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NOTES:

MAIN 1962-1993
Publisher 2000-2002 Online
Publisher 2002-9999 Online

ARTICLE INFORMATION

0033-8230
Radiochimica Acta
48(1-2):29 35 1989
FELMY, AR RAI, D SCHRAMKE, JA
THE SOLUBILITY OF PLUTONIUM HYDROXIDE IN DILUTE-SOLUTION AND IN HIGH-IONI
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Radiochimica Acta *48*, 29–35 (1989)

The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines

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(Received January 13, 1989)

Plutonium / Modeling

Summary

The solubility of $Pu(OH)_3$ is determined in deionized water and in chloride brines that contained Fe powder to maintain Pu in the Pu(III) oxidation state. The presence of aqueous Pu(III) was verified experimentally. The solubility of $Pu(OH)_3$ is several orders of magnitude greater in brines than in deionized water at the same hydrogen ion concentration. The logarithm of the equilibrium constant, extrapolated to zero ionic strength from experiments in deionized water, for the reaction $Pu(OH)_3 \rightleftharpoons Pu^{3+} + 3\,OH^-$ is determined to be -26.2 ± 0.8. The data for solubility in brines are interpreted in terms of the ion-interaction model of Pitzer and coworkers for the excess solution free energy. These solubility data can be explained to within experimental error by a relatively simple ion-interaction model that includes only binary interactions between Pu^{3+} and Cl^-. Ion pairs or ternary interaction parameters for Pu^{3+} were not required in order to predict the solubility of $Pu(OH)_3$ in natural chloride-dominated brines at $-\log[H^+]$ values of <9, where brackets represent concentration.

Introduction

Plutonium is an important component of high-level nuclear wastes. In the geologic disposal of high-level nuclear wastes, the presence of steel and other components in the waste package could result in a reducing environment in which Pu(III) would be expected to be the dominant oxidation state in solution. In addition, because Pu-containing wastes may be placed in repositories in salt, it is necessary to understand the aqueous chemistry of Pu(III) in concentrated natural brines as well as in dilute natural waters.

Plutonium(III) compounds that have both fast precipitation/dissolution kinetics and relatively low solubility can be used to determine upper limits for the Pu concentrations that may be leached from repositories where Pu(III) is stable. One such Pu(III) compound in highly alkaline environments (such as those that would be encountered in proposed salt repository sites) is $Pu(OH)_3$. However, no definitive experimental data for the solubility product of the reaction $[Pu(OH)_3 \rightleftharpoons Pu^3 + 3\,OH^-]$ are available. The logarithm of the solubility product values reported in the literature vary from about -19.7 to -27 [1–8]. These values either are derived from Busey and Cowan's [3] data from experiments titrating $PuCl_3$ solutions with NaOH or are estimated [1, 2, 4, 8]. Because of the large variability in the reported solubility products of $Pu(OH)_3$ and the lack of reliable experimental data, there is a need for experimental evaluation of the solubility product of $Pu(OH)_3$.

One of the overall objectives of our research is to develop models that will predict the solubility of $Pu(OH)_3$, and eventually other actinide-containing solid phases, in complex, multicomponent natural waters. Such models can be used to predict the chemical behavior of natural waters and thereby to support geochemical field investigations. The accuracy of these models is critically dependent on the standard chemical potentials of the aqueous and solid species considered in the model and on the expressions for the activity coefficients of the aqueous species. The accuracy of such geochemical models is usually restricted to relatively dilute solutions ($I \sim 0.1\,M$), principally because they use expressions for the activity coefficient (such as the Debye-Hückel expression) that are valid only in dilute solutions. However, the ion-interaction model of Pitzer [9, 10] for the excess solution free energy has been shown to accurately calculate mineral solubilities in complex natural systems from zero to high concentration [11–14]. This model recognizes that at high concentrations activity coefficients are no longer universal functions of ionic strength but rather depend upon the specific ions present in solution. The necessary ion-interaction parameters are usually determined from osmotic, emf, or solubility data in binary and common-ion ternary systems. Unfortunately, none of these necessary parameters are available for Pu(III) aqueous species.

