3974 *Inorg. Chem.* **2001,** *40,* 3974−3978

An Investigation of the Lead(II)−Hydroxide System

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Received December 18, 2000

A detailed investigation of the Pb(II)/OH^- system has been made in $NaClO_4$ media at 25 °C. Combined UV−vis spectrophotometric−potentiometric titrations at $[\mathrm{Pb(II)}]_T \leq 10$ μM using a long path length cell detected only four mononuclear hydroxide complexes. The values of log $*\beta_{1q}$, for the equilibria $\mathrm{Pb}^{2+}(\mathrm{aq}) + q\mathrm{H_2O} \leftrightarrow \mathrm{Pb(OH)}_q^{(2-q)+}(\mathrm{aq}) + q\mathrm{H}^+(\mathrm{aq})$, were −7.2, −16.1, −26.5, and −38.0 for $q = 1-4$, respectively, at ionic strength $I = 1$ M ($NaClO_4$). Similar results were obtained at $I = 5$ M ($NaClO_4$). No evidence was found for higher order complexes ($q > 4$) even at very high $[\mathrm{OH}^-]/[\mathrm{Pb(II)}]$ ratios, nor for polynuclear species at $[\mathrm{Pb(II)}]_T \leq 10$ μM. Measurements using ^{207}Pb-NMR and Raman spectroscopies and differential pulse polarography (DPP) provided only semiquantitative confirmation. The mononuclear $\mathrm{Pb(OH)}_q^{(2-q)+}(\mathrm{aq})$ complexes are the only hydrolyzed species likely to be significant under typical environmental and biological conditions.

Introduction

Lead is widely used industrially and consequently is ubiquitous throughout the biosphere.[1] The common oxidation state, Pb(II), is highly mobile in the natural environment and is readily accumulated by plants,[2] aquatic organisms, and animals.[3,4] Since Pb(II) is both an acute and a chronic toxin toward human and other animal species,[5] it is of major concern as an environmental pollutant.

Except at low pH, Pb(II) is extensively hydrolyzed,[6,7]

$$p\mathrm{Pb}^{2+}(\mathrm{aq}) + q\mathrm{H_2O} \Leftrightarrow \mathrm{Pb}_p(\mathrm{OH})_q^{(2p-q)+}(\mathrm{aq}) + q\mathrm{H}^+(\mathrm{aq}) \tag{1}$$

forming both "mononuclear" ($p = 1$) and "polynuclear" ($p > 1$) species. Quantification of these equilibria is essential to understanding the behavior of Pb(II) under the near-neutral conditions typical of most environmental and physiological situations. There is also considerable interest in the Pb(II)/OH^- species present at high pH in relation to the electroplating of lead and solder[8] and in the electrowinning of gold.[9]

Because of its importance, numerous studies have been made of the Pb(II)/OH^- system. From their comprehensive review, Baes and Mesmer[6] concluded that, at $[\mathrm{Pb(II)}]_T \approx 10$ μM,[10−12] only $\mathrm{Pb(OH)}_q^{(2-q)+}$, with $q \leq 3$, and $\mathrm{Pb_3(OH)_4}^{2+}$ were formed (Figure 1a). At higher $[\mathrm{Pb(II)}]_T$ an extensive range of poorly characterized polynuclear species is formed (Figure 1b).[6,12,13−15]

However, careful examination of the available data indicates considerable disagreement, especially with respect to the identity of the highest mononuclear complex. Solubility,[16,17] potentiometric,[11] and polarographic[18−21] data indicate that $\mathrm{Pb(OH)_3}^-$ (thermodynamically equivalent in aqueous solution to the so-called[16−22] "biplumbite" ion, $\mathrm{HPbO_2}^-$) is the highest complex formed. This is unusual in the context of the coordination chemistry of Pb(II)[23] but has been rationalized by analogy with Sn(II).[16,24] On the other hand, ultracentrifugation[25] and light-scattering studies[26] indicated that $\mathrm{Pb(OH)_4}^{2-}$ (equivalent in solution to the "plumbite" ion,[17] $\mathrm{PbO_2}^{2-}$) was formed, consistent with the existence of solid-state plumbite salts.[27−29] More recently, a potentiometric study by Ferri et al.[30] reported

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(1) Southwood, T. R. E. *Lead in the Environment, Ninth Report*; Royal Commission on Environmental Pollution: London, 1983.

(2) Chronopoulos, J.; Haidouti, C.; Chronopoulos, S. A.; Massas, I. *Sci. Total Environ.* **1997**, *196*, 91−98.

(3) Branica, M.; Konrad, Z. *Lead in the Marine Environment*; Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment; Pergamon: Oxford, 1977.

(4) Tessier, A.; Turner, D. R. *Metal Speciation and Bioavailability in Aquatic Systems*; Wiley: New York, 1995.

(5) Green, V. A.; Wise, G. W.; Callenbach, J. C. *Toxicity of Heavy Metals in the Environment, Part 1*; Marcel Dekker: New York, 1978.

(6) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.

(7) Richens, D. T. *The Chemistry of Aqua Ions*; Wiley: New York, 1997.

(8) von Frounhofer, J. A. *The Electrochemistry of Lead*; Academic Press: New York, 1979.

(9) Jeffrey, M. I.; Ritchie, I. M.; Labrooy, S. R. In *Electrochemistry in Mineral and Metal Processing IV*; Woods, R., Doyle, F. M., Richardson, P. E., Eds.; Electrochemistry Society: Pennington, NJ, 1996; pp 284−295.

