$t/°C$	$Log_{10}\,{}^*\beta_{m,n}$ (reported)	$Log_{10}\,{}^*\beta_{m,n}$ (accepted)[1]	Ref.
$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+ ({}^*\beta_{3,4})$						
(Li,Na)ClO$_4$						
gl	0.10 NaClO$_4$	0.101	25	−23.7 ± 0.1	−23.69 ± 0.2	2000KAa
gl	0.30 NaClO$_4$	0.305	25	−23.35 ± 0.1	−23.34 ± 0.1	60OLb
gl	1.0 NaClO$_4$	1.051	25	−22.69 ± 0.21	−22.65 ± 0.21	93CWa
gl	3.0 NaClO$_4$	3.503	25	−22.87 ± 0.1	−22.74 ± 0.1	60OLb
gl	3.0 LiClO$_4$	3.481	25	−22.78 ± 0.05	−22.65 ± 0.1	80KIa
gl	3.0 LiClO$_4$	3.481	25	−23.03 ± 0.10	−22.90 ± 0.2	81KOa
$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{2+} + 4H^+ ({}^*\beta_{4,4})$						
(Li,Na,Mg,Ba)ClO$_4$						
gl	0.10 NaClO$_4$	0.101	25	−20.26 ± 0.08	−20.26 ± 0.1	2000KAa[2]
gl	0.30 NaClO$_4$	0.305	25	−19.9 ± 0.1	−19.89 ± 0.1	60OLb
gl	1.0 NaClO$_4$	1.052	25	−19.58 ± 0.02	−19.56 ± 0.06	93CWa
gl	2.0 NaClO$_4$	2.212	25	−19.35 ± 0.02	−19.31 ± 0.2	64HUa
gl	1.5 Mg(ClO$_4$)$_2$	3.392	25	−18.99 ± 0.04	−18.94 ± 0.1	62POa
gl	1.5 Ba(ClO$_4$)$_2$	3.447	25	−19.12 ± 0.02	−19.06 ± 0.1	62POa
gl	3.0 LiClO$_4$	3.481	25	−19.42 ± 0.02	−19.36 ± 0.1	80KIa
gl	3.0 LiClO$_4$	3.481	25	−18.9 ± 0.003	−18.84 ± 0.1	81KOa
gl	3.0 NaClO$_4$	3.503	25	−19.25 ± 0.1	−19.18 ± 0.1	60OLb

Table A2-4 (*Continued*).

Method	Ionic strength		$t/°C$	$\text{Log}_{10}\ {}^*\beta_{m,n}$ (reported)	$\text{Log}_{10}\ {}^*\beta_{m,n}$ (accepted)[1]	Ref.
	Amount concn./ mol dm^{-3}	Molality/ mol kg^{-1}				
(Na,K,Pb)NO$_3$						
gl	0.005 Pb(NO$_3$)$_2$	0.015	25	–20.66	–20.66 ± 0.2	45PEa
gl	0.01 Pb(NO$_3$)$_2$	0.03	25	–20.66	–20.66 ± 0.2	45PEa
gl	0.02 Pb(NO$_3$)$_2$	0.06	25	–20.59	–20.59 ± 0.2	45PEa
gl	0.10 KNO$_3$	0.101	25	–20.40 ± 0.004	–20.40 ± 0.04	80SBa
gl	0.05 Pb(NO$_3$)$_2$	0.151	25	–20.64	–20.64 ± 0.2	45PEa
gl	0.1 Pb(NO$_3$)$_2$	0.302	25	–20.65	–20.65 ± 0.2	45PEa
gl	0.2 Pb(NO$_3$)$_2$	0.607	25	–20.80	–20.80 ± 0.2	45PEa
gl	1.0 KNO$_3$	1.045	25	–21.01	–20.99 ± 0.1	93CWa
gl	0.4 Pb(NO$_3$)$_2$	1.227	25	–20.97	–20.96 ± 0.2	45PEa
gl	2.0 NaNO$_3$	2.138	25	–21.72 ± 0.04	–21.69 ± 0.2	65HUa
$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8{}^{4+} + 4H^+$ (${}^*\beta_{6,8}$)						
(Li,Na)ClO$_4$						
gl	0.10 NaClO$_4$	0.101	25	–43.2 ± 0.1	–43.19 ± 0.1	2000KAa
gl	0.30 NaClO$_4$	0.305	25	–42.66 ± 0.1	–42.64 ± 0.1	60OLb
gl	1.0 NaClO$_4$	1.052	25	–42.43 ± 0.09	–42.36 ± 0.09	93CWa
gl	3.0 LiClO$_4$	3.481	25	–41.68 ± 0.01	–41.49 ± 0.1	81KOa
gl	3.0 LiClO$_4$	3.481	25	–42.33 ± 0.02	–42.14 ± 0.1	80KIa
gl	3.0 NaClO$_4$	3.503	25	–42.14 ± 0.1	–41.94 ± 0.1	60OLb
$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+$ (${}^*\beta_{2,1}$)						
(Na,K,Pb)NO$_3$						
gl	0.005 Pb(NO$_3$)$_2$	0.015	25	–7.19	–7.19 ± 0.2	45PEa
gl	0.01 Pb(NO$_3$)$_2$	0.03	25	–7.15	–7.15 ± 0.2	45PEa
gl	0.02 Pb(NO$_3$)$_2$	0.06	25	–7.10	–7.10 ± 0.2	45PEa
gl	0.05 Pb(NO$_3$)$_2$	0.151	25	–7.05	–7.05 ± 0.2	45PEa
gl	0.1 Pb(NO$_3$)$_2$	0.302	25	–7.05	–7.05 ± 0.2	45PEa
gl	0.2 Pb(NO$_3$)$_2$	0.607	25	–7.05	–7.05 ± 0.2	45PEa
gl	1.0 KNO$_3$	1.045	25	–6.79	–6.79 ± 0.2	93CWa
gl	0.4 Pb(NO$_3$)$_2$	1.227	25	–7.12	–7.12 ± 0.2	45PEa
gl	2.0 NaNO$_3$	2.138	25	–7.11 ± 0.02	–7.11 ± 0.20	65HUa

[1]Constant converted from molar to molal units and including our assigned errors.
[2]Reference for rejected data: [96FOa][a].