The objectives of this study, therefore, are to experimentally evaluate the solubility product of $Pu(OH)_3$ in dilute solutions and to conduct $Pu(OH)_3$ solubility experiments in high-ionic-strength chloride brines to evaluate the applicability of Pitzer's [10] model in interpreting the solubility of $Pu(OH)_3$ in high-ionic-strength solutions. Our results show that 1) the logarithm of the solubility product of $Pu(OH)_3$ is (-26.2 ± 0.8) and is several orders of magnitude lower than the only other experimental value (-19.7; [3]) generally accepted, and 2) the solubility of $Pu(OH)_3$ in high-ionic-strength brines can be accurately predicted with the Pitzer [10] ion-interaction model using only parameters for binary interactions between Pu^{3+} and Cl^-.

Experimental materials and methods

A stock solution of Pu in concentrated HCl was prepared from ^{239}Pu that was purified by ion exchange and electrolytically reduced to Pu(III) immediately before use. The Pu concentration in the stock solution was approximately 1.25 *M*.

Several precautions were taken during the experiments to keep out oxygen and maintain Pu in the Pu(III) oxidation state. First, all experiments were conducted in an inert-atmosphere glove box where CO_2 and O_2 levels were kept low by continuous sparging with a prepurified argon. Second, the brines and deionized water used in the experiments were deoxygenated by bubbling with prepurified Ar for at least 1 h, followed by equilibration with Fe powder to further decrease the soluble O_2 content to levels where Pu(III) is stable. Third, to eliminate inadvertently introduced O_2 during experiments, Fe powder was added in each experiment. The efficiency of the Fe powder for decreasing soluble O_2 has been demonstrated previously [15].

The solubility of $Pu(OH)_3(s)$ is quite sensitive to hydrogen ion concentration, so experiments were conducted over a range of concentrations. The hydrogen ion concentration of the solutions was adjusted with reagent-grade HCl and reagent-grade, carbonate-free NaOH. In the hydrogen ion concentration range investigated, only the Pu^{3+} ion was anticipated to be present in significant concentrations, by analogy with Am^{3+} [16], so hydrolysis of the Pu^{3+} ion should not be a complicating factor in the experiments.

The experiments were conducted in glass centrifuge tubes at 23 ± 2°C. To demonstrate that equilibrium had been achieved in the experiments, solubility was approached from both oversaturation and undersaturation. For the oversaturation experiments, 10 mg of Fe metal and 30 ml of solution were placed in the glass tube, 0.020 ml of Pu(III) stock solution was added (approximately 5 mg Pu), the hydrogen ion concentration was adjusted, and the tube was sealed and placed on an orbital shaker. One of the concerns in preparing $Pu(OH)_3$ precipitates for undersaturation experiments is its possible oxidation during precipitation and during washing of the precipitates. To prevent $Pu(OH)_3$ oxidation by glove box air, the Pu(III) stock solution was added to 10 mg Fe powder in 30 ml of deoxygenated water, the observed pH was adjusted to 12 with carbonate-free NaOH, and the resulting suspension was shaken in a sealed tube for 24 h. The tube was then centrifuged and the supernatant discarded. The precipitate was washed with deoxygenated water adjusted to pH 12. The precipitates were suspended in either deoxygenated deionized water or brine. The pH values of these suspensions were then adjusted to the desired range. The tubes were sealed and placed on an orbital shaker in the glove box.