(10) Throughout this paper square brackets denote concentrations and the subscript T indicates the total or analytical value.

(11) Carell, B.; Olin, A. *Acta Chem. Scand.* **1960**, *14*, 1999−2008.

(12) Olin, A. *Acta Chem. Scand.* **1960**, *14*, 126−150.

(13) Breza, M.; Manova, A. *Collect. Czech. Chem. Commun*. **1995**, *60*, 527−536.

(14) Breza, M.; Manova, A. *Polyhedron* **1999**, *18*, 2085−2090.

(15) Breza, M.; Manova, A. *Collect. Czech. Chem. Commun*. **1999**, *64*, 1269−1273.

(16) Garrett, A. B.; Vellenga, S.; Fontana, C. M. *J. Am. Chem. Soc.* **1939**, *61*, 367−373.

(17) Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry Volume VII*; Longman: London, 1970.

(18) Lingane, J. J. *Chem. Rev.* **1941**, *29*, 1−35.

(19) Vlcek, A. A. *Chem. Listy* 1954, *48*, 1474−1484.

(20) Karnaukhov, A. I.; Kosmatyi, V. E.; Grinevich, V. V. *Ukr. Khim. Zh.* **1984**, *50*, 1086−1088.

(21) Aksel'rud, N. V. *Russ. J. Inorg. Chem.* **1958**, *3*, 23−36.

(22) Pourbaix, M.; De Zoubov, N.; van Leugenhaghe, C.; van Rysselberghe, P. *Atlas d'equilibres electrochimiques*; Gauthier-Villars: Paris, 1963.

(23) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999.

(24) Harrison, P. G. *Chemistry of Tin*; Blackie: Glasgow, 1989.

(25) Johnson, J. S.; Kraus, K. A. *J. Am. Chem. Soc.* **1959**, *81*, 1569−1572.

(26) Pokric, B.; Pucar, Z. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1987−1993.

(27) Byström, A.; Evers, L. *Acta Chem. Scand.* **1950**, *4*, 613−627.

(28) Godinho, O. E. S.; Rohwedder, J. J. R.; Eberlin, M. N.; Aleixo, L. M.; De Oliveira Neto, G. *Talanta* **1991**, *38*, 213-215.

(29) Speranskaya, E. I. *Russ. J. Inorg. Chem.* **1961**, *6*, 1000−1001.

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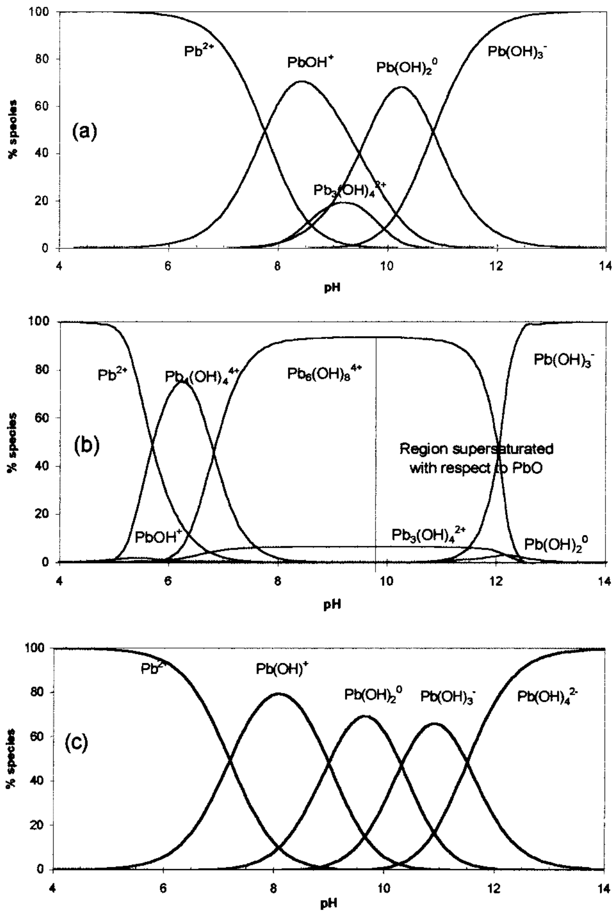

Figure 1. Lead(II) speciation at $I = 1$ M and 25 °C as a function of pH according to Baes and Mesmer[6] at $[\mathrm{Pb(II)}]_T$ of (a) 10 μM and (b) 0.1 M. (c) Present work at $[\mathrm{Pb(II)}]_T = 10$ μM.

mononuclear complexes with $q \leq 6$ (but not 5) at $[\mathrm{OH}^-] \leq 4.2$ M.

Following Byrne and Young,[31] UV−visible spectrophotometry has been applied to the Pb(II)/OH$^-$ system, using a long optical path length cell (Figure S1) at low $[\mathrm{Pb(II)}]_T$ to minimize the possible kinetic and computational problems associated with precipitation[32] and the formation of polynuclear species.[6] Attempts were made to confirm the results using ^{207}Pb nuclear magnetic resonance (NMR) and Raman spectroscopies and differential pulse polarography (DPP).