Table A2-5 Selected equilibrium constants for the reaction: $Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$ at 25 °C.

| Method | Ionic medium | | $t/°C$ | $Log_{10} K_1$ (reported) | $Log_{10} K_1$ (accepted)[1] | Ref.[2] |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
ise	0.25 NaClO$_4$	0.254	25	1.00 ± 0.04	0.99 ± 0.10	63MKc
sp	0.5 NaClO$_4$[3]	0.500	25	0.77	0.77 ± 0.10	2007LUO
ise	0.50 NaClO$_4$	0.513	25	0.83 ± 0.06	0.82 ± 0.10	63MKc
sp	0.50 NaClO$_4$	0.513	25	0.89 ± 0.06	0.88 ± 0.10	82BMc
ise	0.50 NaClO$_4$	0.513	25	0.83 ± 0.01	0.82 ± 0.10	82BMc
sp	0.74 NaClO$_4$[3]	0.740	25	0.70	0.70 ± 0.15	2007LUO
ise	0.75 NaClO$_4$	0.779	25	0.85 ± 0.03	0.83 ± 0.10	63MKc
vlt	1.0 NaClO$_4$	1.052	25	0.96 ± 0.04	0.94 ± 0.10	55KIa
ise	1.0 NaClO$_4$	1.052	25	0.90 ± 0.05	0.88 ± 0.10	63MKc
vlt	1.0 NaClO$_4$	1.052	25	1.18 ± 0.06	1.16 ± 0.30	71BHb
vlt	1.0 NaClO$_4$	1.052	25	0.94 ± 0.03	0.92 ± 0.10	73BHb
sp	1.0 NaClO$_4$	1.052	25	0.98 ± 0.06	0.96 ± 0.10	82BMc
ise	1.0 NaClO$_4$	1.052	25	0.85 ± 0.02	0.83 ± 0.10	82BMc
ise	1.0 NaClO$_4$	1.052	25	0.93 ± 0.02	0.91 ± 010	90HEa
sp	1.12 NaClO$_4$[3]	1.120	25	0.72	0.72 ± 0.10	2007LUO
sp	1.79 NaClO$_4$[3]	1.790	25	0.78	0.78 ± 0.10	2007LUO
vlt	2.0 NaClO$_4$	2.212	25	1.18 ± 0.04	1.14 ± 0.25	57KLa
ise	2.0 NaClO$_4$	2.212	25	1.00 ± 0.09	0.96 ± 0.10	63MKc
sp	2.0 NaClO$_4$	2.212	25	0.82 ± 0.10	0.78 ± 0.10	82BMc
ise	2.0 NaClO$_4$	2.212	25	0.92 ± 0.03	0.88 ± 0.10	82BMc
sp	2.51 NaClO$_4$[3]	2.510	25	0.83	0.83 ± 0.10	2007LUO
sp	3.28 NaClO$_4$[3]	3.280	25	0.94	0.94 ± 0.10	2007LUO
ise	3.0 NaClO$_4$	3.503	25	1.16 ± 0.06	1.09 ± 0.10	63MKc
sp	4.11 NaClO$_4$[3]	4.110	25	0.98	0.98 ± 0.10	2007LUO
sp	4.52 NaClO$_4$[3]	4.520	25	1.10	1.10 ± 0.10	2007LUO
ise	4.0 NaClO$_4$	4.950	25	1.30 ± 0.02	1.21 ± 0.10	63MKc
ise	4.0 NaClO$_4$	4.950	25	1.19 ± 0.11	1.10 ± 0.11	71VIa
sp	4.0 NaClO$_4$	4.950	25	1.13 ± 0.18	1.04 ± 0.18	71VIb
sp	4.98 NaClO$_4$[3]	4.980	25	1.24	1.24 ± 0.10	2007LUO
emf	5.0 NaClO$_4$[3]	5.000	25	1.15 ± 0.02	1.15 ± 0.10	88FSb
sp	5.89 NaClO$_4$[3]	5.890	25	1.48	1.48 ± 0.15	2007LUO

[1]Constant converted from molar to molal units and including our assigned errors.
[2]References for rejected data: [88PBb][a], [87KSd][n], [83BPa][b], [76FSa][n], [74MId][o], [73VIa][e,h], [73HHb][b,e,i], [66VSa][d].
[3]Reported on the molality (mol kg^{-1}) scale.

Table A2-6 Selected equilibrium constants for the reaction: $Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(aq)$ at 25 °C.

Method	Ionic medium		$t/°C$	$Log_{10} \beta_2$ (reported)	$Log_{10} \beta_2$ (accepted)[1]	Ref.[2]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
ise	0.25 NaClO$_4$	0.254	25	1.48 ± 0.16	1.47 ± 0.15	63MKc
sp	0.5 NaClO$_4$[3]	0.500	25	1.16	1.16 ± 0.15	2007LUO
ise	0.50 NaClO$_4$	0.513	25	1.15 ± 0.09	1.13 ± 0.15	63MKc
sp	0.50 NaClO$_4$	0.513	25	1.13 ± 0.04	1.11 ± 0.15	82BMc
ise	0.50 NaClO$_4$	0.513	25	1.34 ± 0.001	1.32 ± 0.15	82BMc
sp	0.74 NaClO$_4$[3]	0.740	25	1.11	1.11 ± 0.15	2007LUO
ise	0.75 NaClO$_4$	0.779	25	1.46 ± 0.03	1.43 ± 0.30	63MKc
vlt	1.0 NaClO$_4$	1.052	25	0.87 ± 0.04	0.83 ± 0.30	55KIa
ise	1.0 NaClO$_4$	1.052	25	1.36 ± 0.08	1.32 ± 0.15	63MKc
vlt	1.0 NaClO$_4$	1.052	25	1.18 ± 0.06	1.14 ± 0.15	71BHb
vlt	1.0 NaClO$_4$	1.052	25	1.08 ± 0.04	1.04 ± 0.15	73BHb
ise	1.0 NaClO$_4$	1.052	25	1.08 ± 0.04	1.04 ± 0.15	90HEa
sp	1.0 NaClO$_4$	1.052	25	1.30 ± 0.08	1.26 ± 0.15	82BMc
ise	1.0 NaClO$_4$	1.052	25	1.24 ± 0.02	1.20 ± 0.15	82BMc
sp	1.12 NaClO$_4$[3]	1.120	25	1.10	1.10 ± 0.15	2007LUO
sp	1.79 NaClO$_4$[3]	1.790	25	1.22	1.22 ± 0.15	2007LUO
vlt	2.0 NaClO$_4$	2.212	25	1.15 ± 0.04	1.06 ± 0.15	57KLa
ise	2.0 NaClO$_4$	2.212	25	1.41 ± 0.07	1.32 ± 0.15	63MKc
sp	2.0 NaClO$_4$	2.212	25	1.33 ± 0.08	1.24 ± 0.15	82BMc
ise	2.0 NaClO$_4$	2.212	25	1.27 ± 0.04	1.18 ± 0.15	82BMc
sp	2.51 NaClO$_4$[3]	2.510	25	1.32	1.32 ± 0.15	2007LUO
sp	3.28 NaClO$_4$[3]	3.280	25	1.51	1.51 ± 0.15	2007LUO
ise	3.0 NaClO$_4$	3.503	25	1.70 ± 0.04	1.57 ± 0.15	63MKc
sp	4.11 NaClO$_4$[3]	4.110	25	1.65	1.65 ± 0.15	2007LUO
sp	4.52 NaClO$_4$[3]	4.520	25	1.80	1.80 ± 0.15	2007LUO
ise	4.0 NaClO$_4$	4.950	25	2.18 ± 0.03	1.99 ± 0.15	63MKc
ise	4.0 NaClO$_4$	4.950	25	1.86 ± 0.16	1.67 ± 0.16	71VIa
sp	4.0 NaClO$_4$	4.950	25	1.90 ± 0.14	1.71 ± 0.15	71VIb
sp	4.98 NaClO$_4$[3]	4.980	25	1.95	1.95 ± 0.15	2007LUO
emf	5.0 NaClO$_4$[3]	5.000	25	1.78 ± 0.02	1.78 ± 0.15	88FSb
sp	5.89 NaClO$_4$[3]	5.890	25	2.41	2.41 ± 0.30	2007LUO