The experimental solutions were sampled after equilibration for 1 to 24 days. Eh values were measured with a platinum electrode calibrated with quinhydrone buffer solution. Solution aliquots were removed and passed through Amicon Centriflo® cones of 0.0018-μm pore size and analyzed for Pu concentration by liquid-scintillation alpha counting. To ensure that adsorption or precipitation of Pu onto the filters did not affect the results, the filters were preadjusted to the sample pH and pretreated with an aliquot of sample solution before they were used to filter the sample for analysis [17]. To determine whether the Pu(III) oxidation state was maintained during the experiments, selected samples were analyzed by solvent extraction to separate the Pu(III) + Pu(IV) oxidation states [17]. The solution pH was measured with a combination glass electrode (Orion-Ross®) calibrated against pH buffer solutions. During pH and Eh measurements, the electrodes were sealed in the tubes to minimize O_2 introduction into the tube from the glove box atmosphere.

The constituent concentrations in the Permian Basin brines, PBB1 and PBB3, were determined by inductively coupled-plasma chromatography (ICP) analysis. The molality of hydrogen ion in these brines was calculated from the observed pH meter reading according to a modified form of a Gran titration performed by Peterson and Peterson (unpublished data; see [18] for details of the titration procedure, [19–20] for a general discussion). In this method, the observed pH [pH(obs)] is equal to

$$\mathrm{pH(obs)} = pc_{\mathrm{H}^+} - A \quad (1)$$

where c_{H^+} is the concentration in molarity units and the constant A is defined by

$$A = \log \gamma_{\mathrm{H}^+} + \frac{F}{2.303\mathrm{RT}} \Delta E_j \quad (2)$$

where γ_{H^+} is the convention-dependent molarity-scale activity coefficient of H^+ and ΔE_j is the difference in liquid junction potential between standards and solutions. Neither term on the right side of eq. (2) is experimentally measurable but the combination of them, A, in eq. (2) can be measured.

Rewriting eq. (1) in terms of logarithms and then taking the antilog of both sides yields

$$\mathrm{H^+(obs)} = 10^A c_{\mathrm{H}^+} \quad (3)$$

The constant A is then obtained by a modified Gran titration in which the moles of added acid per liter is plotted against H^+(obs) (i.e., the negative of the antilog of the pH meter reading). The logarithm of the slope of this curve is the correction factor A needed to convert the observed pH to pc_{H^+}. The concentration in molarity units was then corrected to molality using the measured density. The values of A and the measured densities for PBB1 and PBB3 brines are given in Table 1.

Table 1. Measured densities and A parameters (Eq. 2) for permian basin brines

	PBB1	PBB3
Density (g/cm^3)	1.17	1.23
A	0.68	1.43

Results and discussion

The details of the solubility results for all experiments are plotted in Figure 1. Oxidation-state analyses of samples (Table 2) selected from among those reported in Figure 1 indicate that the Pu was present predominantly in the reduced oxidation states. These results, in conjunction with 1) the very low measured redox potentials (approximately −300 mV at the observed pH) where Pu(III) is the stable oxidation state and 2) the fact that measurable quantities of Pu(IV) will not be present at these pH values [as a result of the formation of insoluble Pu(IV) hydrous oxides [17], indicate that the aqueous Pu was primarily Pu(III). Therefore, it can be concluded that the powdered metallic Fe successfully maintained low redox potentials in the experiments so that Pu(III) was the stable oxidation state. The fact that log Pu concentrations as a function of pc_{H^+} in deionized water experiments conform closely to a slope of 3 further justifies the conclusion that the Pu present in the aqueous state is Pu(III). These results also strongly indicate that significant hydrolysis of Pu^{3+} does not occur.