Experimental Section

Materials and Equipment. Solutions were prepared using calibrated A-grade volumetric glassware and high-purity water (Millipore Milli-Q system), boiled and purged with high-purity N_2. Stock solutions of ∼8 M were prepared from $\mathrm{NaClO_4 \cdot }x\mathrm{H_2O}$ (Aldrich, USA, "99.99%"), filtered (0.45 μm), and analyzed (±0.1%) gravimetrically.[33] Stock solutions of ca. 8 M NaOH ($[\mathrm{Na_2CO_3}]_T < 4$ mM)[34] were prepared from analytical grade reagent (Ajax, Australia, 97%) and standardized (±0.2%) potentiometrically against HCl (BDH, concentrated volumetric standard). $\mathrm{HClO_4}$ stock solutions (∼0.1 M) were prepared from ∼70% $\mathrm{HClO_4}$ (BDH, UK, AR) and standardized (±0.2%) against NaOH (BDH, CVS) using methyl orange.[33] Dilute $\mathrm{Pb(ClO_4)_2}$ stock solutions (∼0.01 M) were prepared by dissolving freshly precipitated white "lead hydroxide" in $\mathrm{HClO_4}$. Concentrated $\mathrm{Pb(ClO_4)_2}$ solutions (∼1 M) were prepared by dissolving excess "basic" lead carbonate, $\mathrm{Pb(OH)_2 \cdot PbCO_3}$(s) (BDH, LR), in 2 M $\mathrm{HClO_4}$ and filtering (0.45 μm). The exact concentration of $\mathrm{Pb^{2+}}$ was determined (±0.2%) titrimetrically against EDTA (BDH, CVS) using Eriochrome Black T.[33]

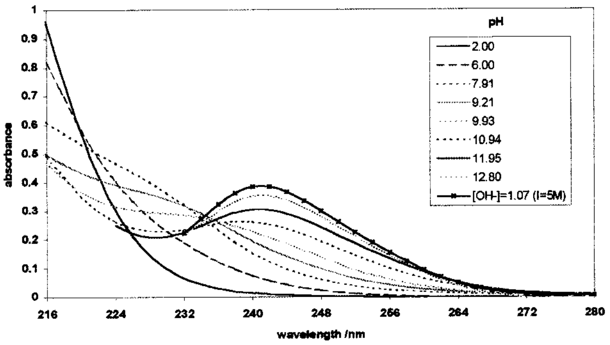

Figure 2. Representative background-subtracted UV−vis absorption spectra of 9.0 μM $\mathrm{Pb(ClO_4)_2}$ at $I = 1$ M ($\mathrm{NaClO_4}$), $2 \leq \mathrm{pH} \leq 13$; and of 8.0 μM $\mathrm{Pb(ClO_4)_2}$ at $I = 5$ M ($\mathrm{NaClO_4}$) at high $[\mathrm{OH}^-]$ (truncated at 232 nm due to the high background absorbance).

UV−Vis Spectrophotometric Titrations. Absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer using a combined spectrophotometric−potentiometric titration cell (Figure S1[35]). The optical path length was measured as 10.76 ± 0.05 cm using $\mathrm{K_2Cr_2O_7}$.[36] Solutions were stirred with a PTFE-coated magnetic bar driven by a magnetic rotor (Metrohm, Switzerland, model E402) mounted at 90° to the cell.

The cell temperature was maintained at 25.0 ± 0.05 °C using a circulator−thermostat (Grant Instruments, UK, model SB3/74GB) and was monitored with a calibrated mercury thermometer (NIST-traceable). Where appropriate, a glass electrode (Metrohm, model 6.0101.000) and Ag/AgCl reference electrode were used, in conjunction with a 1 or 5 M $\mathrm{NaClO_4}$ salt bridge to monitor the solution pH. The electrodes were calibrated ex situ in terms of $[\mathrm{H^+}]$, and throughout this paper $\mathrm{pH} = -\log[\mathrm{H^+}]$. All titrations were performed under N_2 at constant ionic strength I $(= {}^1/_2\sum c_i z_i^2)$. Titrant was added from a piston buret (Metrohm Dosimat, model 665, calibrated accuracy ±0.1%), and potentials were measured to ± 0.1 mV after 1−5 min of equilibration.

Background spectra (Figure S2) were obtained by titrating $\mathrm{H^+}$ with $\mathrm{OH^-}$ at $I = 1$ or 5 M ($\mathrm{NaClO_4}$). Complexation at constant I was measured by titrating $[\mathrm{Pb(II)}]_T = 5$−10 μM in 0.01 M $\mathrm{H^+}$ with $\mathrm{OH^-}$. Precipitation was monitored using absorbances at $\lambda > 300$ nm. All spectra were recorded from 190 to 800 nm. However, only the data from 216 to 300 nm at pH < 10.8, and 232 to 300 nm at higher pH values, were processed because of the spectral contribution from $\mathrm{OH^-}$ at short λ (Figure S2) and the absence of information at longer λ (Figure 2). The minimum wavelength selected, $\lambda_{\min}$, corresponded to a change in background absorbance ≤0.1 and a total absorbance ≤1.0. Background spectra at the required pH were obtained by linear interpolation of spectra from closely spaced pH intervals, and were subtracted from the Pb(II)-containing solutions, using EXCEL. The background-subtracted spectra were evaluated with the program SPECFIT.[37,38]

Differential Pulse Polarography. DPP measurements were performed as titrations under N_2 at 25.0 ± 0.05 °C, with $[\mathrm{Pb(II)}]_T \leq 10$ μM at $I = 1$ or 5 M ($\mathrm{NaClO_4}$), using a Metrohm Polarecord E 506 and polarography stand E505, with a pulse of 30 mV and a drop time of

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(30) Ferri, D.; Salvatore, F.; Vasca, E. *Ann. Chim.* **1989**, *79*, 1−13.