[1]Constant converted from molar to molal units and including our assigned errors.
[2]References for rejected data: [88PBb][a], [87KSd][n], [83BPa][b], [76FSa][n], [74MId][o], [73VIa][e,h], [66VSa][d].
[3]Reported on the molality (mol kg^{-1}) scale.

Table A2-7 Selected equilibrium constants for the reaction: $Pb^{2+} + 3Cl^- \rightleftharpoons PbCl_3^-$ at 25 °C.

Method	Ionic medium Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}	$t/$°C	$Log_{10} \beta_3$ (reported)	$Log_{10} \beta_3$ (accepted)[1]	Ref.[2]
sp	0.5 NaClO$_4$ [3]	0.500	25	0.95	0.95 ± 0.25	2007LUO
sp	0.74 NaClO$_4$ [3]	0.740	25	0.92	0.92 ± 0.25	2007LUO
ise	0.75 NaClO$_4$	0.779	25	1.20 ± 0.08	1.15 ± 0.25	63MKc
vlt	1.0 NaClO$_4$	1.052	25	1.37 ± 0.04	1.30 ± 0.25	55KIa
ise	1.0 NaClO$_4$	1.052	25	1.45± 0.06	1.38 ± 0.25	63MKc
vlt	1.0 NaClO$_4$	1.052	25	1.72 ± 0.07	1.65 ± 0.25	73BHb
sp	1.0 NaClO$_4$	1.052	25	1.17 ± 0.18	1.10 ± 0.25	82BMc
ise	1.0 NaClO$_4$	1.052	25	1.09 ± 0.04	1.03 ± 0.25	82BMc
ise	1.0 NaClO$_4$	1.052	25	1.72 ± 0.05	1.65 ± 0.45	90HEa
sp	1.12 NaClO$_4$ [3]	1.120	25	0.95	0.95 ± 025	2007LUO
sp	1.79 NaClO$_4$ [3]	1.790	25	1.07	1.07 ± 0.25	2007LUO
vlt	2.0 NaClO$_4$	2.212	25	1.49 ± 0.04	1.36 ± 0.25	57KLa
ise	2.0 NaClO$_4$	2.212	25	1.48 ± 0.06	1.35 ± 0.25	63MKc
sp	2.0 NaClO$_4$	2.212	25	1.23 ± 0.06	1.10 ± 0.25	82BMc
ise	2.0 NaClO$_4$	2.212	25	1.43 ± 0.02	1.3 0 ± 0.25	82BMc
sp	2.51 NaClO$_4$ [3]	2.510	25	1.30	1.30 ± 0.25	2007LUO
sp	3.28 NaClO$_4$ [3]	3.280	25	1.54	1.54 ± 0.25	2007LUO
ise	3.0 NaClO$_4$	3.503	25	1.97 ± 0.05	1.77 ± 0.25	63MKc
sp	4.11 NaClO$_4$ [3]	4.110	25	1.78	1.78 ± 0.25	2007LUO
sp	4.52 NaClO$_4$ [3]	4.520	25	1.93	1.93 ± 0.25	2007LUO
ise	4.0 NaClO$_4$	4.950	25	2.43 ± 0.03	2.15 ± 0.25	63MKc
ise	4.0 NaClO$_4$	4.950	25	2.03 ± 0.14	1.75 ± 0.25	71VIa
sp	4.0 NaClO$_4$	4.950	25	2.08 ± 0.25	1.80 ± 0.25	71VIb
sp	4.98 NaClO$_4$ [3]	4.980	25	2.16	2.16 ± 0.25	2007LUO
emf	5.0 NaClO$_4$ [3]	5.000	25	1.95 ± 0.01	1.95 ± 0.25	88FSb
sp	5.89 NaClO$_4$ [3]	5.890	25	2.57	2.57 ± 0.25	2007LUO

[1]Constant converted from molar to molal units and including our assigned errors.
[2]References for rejected data: [88PBb][a], [87KSd][n], [83BPa][b], [76FSa][n], [74MId][o], [73VIa][e,h], [71BHb][j], [66VSa][d].
[3]Reported on the molality (mol kg^{-1}) scale.

Table A2-8 Selected equilibrium constants for the system Pb^{2+}–H^+–CO_3^{2-} at 25 °C and 10^5 Pa (1 bar).