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Table 2. Results of oxidation state analyses of Pu by solvent extraction from a selected set of duplicate samples

Sample[a] number	Eh(mV)	pH[b]	Pu(III) and Pu(IV) (%)	Pu(V) and Pu(VI) (%)	Nonextractable Pu(%)	Total (%)
Deionized water, oversaturation experiments						
222- 7	−294	6.86	88.9; 92.1	3.1; 4.9	0.1; 0.1	93.9; 95.3
224- 7	−355	6.83	46.6; 85.5	8.7; 51.8	0.1; 0.3	94.3; 98.7
225A-8	−278	6.62	88.2; 88.6	1.1; 2.4	0.1; 0.1	89.8; 90.7
226- 8	−352	7.80	89.6; 92.3	1.9; 2.0	0.8; 0.8	92.4; 95.0
228- 8	−311	8.08	82.9; 83.9	1.0; 1.8	1.2; 1.3	85.9; 86.2
230- 8	−282	7.28	67.0; 70.8	2.1; 2.6	0.1; 0.1	69.7; 73.0
Deionized water, undersaturation experiments						
282-21	−314	7.18	94.7; 95.2	nm[c]	0.6; 2.3	95.3; 97.5
PBB1, oversaturation experiments						
241-14	−269	8.08	94.2; 94.5	1.2; 1.4	0.5; 0.5	95.9; 96.4
PBB1, undersaturation experiments						
267-13	−284	7.88	95.1; 95.8	nm	3.6; 4.5	98.7; 100.3
266-19	−252	8.28	89.3	nm	7.5	96.8
271-19	−338	9.15	18.4	nm	85.9	104.3
PBB3, oversaturation experiments						
255-10	−256	6.39	69.0; 72.6	12.2; 19.3	0.2; 0.2	85.0; 88.5
259-10	−286	6.80	86.7; 86.8	5.0; 7.5	0.2; 0.2	92.0; 94.4
PBB3, undersaturation experiments						
275-14	−367	6.81	92.0; 92.2	nm	1.3; 1.5	93.5; 93.5
278-14	−307	7.32	92.7; 93.1	nm	2.0; 4.0	94.7; 97.1

[a] Numbers after the dash represent equilibration period in days.
[b] Represents the observed pH meter reading. [c] nm = not measured.

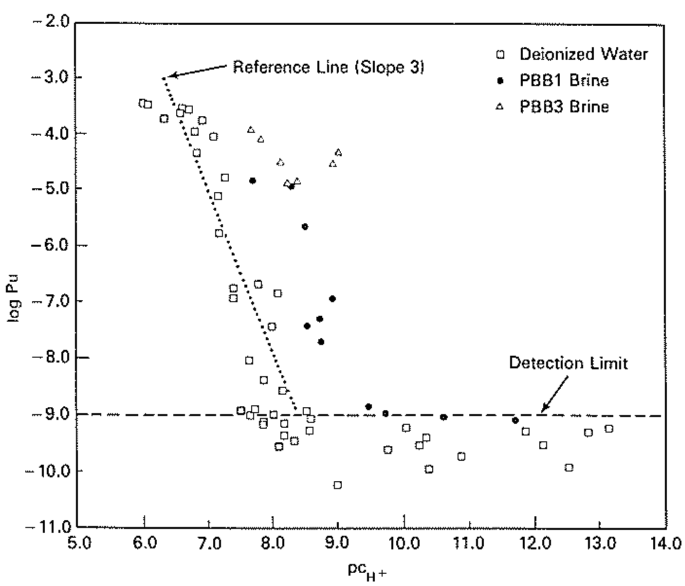

Fig. 1. Plutonium concentrations contacting $Pu(OH)_3(s)$ in 0.0018-μm filtrates as a function of the measured negative logarithm of the H^+ molarity (pc_{H^+}).