(31) Byrne, R. H.; Young, R. W. *J. Solution Chem.* **1982**, *4*, 127−136.

(32) The white solid, generally thought of as $\mathrm{Pb(OH)_2}$(s), which precipitates instantly when solutions containing Pb(II) and $\mathrm{OH^-}$ are mixed is often a "basic lead salt" Pb(OH)X (s), where X = $\mathrm{NO_3^-}$, $\mathrm{CO_3^{2-}}$, $\mathrm{ClO_4^-}$, etc. Solid $\mathrm{Pb(OH)_2}$ is believed to form at low $[\mathrm{Pb(II)}]_T$ or in the presence of counterions (e.g., acetate) that form reasonably soluble basic lead salts,[17] but it is unstable with respect to dehydration to form the more stable lead oxides.[17]

(33) Jeffery, H.; Bassett, L.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman: New York, 1989.

(34) Sipos, P.; May, P. M.; Hefter, G. T. *Analyst* **2000**, *125*, 955−958.

(35) See the Supporting Information.

(36) Haupt, G. W. *J. Opt. Soc. Am.* **1952**, *42*, 441−447.

(37) Maeder, M.; Zuberbuhler, A. D. *Anal. Chem.* **1990**, *62*, 2220−2224.

(38) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1985**, *32*, 257−264.

Table 1. Formation Constants of the Hydrolysis Products of Lead(II) at 25 °C from Selected Literature Studies and Results of This Study

			log $^*\beta_{1q}$						
ionic strength/M	$[Pb(II)]_T$/mM[a]	$[OH^-]_T$/M[a,b]	$Pb(OH)^+$	$Pb(OH)_2^0$	$Pb(OH)_3^-$	$Pb(OH)_4^{2-}$	method[c]	ref	year
0.3 ($NaClO_4$)	0.3−10	0.003−0.4		−17.2	−28.0		Pb(Hg)	11	1960
0.3 ($NaClO_4$)	1.3−80	(5−8)	−7.8				Pb(Hg)	12[d]	1960
1 ($NaClO_4$)	1−10	(5.5−8.5)	−7.8				Pb(Hg), cal	63[d]	1993
2 ($NaClO_4$)	0.1−100	(5.5−7.5)	−7.9				Pb(Hg)	64[d]	1964
3 ($NaClO_4$)	0.3−10	0.003−0.4		−17.5	−29.0		Pb(Hg)	11	1960
3 ($NaClO_4$)	1.3−80	(5−8)	−7.9				Pb(Hg)	12[d]	1960
5 ($NaClO_4$)	0.7−4	0.4−4			−30.3[e,f]	−45.6[e,f]	Pb(Hg)	30	1989
0					−28.1[g]		Pol	19	1954
0.1 (KNO_3)	$10^{-3}-10^{-2}$	(7−11)	−6.8[h]	−16.1[h]			ASV	47	1976
0.1 (KNO_3)	$10^{-2}-10$	(5.5−6.5)	−7.4[h]	−14.2[h]			Pb(Hg)	65[d]	1977
1 (KNO_3)	1−50	(5.5−8.5)	−7.94				Pb(Hg), cal	63[d]	1993
1 (KNO_3)	0.5	0.01−1			−27.2[h]		Pol	18	1941
2 (KNO_3)	0.3	0.3−2			−29.5[h]		IC	20	1984
1 ($NaClO_4$)	$5 \times 10^{-3}-10^{-2}$	(2−12.6)	−7.2 ± 0.3[i] {6.6}[j]	−16.1 ± 0.5[i] {11.4}[j]	−26.5 ± 0.5[i] {14.8}[j]	−38.0 ± 0.3[i] {17.1}[j]	UV−vis	this study	
5 ($NaClO_4$)	9×10^{-3}	(2−12.5)	−7.2 ± 0.3[i] {7.6}[j]	−16.2 ± 0.2[i] {13.4}[j]	−26.7 ± 0.7[i] {17.6}[j]	−38.7 ± 0.8[i] {20.4}[j]	UV−vis		

[a] Approximate reported total concentration range. [b] Values in parentheses are pH ranges. [c] Abbreviations: Pb(Hg), potentiometry with a lead amalgam electrode; cal, calorimetry; pol, polarography; ASV, anodic stripping voltammetry; IC, inverse chronoamperometry; UV−vis, UV−vis spectrophotometry. [d] Polynuclear species are also reported. [e] log $^*\beta_{16} = -76.1$ also reported. [f] Recalculated using a pK_w of 14.8 ($I = 5$ M $NaClO_4$).[44] [g] Recalculated using a pK_w of 14.0 ($I = 0$).[6] [h] Recalculated using a pK_w of 13.8 ($I = 0.1$ M KNO_3), 13.7 ($I = 1$ M KNO_3), and 13.9 ($I = 2$ M KNO_3).[66] [i] Uncertainty expressed as the standard deviation of all of the log $^*\beta_{pq}$ values (Table S1). [j] Log β_{pq} values as defined in eq 3.

0.4 s. Potentials were measured (±0.2 mV) relative to a Ag/AgCl reference electrode using a 1 or 5 M $NaClO_4$ salt bridge, and a Pt wire as the auxiliary electrode.