Method	Ionic medium		$t/°C$	$Log_{10} K$ (reported)	$Log_{10} K$ (accepted)[1]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3(aq)$ $(K_1)^2$						
sol	0.30 NaClO$_4$	0.305	25	5.40 ± 0.10	5.39 ± 0.40	82BSa
vlt	0.70 NaClO$_4$	0.725	25	5.36 ± 0.01	5.34 ± 0.30	80SVa
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$ $(\beta_2)^3$						
sol	0.30 NaClO$_4$	0.305	25	8.86 ± 0.10	8.84 ± 0.40	82BSa
vlt	0.70 NaClO$_4$	0.725	25	8.59 ± 0.05	8.56 ± 0.30	80SVa
sol	1.0 NaClO$_4$	1.052	25	9.0 ± 0.10	8.96 ± 0.30	69BAc
ise	3.0 NaClO$_4$	3.505	25	8.9 ± 0.10	8.77 ± 0.20	87FGb
$Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons PbHCO_3^+$						
gl	3.0 NaClO$_4$	3.505	25	–6.09 ± 0.04	–6.02 ± 0.10	92NEa
$2Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons Pb_2CO_3^{2+} + 2H^+$						
gl	3.0 NaClO$_4$	3.505	25	–10.51 ± 0.37	–10.44 ± 0.4	92NEa
$3Pb^{2+} + H_2O + CO_2(g) \rightleftharpoons Pb_3CO_3^{4+} + 2H^+$						
gl	3.0 NaClO$_4$	3.505	25	–9.20 ± 0.01	–9.20 ± 0.20	92NEa
$Pb^{2+} + CO_3^{2-} + OH^- \rightleftharpoons Pb(CO_3)OH^-$						
ise	3.0 NaClO$_4$	3.505	25	10.9 ± 0.3	10.77 ± 0.4	87FGb

[1]Constant corrected from molar to molal units and including our assigned errors.
[2]References for rejected data: [87AZa][o], [80SRa][d,e], [79BKa][a,b], [76BHa][b,d], [75EAa][b,c], [69BAc][h,j], [78PBa][a,b,d].
[3]References for rejected data: [80SRa][d,e], [76BHa][b,d], [69FFa][a,b], [68BAb][d,e], [59FBa][a,b], [78PBa][a,b,d].

Table A2-9 Selected equilibrium constants for the reaction: $Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4(aq)$ in NaClO$_4$ or LiClO$_4$ media at 25 °C.

Method	Ionic medium		$t/°C$	$Log_{10} K_1$ (reported)[1]	$Log_{10} K_1$ (accepted)[2]	Ref.[3]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
sol, con	0 corr	0 corr	25	2.62 ± 0.05	2.62 ± 0.10	60RKa
con, ise(Pb)	0 corr	0 corr	25	2.72 ± 0.03	2.72 ± 0.05	70GNa
ise(Pb)	0 corr	0 corr	25	2.77 ± 0.03	2.77 ± 0.05	85SBa
oth[4]	0.7 NaClO$_4$	0.725	23	1.05 ± 0.02	1.04 ± 0.05	82ROa
pol	1.0 NaClO$_4$	1.051	25	1.20 ± 0.03	1.19 ± 0.05	89NWa
sol	3.0 LiClO$_4$	3.482	25[5]	0.65 ± 0.05	0.58 ± 0.10	90CSa
pol	3.0 NaClO$_4$	3.503	25	0.74 ± 0.02	0.66 ± 0.05	72BHb

[1]Uncertainties as given by the original authors or calculated by the reviewer from the spread of values given by the original authors.
[2]Constant converted from molar to molal units; errors assigned by reviewer (see text).
[3]References for rejected data: [61KOa][j], [69DIa][i,j], [78PB][b,h,i].
[4]By electrophoresis.
[5]Data also reported at other temperatures.

Table A2-10 Reported equilibrium constants for the reaction: $Pb^{2+} + 2SO_4^{2-} \rightleftharpoons Pb(SO_4)_2^{2-}$ in $NaClO_4$ or $LiClO_4$ media at 25 °C.

Method	Ionic medium		$t/°C$	$Log_{10}\,\beta_2$ (reported)[1]	$Log_{10}\,\beta_2$ (accepted)[2]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
sol, con	0 corr	0 corr	25	3.47 ± 0.05	3.5 ± 0.1	60RKa
oth[3]	0.70 NaClO$_4$	0.725	23	1.18 ± 0.03	1.2 ± 0.1	82ROa
sol	3.0 LiClO$_4$	3.482	25[4]	0.7 ± 0.1	0.6 ± 0.2	90CSa
pol	3.0 NaClO$_4$	3.503	25	2.00 ± 0.02	1.9 ± 0.1	72BHb

[1]Uncertainties as given by the original authors or calculated by the reviewer from the spread of values given by the original authors.
[2]Constant corrected from molar to molal units; errors assigned by reviewer (see text).
[3]By electrophoresis.
[4]Data also reported at other temperatures.

Table A2-11 Selected stability constants for the system Pb^{2+}–H^+–PO_4^{3-} at 25 °C.

Method	Ionic medium	$t/°C$	$Log_{10}\,K$ (reported)	$Log_{10}\,K$ (accepted)[1]	Ref.
	Molality/ mol kg^{-1}				
$Pb^{2+} + HPO_4^{2-} \rightleftharpoons PbHPO_4(aq)$					
sol	→ 0 (dil. H$_3$PO$_4$)	25	3.1 ± 0.8[2]		72NRc
gl	0.101 NaClO$_4$	25	3.27 ± 0.04	3.3 ± 0.2	74RMa
$Pb^{2+} + H_2PO_4^- \rightleftharpoons PbH_2PO_4^+$					
sol	→ 0 (dil. H$_3$PO$_4$)	25	1.5 ± 0.5[2]		72NRc
gl	0.101 NaClO$_4$	25	2.37		74RMb
$Pb^{2+} + 2HPO_4^{2-} \rightleftharpoons Pb(HPO_4)_2^{2-}$					
gl	0.101 NaClO$_4$	25	5.64		74RMb

[1]Constant including our assigned errors.
[2]Corrected to $I_m = 0$ using the Davies equation.

Table A2-12 Selected solubility constant data for PbO(s) (red) and PbO(s) (yellow) at 25 °C.

Method	Ionic medium		$t/°C$	$\text{Log}_{10} K_{sn}°$ (reported)	$\text{Log}_{10} K_{sn}°$ (accepted)[1]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
PbO(s) (red) + H$_2$O $\rightleftharpoons$ Pb(OH)$_2$(aq) ($K_{s2}°$)						
emf	var.	0 corr	25	−4.45	−4.45 ± 0.1	39GVa
sol	var.	0 corr	25	−4.3 ± 0.1	−4.3 ± 0.1	75TUG
PbO(s) (red) + 2H$_2$O $\rightleftharpoons$ Pb(OH)$_3^-$ + H$^+$ ($K_{s3}°$)[2]						
ise	var.	0 corr	25	−15.37	−15.37 ± 0.1	21GLa
sol	var.	0 corr	25	−15.36 ± 0.08	−15.36 ± 0.08	28RSa
emf	var.	0 corr	25	−15.37	−15.37 ± 0.1	39GVa
sol	var.	0 corr	25	−15.33 ± 0.1	−15.33 ± 0.1	75TUG
PbO(s) (red) + H$_2$O $\rightleftharpoons$ PbOH$^+$ + OH$^-$ ($K_{s1}°$)						
sol	var.	0 corr	25	−8.96 ± 0.1	−8.96 ± 0.1	75TUG
PbO(s) (yellow) + H$_2$O $\rightleftharpoons$ Pb(OH)$_2$(aq) ($K_{s2}°$)						
emf	var.	0 corr	25	−4.00	−4.00 ± 0.1	39GVa
PbO(s) (yellow) + 2H$_2$O $\rightleftharpoons$ Pb(OH)$_3^-$ + H$^+$ ($K_{s3}°$)[3]						
sol	var.	0 corr	25	−15.16 ± 0.07	−15.16 ± 0.07	28RSa
sol	var.	0 corr	25	−15.1	−15.1 ± 0.1	29TOa
emf	var.	0 corr	25	−15.13	−15.13 ± 0.1	39GVa