The solubilities of $Pu(OH)_3$ in dilute solution and in brines differ significantly (Fig. 1). For example, at a measured pc_{H^+} of approximately 9, the deionized water samples show total Pu concentrations at or below the detection limit of approximately $10^{-9.0}$ M; in contrast, the PBB1 brine shows a solubility of approximately $10^{-7.5}$ M and the PBB3 brine shows a solubility of approximately $10^{-4.5}$ M. Thus, at a pc_{H^+} of approximately 9, the solubility of $Pu(OH)_3$ changes by at least four orders of magnitude between deionized water and the PBB3 brine. As we will demonstrate in the next section, these large differences in solubility are related both to the differences in ionic strength among the solutions (i.e., $I \sim 0$ for deionized water, ~ 6 for PBB1 brine, and ~ 10 for PBB3 brine), and to the specific ions present in the solution. In that regard, the PBB1 brine is predominantly a NaCl brine, whereas the PBB3 brine is predominantly a $MgCl_2$ brine (Table 3).

Table 3. Analyzed compositions of PBB1 and PBB3 solutions used in the experiments

Element/species	PBB1 (mg/l)	PBB3 (mg/l)
Ca	1,346	17,300
K	86.6	11,400
Mg	121	50,600
Na	120,400	27,200
Si	–	45.4
Sr	20	17.8
Br^-	140	3,346
Cl^-	163,000	220,000
HCO_3^-	36	5.6
SO_4^{2-}	4,220	420
ph[a]	6.63	6.37

[a] Observed pH only.

Thermodynamic analysis

The objective of this section is to develop a thermodynamic model that will explain the large differences in

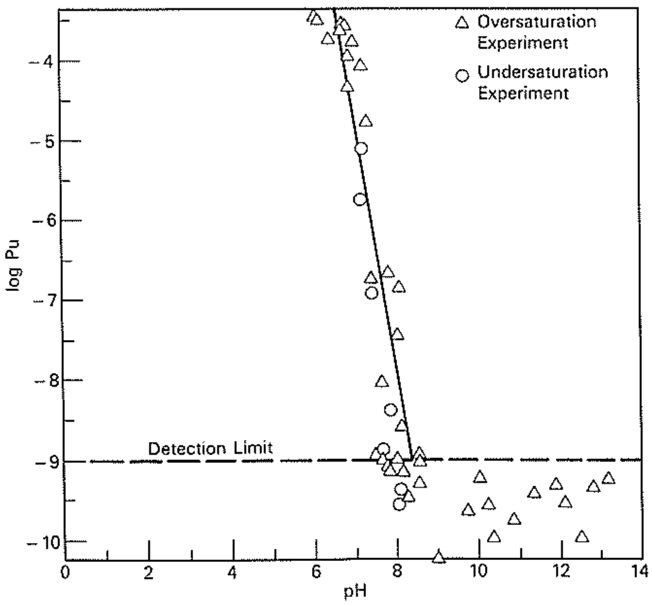

Fig. 2. Plutonium concentrations in 0.0018-μm filtrates in equilibrium with $Pu(OH)_3$, as a function of pH. Solid line depicts a calculated best fit line of slope 3.

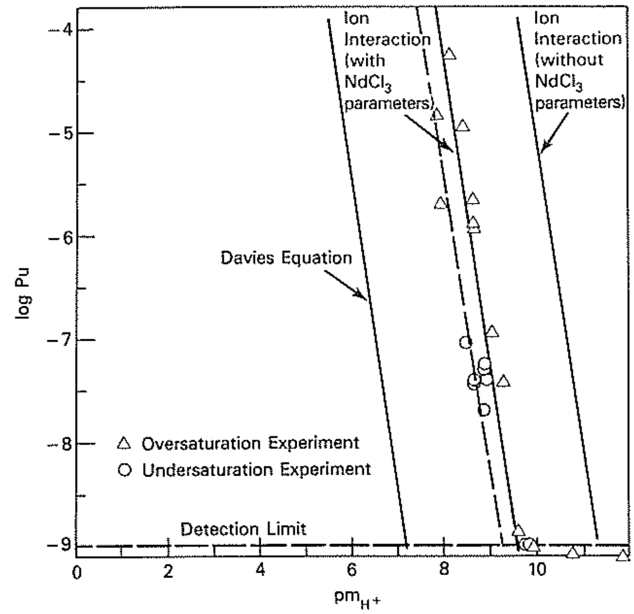

Fig. 3. Calculated and experimental solubilities in PBB1 brine as a function of the negative logarithm of the molality of hydrogen ion (pm_{H^+}). Calculated solubilities use either the Davies equation of Pitzer's ion-interaction model with different parameters. Dashed line represents calculations using large values for the Pu^{3+} ternary interaction parameters.