Formation constants (β_{1q}) corresponding to the equilibria

$$Pb^{2+} + qOH^- \Leftrightarrow Pb(OH)_q^{(2-q)+} \tag{2}$$

where

$$\log {}^*\beta_{1q} = \log \beta_{1q} - q(pK_w) \tag{3}$$

were obtained from the experimental polarographic formation function[39−43] using the DeFord−Hume approach.[42,43] pK_w was taken to be 13.77 at $I = 1$ M ($NaClO_4$) and 14.80 at $I = 5$ M ($NaClO_4$).[44]

^{207}Pb-NMR Spectroscopy. ^{207}Pb-NMR measurements were made at $[Pb(II)]_T = 5$ mM and 0.05 M < $[OH^-]$ < 5 M at $I = 5$ M ($NaClO_4$) in a 4 mm diameter PTFE tube fitted inside a 5 mm quartz NMR tube. Some (solubility-constrained) measurements were made at higher $[Pb(II)]_T$. Spectra were recorded on a Bruker Avance DPX300 pulse Fourier transform NMR spectrometer at 25 ± 1 °C using 3200 scans. The magnetic field was adjusted to give a ^{207}Pb resonance for tetramethyllead (TML) at 62.76179 MHz. Chemical shifts were reported relative to TML by assigning a shift of −2872.7 ppm to an external reference of 0.093 M $Pb(ClO_4)_2$ in water.[45]

Raman Spectroscopy. Solutions of NaOH (0.1−7 M) were saturated with an appropriate Pb(II) compound for a few days. Supernatant solutions were then withdrawn and analyzed for $[Pb(II)]_T$ by ICPAES. Raman spectra were recorded using a Nicolet Magna-IR 850 (series II) Fourier transform spectrometer (YVO_4 laser, 1.5 W at 1056 nm). Spectra were recorded (16384 scans) with a resolution of 4 cm^{-1} and background-subtracted using the Galactic Grams 5.2 software. Polarized spectra were recorded with an ISA Labram 1B dispersive Raman spectrometer (argon laser at 514 nm) with a resolution of 1.3 cm^{-1}.

Results and Discussion

UV−Visible Spectrophotometry. Background Spectra. At low pH the background absorbance (A) was significant only at $\lambda < 220$ nm, but at higher pH it increased markedly and shifted to longer λ (Figure S2[35]).[46]

Pb^{2+} Solutions. Details of the spectrophotometric data are summarized in Table S1.[35] Background-subtracted spectra of 9 μM Pb(II) in 1 M ($NaClO_4$) showed (Figure 2) four isosbestic points, at 219, 223, 234, and 231 nm. The near-zero A (<0.05, equivalent to $A < 0.005$ in a conventional 1 cm path length cell) at $\lambda > 300$ nm indicated that the solutions were homogeneous. At pH ≤ 10.4, absorbances from 216 to 300 nm were consistent with the presence of Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2^0$, and $Pb(OH)_3^-$. At higher pH, a further species, $Pb(OH)_4^{2-}$, was detected, producing a single Gaussian band at $[OH^-]_T \geq 0.25$ M (Figure 2). No evidence was found for any higher order complex at $[OH^-]_T/[Pb(II)]_T \leq 5 \times 10^5$.

The species $Pb_3(OH)_4^{2+}$, well-established potentiometrically,[6,12] should be present at significant levels at $[Pb(II)]_T = 10$ μM if the model of Baes and Mesmer (Figure 1a) is correct. However, optimizations that included any polynuclear species did not converge or gave unrealistic calculated spectra. Furthermore, the spectra were independent of $[Pb(II)]_T$ over the range 5-10 μM, consistent with the absence of polynuclear species. Spectra were independent of time for at least several weeks, ruling out significant kinetic complications. Carbonato complexes[47] were shown to be absent by addition of 50 μM carbonate (at pH ∼ 10), which is well above likely contamination levels.[34]

The stability constants (log $^*\beta_{1q}$) obtained for the four mononuclear $Pb(OH)_q^{(2-q)+}$ complexes detected by UV−vis spectrophotometry are summarized in Table 1, which also gives the log β_{1q} values (eq 2) calculated via eq 3. As found previously,[11,12] the log $^*\beta_{1q}$ values show almost no dependence on ionic strength, because of the variation of pK_w with I.[44] The β_{1q} do show the expected increase with I.

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(39) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1966.
(40) Meites, L. *Polarographic Techniques*, 2nd ed.; Wiley: New York, 1965.
(41) Bond, A. M. *Coord. Chem. Rev.* **1971**, *6*, 377−405.
(42) Heath, G. A., Hefter, G. T. *J. Electroanal. Chem.* **1977**, *84*, 295.
(43) DeFord, D. D.; Hume, D. N. *J. Am. Chem. Soc.* **1951**, *73*, 5321−5322.
(44) Turonek, M. L.; Hefter, G. T.; May, P. M. *Talanta* **1998**, *45*, 931−934.
(45) Harrison, P. G.; Healy, H. A.; Steel, A. T. *J. Chem. Soc., Dalton Trans.* **1983**, 1845−1848.
(46) Sipos, P.; May, P. M.; Hefter, G. T.; Kron, I. *J. Chem. Soc., Chem. Commun.* **1994**, 2355−2356.
(47) Bilinski, H.; Huston, R.; Stumm, W. *Anal. Chim. Acta* **1976**, *84*, 157−164.