[1]Constant corrected from molar to molal units and including our assigned errors.
[2]References for rejected data: [22ARa][a], [23HEa][a].
[3]References for rejected data: [22ARa][a].

Table A2-13 Selected solubility constant data for PbCO$_3$(s) (cerussite) and Pb$_2$(CO$_3$)Cl$_2$ (s) (phosgenite).

Method	Ionic medium		$t/°C$	$\text{Log}_{10} K_{s0}$ (reported)	$\text{Log}_{10} K_{s0}$ (accepted)[1]	Ref.
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
PbCO$_3$(s) $\rightleftharpoons$ Pb^{2+} + CO$_3^{2-}$ (K_{s0})[2]						
gl	0 corr	0 corr	25	−13.13	−13.13 ± 0.10	61NMc
gl	0 corr	0 corr	25	−13.24	−13.24 ± 0.10	59UGa
gl	0.3 NaClO$_4$	0.305	25	−12.15 ± 0.05	−12.14 ± 0.20	82BSa
Pb(CO$_3$)$_{0.5}$Cl(s) $\rightleftharpoons$ Pb^{2+} + 0.5CO$_3^{2-}$ + Cl$^-$ (K_{s0})[3]						
gl	0 corr	0 corr	25	−9.97	−9.97 ± 0.10	63NMd
gl	0 corr	0 corr	25	−9.84	−9.84 ± 0.15	62NMf

[1]Constant converted from molar to molal units and including our assigned errors.
[2]References for rejected data: [77BLc][b,d], [28RSa][d,e], [13APa][a,c], [07PLa][a,e].
[3]References for rejected data: [62NMg][a,l].

Table A2-14 Selected solubility constant data for the reaction: $PbSO_4(s) \rightleftharpoons Pb^{2+} + SO_4^{2-}$ at 25 °C.

Method	Ionic medium		$t/°C$	$Log_{10} K_{s0}$ (reported)[1]	$Log_{10} K_{s0}$ (accepted)[2]	Ref.[3]
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}				
sol, emf	0 corr	0 corr	25[4]	–7.80	–7.80 ± 0.05	31CMa
sol	0 corr	0 corr	25	–7.80	–7.80 ± 0.05	34LEa
sol	0 corr	0 corr	25	–7.80	–7.79 ± 0.05	46TMa
sol	0 corr	0 corr	25	–7.82	–7.82 ± 0.05	58JAa
sol	0 corr	0 corr	25	–7.78 ± 0.05	–7.78 ± 0.05	60RKa
recalc (sol)	0 corr	0 corr	25[4]	–7.76	–7.76 ± 0.05	92PKa
sol	1.0 NaClO$_4$	1.051	25	–6.20[5]	–6.15 ± 0.05	61RSa

[1]Uncertainties as given by the original authors or calculated by the reviewer from the spread of values given by the original authors.
[2]Constant converted from molar to molal units; errors assigned by reviewer (see text).
[3]References for rejected data: [03BOb]^{c,l}, [07PLa]^{c,l}, [08KOa]^{c,l}, [42KPa]^c, [55SIa]^m, [62ETc]^j, [66NHb]^{b,e}, [69DIa]^{i,j}.
[4]Data also reported at other temperatures.
[5]A value of –6.38 was also given after making allowance for the complexation of SO_4^{2-} by Na^+.

Table A2-15 Selected solubility constant data for lead(II)-phosphates.

Method	Ionic medium Molality/ mol kg^{-1}	$t/°C$	$Log_{10} K_{s0}$ (reported)	$Log_{10} K_{s0}$ (accepted)[1]	Ref.
$Pb(H_2PO_4)_2(s) \rightleftharpoons Pb^{2+} + 2H_2PO_4^-$					
sol	→ 0 (0.1 NaCl)^2	25	–9.84		73NRa
$PbHPO_4(s) \rightleftharpoons Pb^{2+} + HPO_4^{2-}$					
sol	→ 0 (0.02 NaCl)^3	37	–11.36		32JPa
sol	→ 0 (dil. H$_3$PO$_4$)^2	25	–11.43 ± 0.1	–11.4 ± 0.3	72NRc
$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+} + 2PO_4^{3-}$					
sol	→ 0 (0.02 NaCl)^3	37	–43.5		32JPa^4
ise	dil. NaH$_2$PO$_4$	30	–42.0		69AWA
sol	→ 0 (dil. H$_3$PO$_4$)^2	25	–44.4	–44.4 ± 1.0	72NRc
$Pb_4O(PO_4)_3(s) + 2H^+ \rightleftharpoons 4Pb^{2+} + 2PO_4^{3-} + H_2O$					
sol	→ 0 (0.1 KOH)^2	25	–48.9		72NRc
$Pb_5(PO_4)_3X_2(s) \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + X^-$					
sol	→ 0 (0.16 NaCl)^3	37	–79.1 (X = Cl)		32JPa
sol	→ 0 (0.1 NaCl)^2	25	–84.4 (X = Cl)	–84.4 ± 2.0	73NRa
sol	→ 0 (0.1 NaF)^2	25	–71.6 ± 0.1 (X = F)		73NRb
sol	→ 0 (0.1 NaBr)^2	25	–78.1 ± 0.1 (X = Br)		73NRb
sol	→ 0 (0.1 KOH)^2	25	–76.8 (X = OH)		72NRc

[1]Constant including our assigned errors.
[2]Correction to $I = 0$ with Davies equation.
[3]Correction to $I = 0$ with Debye–Hückel equation.
[4]Reference for rejected data: [29MJa]^h.

Table A2-16 Reaction enthalpies for the formation of $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$ at 25 °C in $NaClO_4$ media.

| Method | Ionic medium | | $t/°C$ | $\Delta_r H$ | Ref. |
	Amount concn./mol dm^{-3}	Molality/ mol kg^{-1}	(kJ mol^{-1})	(reported)	
$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$					
cal	1.0 $NaClO_4$	1.052	25	24 ± 8	93CWa
$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+$					
cal	3.0 $NaClO_4$	3.503	25	110.8 ± 3.3	62COa
cal	3.0 $LiClO_4$	3.481	25	61.6 ± 2.0	81IOa
cal	1.0 $NaClO_4$	1.052	25	112 ± 5	93CWa
$3Pb^{2+} + 5H_2O \rightleftharpoons Pb_3(OH)_5^+ + 5H^+$					
cal	1.0 $NaClO_4$	1.052	25	146 ± 3	93CWa
$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$					
cal	3.0 $NaClO_4$	3.503	25	83.91 ± 0.50	62COa
cal	3.0 $LiClO_4$	3.481	25	81.4 ± 0.4	81IOa
cal	1.0 $NaClO_4$	1.052	25	86 ± 1	93CWa
$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+$					
cal	3.0 $NaClO_4$	3.503	25	206.8 ± 3.3	62COa
cal	3.0 $LiClO_4$	3.481	25	242.8 ± 1.1	81IOa
cal	1.0 $NaClO_4$	1.052	25	215 ± 3	93CWa