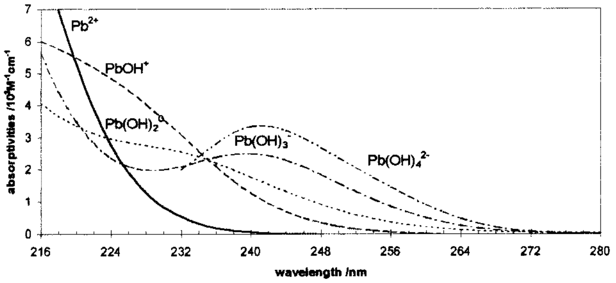

Figure 3. UV−vis spectra of the individual mononuclear Pb-$(OH)_q^{(2-q)+}$(aq) at $I = 1$ M ($NaClO_4$) and 25 °C.

The uncertainties in the constants are larger than those typically achieved for uncomplicated systems[48] but are similar to or better than those previously reported using other techniques (Table 1).[11,12,30] These uncertainties reflect the difficulties of making accurate absorbance measurements at short λ and the feebleness of the buffering at low $[Pb(II)]_T$ for $4 < pH < 9$. Radiotracer measurements indicate that the adsorption of Pb(II) species on the cell walls should be negligible.[49]

The deconvoluted spectra of the individual complexes (Figure 3) show a systematic shift to longer λ with increasing OH^- coordination. The charge-transfer band for Pb^{2+}(aq) has a distinct peak (not shown for representational convenience) at 210 nm with $\epsilon_{max} = 11.8 \times 10^3\ M^{-1}\ cm^{-1}$. For $PbOH^+$(aq) only a broad absorption band is seen, centered at ~210 nm with $\epsilon_{max} \sim 6 \times 10^3\ M^{-1}\ cm^{-1}$. The band for $Pb(OH)_2^0$(aq) is also broad with a barely discernible shoulder at 227 nm ($\epsilon_{max} = 2.8 \times 10^3\ M^{-1}\ cm^{-1}$). $Pb(OH)_3^-$(aq) shows one resolved peak at 239 nm ($\epsilon_{max} = 2.5 \times 10^3\ M^{-1}\ cm^{-1}$) which is close to but distinguishable from that for $Pb(OH)_4^{2-}$(aq) at 241 nm ($\epsilon_{max} = 3.4 \times 10^3\ M^{-1}\ cm^{-1}$).

The species distribution calculated from the present spectrophotometric results for a $[Pb(II)]_T = 10\ \mu M$ solution is shown in Figure 1c. This differs from that of Baes and Mesmer[6] (Figure 1a) specifically with respect to the presence of $Pb(OH)_4^{2-}$ and the absence of $Pb_3(OH)_4^{2+}$.

Differential Pulse Polarography. The high sensitivity of DPP enables a low $[Pb(II)]_T$ to be used, and this technique is applicable in the presence of precipitation, provided that the complexation kinetics are rapid and the precipitation is sufficiently slow.[42,50] Table S2[35] summarizes the DPP data obtained for the Pb(II)/OH^- system at $I = 5$ M ($NaClO_4$). Similar data were obtained under other conditions (Figure S3[35]). All polarograms were well defined, with half-widths (full widths at half-maximum, fwhm) of 51.5 ± 1.5 mV (theoretical is 51.5 mV).[51]

Unfortunately, DPP is of limited use for calculating the Pb(II)/OH^- stability constants. First, β_{11} cannot be reliably determined[18,19] because of the weak buffering at low [Pb(II)] and $[OH^-]$. Second, as found by earlier workers,[18,19] the DPP data at high $[OH^-]$ are inconsistent with the stepwise model of complex formation, vitiating quantification of any higher order complexes.[52]

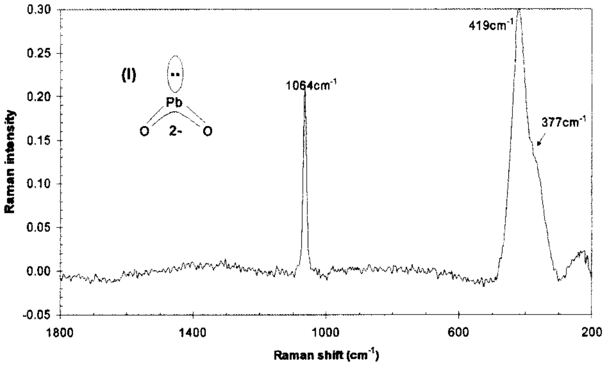

Figure 4. Background-subtracted Raman spectrum of a 7 M NaOH solution saturated with massicot (yellow PbO) at ~25 °C; $[Pb(II)]_T$ ~ 0.1 M.

Nevertheless, the DPP data could be used to estimate the stability constants of the middle order complexes. Assuming the present spectrophotometric values of β_{11} (Table 1), values of $\log \beta_{12} = 11.2 \pm 0.1$ and $\log \beta_{13} = 13.18 \pm 0.05$ (at $I = 1$ M ($NaClO_4$)) and $\log \beta_{12} = 12.8 \pm 0.2$ and $\log \beta_{13} = 14.53 \pm 0.05$ (at $I = 5$ M ($NaClO_4$)) are obtained. β_{12} is in reasonable agreement with the spectrophotometric values (Table 1), but the β_{13} results, which agree well with previous polarographic studies,[18,19] are lower probably because of the effect referred to above.