APPENDIX 3

SIT plots for Pb^{2+} + L systems
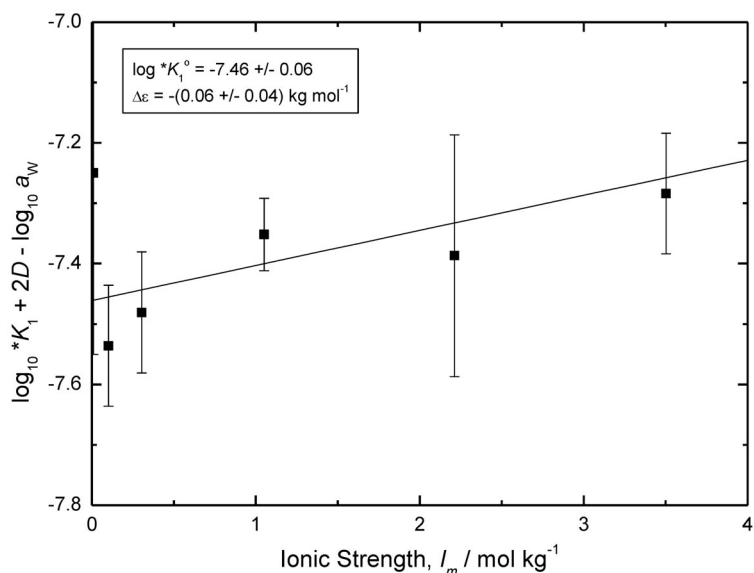
Fig. A3-1 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} {}^*K_1 - (z^2)D - \log_{10} a(H_2O)$ (eq. 3, Section 5) for reaction 4 using selected data for perchlorate media, 25 °C (Table A2-1).
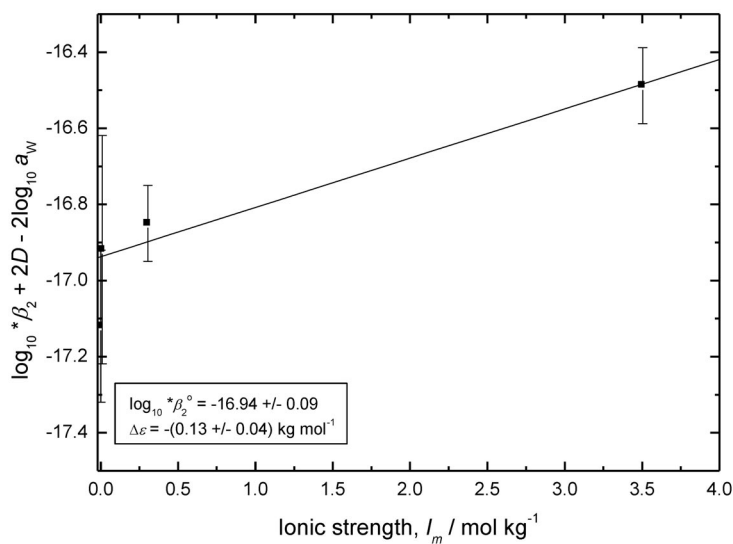
Fig. A3-2 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} {}^*\beta_2 - (z^2)D - 2 \log_{10} a(H_2O)$ for reaction 5 using selected data for perchlorate media, 25 °C (Table A2-2).
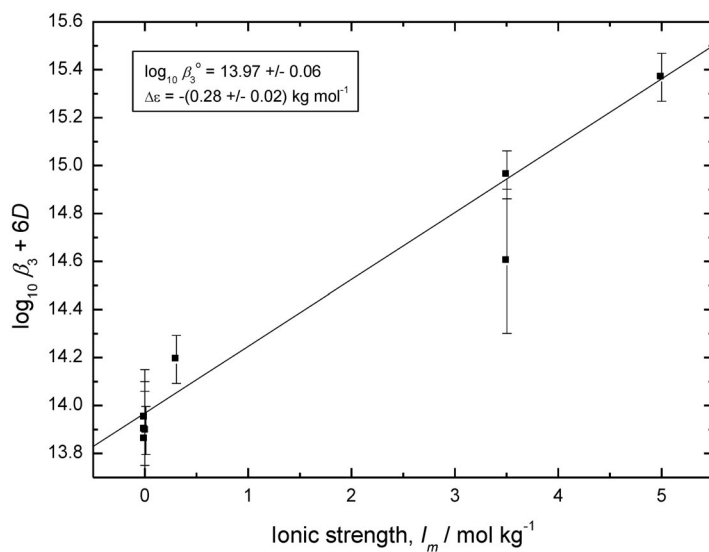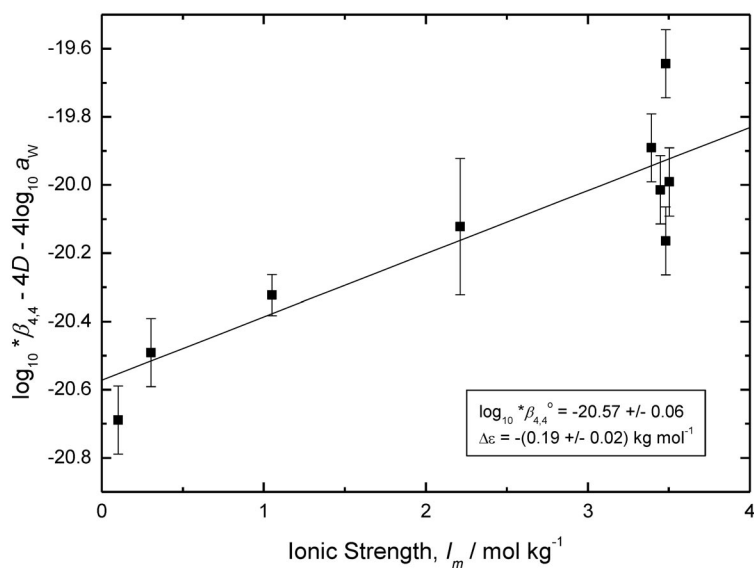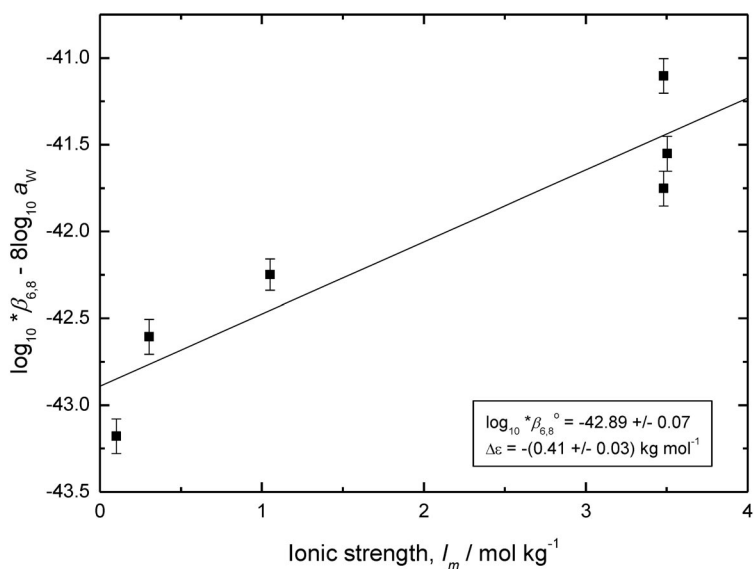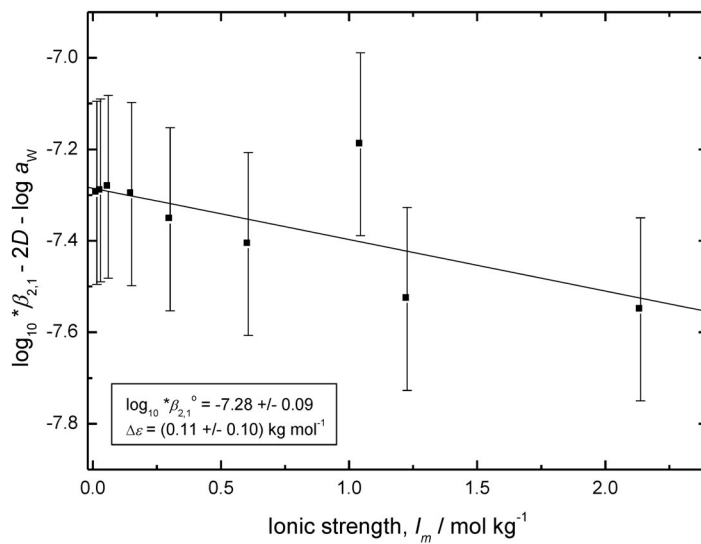
Fig. A3-3 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} \beta_3 - (z^2)D$ for reaction 6 using selected data for perchlorate media, 25 °C (Table A2-3).
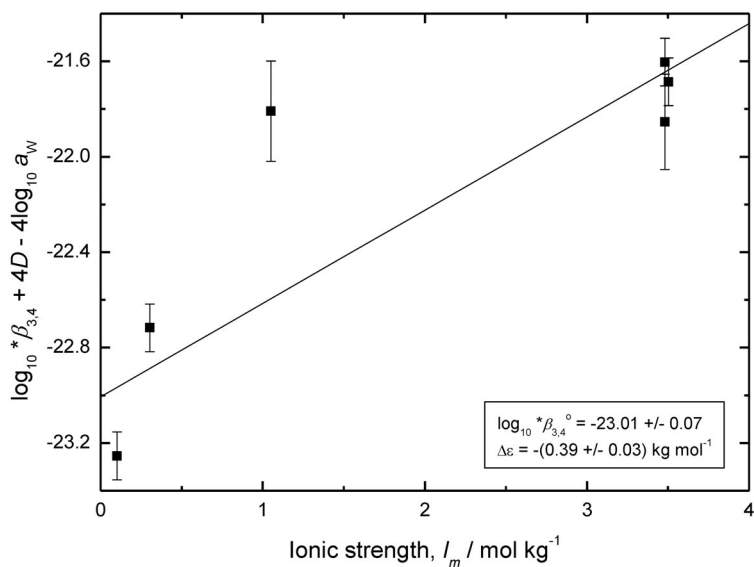
Fig. A3-4 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} {}^*\beta_{3,4} - (z^2)D - 4 \log_{10} a(H_2O)$ for reaction 8 using selected data for perchlorate media, 25 °C (Table A2-4).