^{207}Pb-NMR Spectroscopy. Very large variations in $\delta(^{207}Pb)$ were observed with changes in pH, shifting from −2813.9 ppm at $[H^+]_T = 0.01$ M to 1066.3 ppm at $[OH^-]_T = 5$ M. Unfortunately, $\delta(^{207}Pb)$ is also sensitive to the overall solution "environment";[45,53] e.g, at $[Pb(II)]_T = 0.1$ M and $[H^+] = 0.01$ M, where only Pb^{2+}(aq) should be present, the signal moved from −2872.0 to −2812.0 ppm as I increased from 0.3 to 5 M ($NaClO_4$).

Because of the precipitation of "$Pb(OH)_2$(s)", NMR measurements were restricted to solutions with a significant excess of OH^-. Only one signal of constant intensity and width (fwhm = 7.5 Hz) was observed throughout (Figure S4[35]), consistent with fast complex formation. The variation of $\delta(^{207}Pb)$ for $0.2 \le [OH^-] \le 5$ M at $I = 5$ M ($NaClO_4$) was consistent with the presence of two complexes. However, the small change ($\Delta\delta = 22$ ppm) is probably caused by "environmental" effects rather than a speciation change.

Raman Spectroscopy. Background-subtracted Raman spectra of solutions of NaOH saturated with yellow PbO (massicot) or other Pb(II) sources showed two distinct bands, at around 419 and 1064 cm^{-1} (Figure 4). The latter was shown not to be due to CO_3^{2-} by deliberate addition. Integrated intensities of both bands were linearly dependent on $[Pb(II)]_T$ (ICPAES) at $0.1\ M \le [OH^-]_T \le 7$ M. Band positions and shapes were independent of $[Pb(II)]_T$ and $[OH^-]_T$, indicating that only one mononuclear complex was present. Both main bands were strongly polarized and were therefore assigned to A_{1g} vibrational modes.[54] The band at 1064 cm^{-1} is of higher energy than the Pb−O stretching in $Pb_4(OH)_4^{4+}$ (404 cm^{-1}),[55] possibly suggesting that $Pb(OH)_4^{2-}$(aq) might exist as PbO_2^{2-} (**I** in Figure 4), which has C_{2v} symmetry with $2A_{1g} + B_2$ Raman active vibrational modes.[56,57]

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(48) Rossotti, H. *The Study of Ionic Equilibria: An Introduction*; Longman: London, 1978.

(49) Benes, P.; Sanyal, A. S.; Kristofikova, Z.; Obdrzalek, M. *Radiochim. Acta* **1981**, *28*, 35−38.

(50) Bond, A. M.; Hefter, G. T. *J. Electroanal. Chem.* **1972**, *34*, 227−237.

(51) Bond, A. M. *Modern Polarographic Methods in Analytical Chemistry*; Marcel Dekker: New York, 1980.

(52) Perera, W. N. Ph.D. Thesis, Murdoch University, Western Australia, 2001.

(53) Laszlo, P. *NMR of Newly Accessible Nuclei Vol 2, Chemically and Biochemically Important Elements*; Academic Press: New York, 1983.

(54) Schrader, B. *Infrared and Raman Spectroscopy*; VCH: New York, 1995.

(55) Maroni, V. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1967**, *89*, 45−48.

(56) Bishop, D. M. *Group Theory and Chemistry*; Clarendon: Oxford, 1973.

(57) Fadini, A.; Schnepel, F. M. *Vibrational Spectroscopy Methods and Applications*; Ellis Horwood: Chichester, 1989.

Mononuclear Complexes. The present UV−vis spectrophotometric results provide clear-cut evidence for four mononuclear $Pb(OH)_q^{(2-q)+}$ complexes ($q \leq 4$) alone. No evidence for higher order or polynuclear complexes was found at $[Pb(II)]_T \leq 10$ μM with $[OH^-]/[Pb(II)]_T \leq 5 \times 10^5$. The $*\beta_{1q}$ values lie within the ranges reported in previous investigations, although they are somewhat lower (the β_{1q} values are higher) than those determined by potentiometry (Table 1).

The most recent potentiometric study[30] requires comment. The formation constants obtained by Ferri et al.[30] using the cell Ag|AgBr|test solution|Pb(Hg) depend critically on the activity coefficient corrections derived via the Pitzer formalism. The need to estimate many of the required interaction parameters introduces unknown uncertainties into their results, as does their use of a cell without a liquid junction.[48] Furthermore, Ferri et al.[30] reported $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, and $Pb(OH)_6^{4-}$ but not $Pb(OH)_5^{3-}$. Although "missing" complexes in a stepwise sequence are known, they are rare. No other study has found any evidence for $Pb(OH)_6^{4-}$ in solution nor in the solid state, and its existence is inconsistent with all of the present (UV−vis, NMR, and Raman) spectroscopic data.

It is also notable that all studies employing lead amalgam electrodes have reported anomalies at high $[OH^-]$. The polarographic data (where a lead amalgam is generated in situ) and the data of Ferri et al.[30] have already been discussed. Carell and Olin[11] had to postulate the existence of a highly improbable $(OH)_2^{2-}$ species to rationalize their Pb(Hg) potentiometric data at $[OH^-] > 0.2$ M, and Karnaukhov et al. reported anomalies using inverse chronoamperometry.[20]

These effects are *not* due to activity coefficient variations, as has been speculated,[11,18] because extensive isopiestic measurements[58] on $NaOH/NaClO_4$ mixtures show no unusual behavior. The likely cause is that Pb(Hg) electrodes are not thermodynamically stable at high $[OH^-]$,[22,23] although the rate of corrosion must be sufficiently slow such that stable mixed potentials are observed.[59] If this is so, reliable thermodynamic information cannot be obtained on the $Pb(II)/OH^-$ system from measurements employing any variant of Pb(Hg) electrodes.