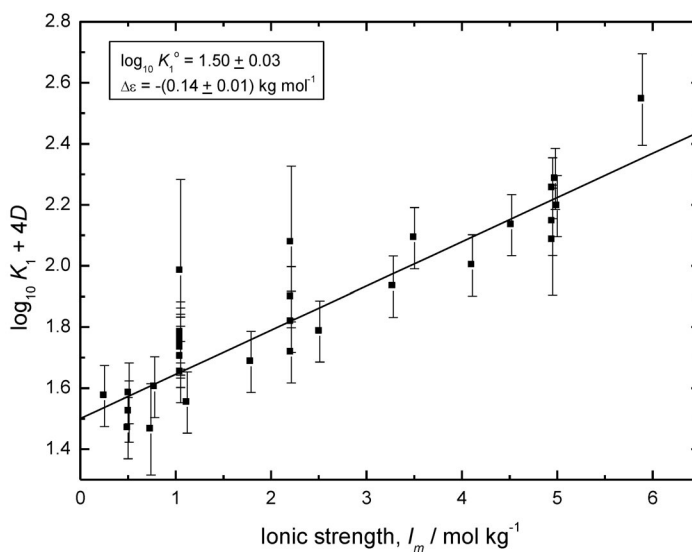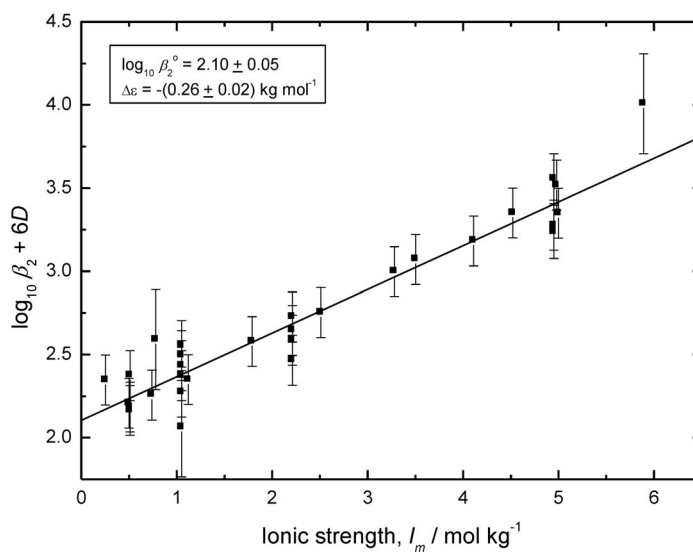**Fig. A3-5** Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} {}^*\beta_{4,4} - (z^2)D - 4\log_{10} a(H_2O)$ for reaction 9 using selected data for perchlorate media, 25 °C (Table A2-4).

Fig. A3-6 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} \beta_{6,8} - 8\log_{10} a(H_2O)$ for reaction 10 using selected data for perchlorate media, 25 °C (Table A2-4).
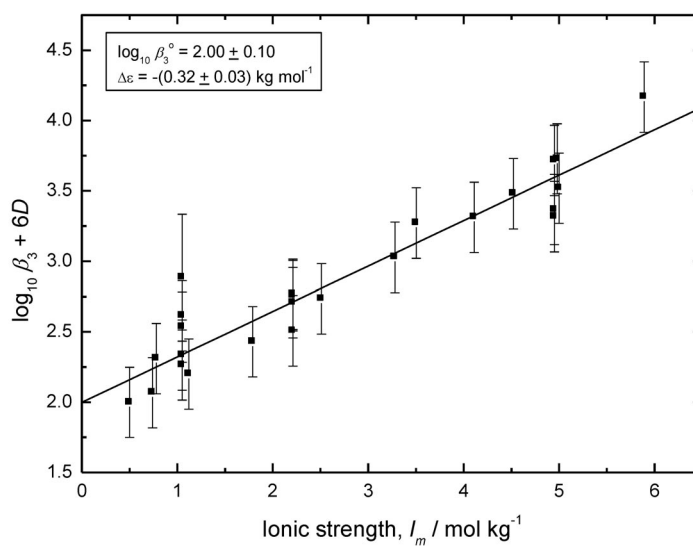
Fig. A3-7 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} {}^{*}\beta_{2,1} - \Delta(z^2)D - \log_{10} a(H_2O)$ for reaction 11 using selected data for nitrate media, 25 °C (Table A2-4).
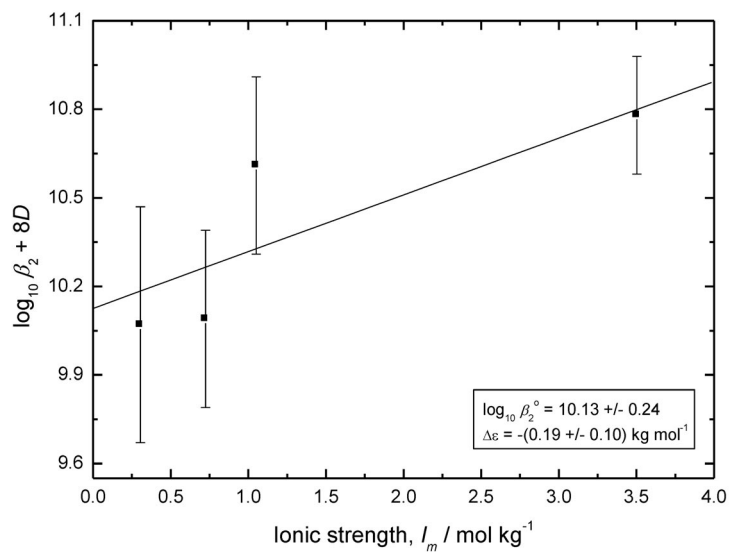

Fig. A3-8 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 12 using selected data for perchlorate media, 25 °C (Table A2-5).
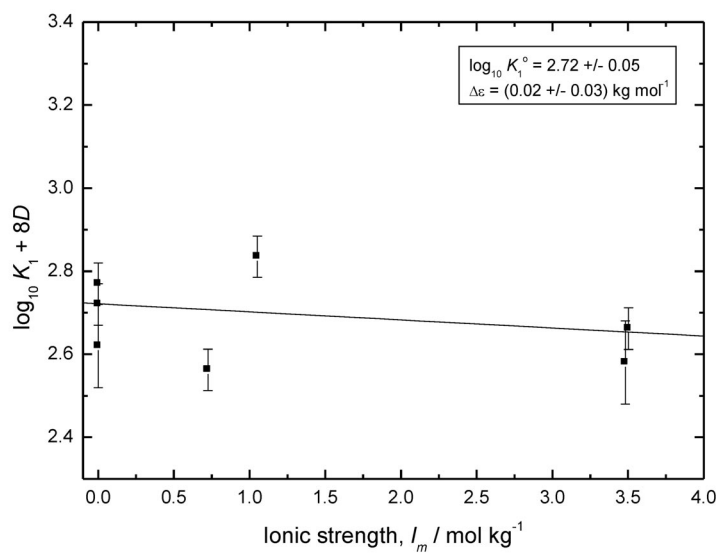
Fig. A3-9 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 13 using selected data for perchlorate media, 25 °C (Table A2-6).

Fig. A3-10 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} \beta_3 - \Delta(z^2)D$ for reaction 14 using selected data for perchlorate media, 25 °C (Table A2-7).

Fig. A3-11 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} \beta_2 - \Delta(z^2)D$ for reaction 17 using selected data for perchlorate media, 25 °C (Table A2-8).

Fig. A3-12 Extrapolation to $I_m = 0$ mol kg^{-1} of $\log_{10} K_1 - \Delta(z^2)D$ for reaction 26 using selected data for perchlorate media, 25 °C (Table A2-9).