It is useful to consider the insights offered by other techniques. The (rather old) solubility measurements[16,17] indicate formation of only $Pb(OH)_3^-$. However, as these studies were not conducted at constant I and the precise nature of the solid formed was unknown,[17,32] little weight can be given to these data.

Pokric and Pucar,[26] using the Tyndall effect, showed that the charge of the soluble species in equilibrium with the precipitate under highly alkaline conditions was −2, which they attributed to a polynuclear species, even though their $[Pb(II)]_T$ was $<10^{-4}$ M. However, an identical result obtained by Johnson and Kraus[25] using ultracentrifugation, which is mass and size sensitive, was consistent with the presence of $Pb(OH)_4^{2-}$. If indeed only $Pb(OH)_4^{2-}$ is present at high $[OH^-]_T$, then, using the solubility products $\log *K_{s0} = 9.1$ and $\log *K_{s4} = -29.22$, from Pokric and Pucar's Figure 1, and their equation[26]

$$\mathrm{pH} = (1/n)(\log *K_{sq} - \log [Pb(OH)_q^{\ n}]) \qquad (4)$$

a value of $\log *\beta_{14} = -38.32$ is obtained at $I = 0.5$ M, 20 °C. This result is close to the present spectrophotometric value of −38.0 (at $I = 1$ M, 25 °C, Table 1).

Finally, a number of workers[60−62] have predicted β_{13} and β_{14} on the basis of empirical correlations using the relatively uncontroversial values of β_{11} and β_{12}. These predicted values are also close to those obtained from the present spectrophotometric experiments (Table 1).

Polynuclear Complexes. A variety of polynuclear complexes have been reported, but, except for $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$, they have not been well characterized.[6] Although such species are favored at higher $[Pb(II)]_T$, Baes and Mesmer's[6] model, based largely on Carell and Olin's constants,[11,12] suggests that $Pb_3(OH)_4^{2+}$ remains significant even at $[Pb(II)]_T \approx 10$ μM (Figure 1a). Unless this species does not have an absorption band in the UV−vis region, which seems improbable, the present spectrophotometric data clearly show that $Pb_3(OH)_4^{2+}$ does not form to a significant extent under such conditions. It is readily shown that the distribution plot in Figure 1c, which uses the present formation constants for the mononuclear species, is unaffected by the inclusion of Olin's[12] formation constant for $Pb_3(OH)_4^{2+}$. Similar results are obtained upon inclusion of any of the other polymeric species.[6] It is concluded that Baes and Mesmer's model[6] overestimates the magnitude of the polymeric species and underestimates the formation of the mononuclear species. That is, when proper allowance is made for the formation of $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$, polynuclear species are *not* significant at low $[Pb(II)]_T$ over the entire pH range.

Conclusions

UV−vis spectrophotometry of the $Pb(II)/OH^-$ system ($[Pb(II)]_T \leq 10$ μM and $[OH^-]_T \leq 5$ M) reveals the presence of only four species: $Pb(OH)_q^{(2-q)+}$ ($q = 1-4$). These mononuclear complexes are the only hydrolysis products of Pb(II) that are likely to be important under typical environmental and biological conditions. Other techniques gave only semiquantitative confirmation, and it appears that methods employing Pb(Hg) electrodes are unsuitable for studying this difficult system.

Acknowledgment. The authors thank P. M. May for helpful discussions, G. Whiting (Hi Tech Glass, Perth, Western Australia) for constructing the cell, L. Byrne (University of Western Australia) and T. Osborne (Murdoch University) for assistance with the NMR measurements, B. van Bronswijk (Curtin University of Technology) for the polarized Raman spectra, and Stanley (Murdoch University) for assistance with the speciation plots.

Supporting Information Available: Tables S1 and S2; Figures S1, S2, S3, and S4. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001415O

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(58) Huang Fu, J. H.; May, P. M.; Hefter, G. T. Unpublished observations.
(59) Girciene, O.; Visomirskis, R. *Chemija* **1995**, *4*, 54−60; *Chem. Abstr.* **1996**, *124*, 69812).
(60) Parkhurst, L. *ACS Symp. Ser.* **1990**, *416*, 30−43.
(61) Brown, P. L.; Wanner, H. *Predicted Formation Constants, Using the Unified Theory of Metal Ion Complexation*; OECD Nuclear Energy Agency: Paris, 1987.
(62) Povar, G. *Russ. J. Inorg. Chem.* **1993**, *38* 1782−1786.
(63) Cruywagen, J. J.; van de Water, R. F. *Talanta* **1993**, *40*, 1091−1095.
(64) Hugel, R. *Bull. Soc. Chim. Fr.* **1964**, 1462−1469.
(65) Birraux, J. C.; Landry, L.; Haerdi, W. *Anal. Chim. Acta* **1977**, *93*, 281−285.
(66) Kron, I.; Marshall, S. L.; May, P. M.; Hefter, G.; Konigsberger, E. *Monatsh. Chem.* **1995**, *126*, 819−837.