$Pu(OH)_3$ solubility found for deionized water and for the high-ionic-strength brines. To proceed, we must establish the standard chemical potentials for aqueous Pu^{3+} ion and $Pu(OH)_3(s)$.

The standard chemical potential ($\mu°/RT = -233.4$) of $Pu^{3+}(aq)$ was taken from Fuger and Oetting [21]. The standard chemical potential of $Pu(OH)_3(s)$ was obtained from a nonlinear least-squares analysis [22] of our solubility data in deionized water [$\mu°/RT\,(Pu(OH)_3) = -484.0$].

In this analysis, the modified form of the extended Debye-Hückel equation given by Pitzer [9] was used. Combining the standard chemical potentials of $Pu^{3+}(aq)$ and $Pu(OH)_3(s)$ with the standard chemical potential of hydroxide ion ($\mu°/RT = -63.435$) taken from Harvie *et al.* [12] gives a log K of -26.2 ± 0.8 for the dissolution reaction of $Pu(OH)_3$,

$$Pu(OH)_3(s) \rightleftharpoons Pu^{3+}(aq) + 3\,OH^-(aq). \quad (4)$$

Figure 2 shows the agreement between our model calculations (solid line) and the experimental data for the deionized water samples. The agreement is quite good. The ordinate of this figure is in pH units. (Note that pH is an operationally defined quantity, not a thermodynamic quantity; see [12]). As mentioned in the section on experimental methods, only the combination of the convention-dependent activity coefficient and the liquid junction potential can be experimentally measured (eq. 2). However, in these deionized water experiments, activity coefficients are all universal functions of ionic strength and have the same convention-dependent values (~0.91). In these dilute solutions, it is also a reasonable assumption to neglect the difference in liquid junction potential between standards and experimental solutions. Under these conditions, a measured pH reading can be consistently interpreted as the negative of the logarithm of the activity of hydrogen ion. We have used this assumption in the calculations shown in Figure 2.

With the standard chemical potential of $Pu(OH)_3(s)$ determined from our experiments in deionized water, we can use models of the excess solution free energy to predict the solubility of $Pu(OH)_3$ in multicomponent solutions. The simplest such models assume the activity coefficients are universal functions of ionic strength. One commonly used example of such a model is the Davies equation [23]. In this model, the ion activity coefficients are given by

$$\log \gamma_i = -0.509\, Z_i^2\,[I^{1/2}/(1 + I^{1/2}) - 0.3\, I] \quad (5)$$

where γ_i is the activity coefficient of species i, Z_i the charge on species i and I the ionic strength.

We have used this simple model to predict the solubility of $Pu(OH)_3(s)$ in the PBB1 brine, which is a predominantly NaCl brine. A comparison between this model calculation and the experimental solubility data is shown in Figure 3. As expected, this model gives very poor results. In fact, the calculated solubility differs by approximately 7 orders of magnitude at the same molality of H^+. This calculation clearly demonstrates the very large errors that can occur if poor or inappropriate models of the excess solution free energy are used for concentrated solutions.

The principal problem with these simple models of the excess solution free energy is that at high concentrations, activity coefficients are no longer universal functions of ionic strength but rather are dependent on the specific ions present in solution. Such specific ion-interaction effects, related to short-range forces among ions, are included in the ion-interaction model of Pitzer [9, 10]. This model emphasizes a detailed description of the specific ion interaction in the solution. The effects of the specific ion interactions in the excess solution free energy are contained within the expressions for the activity coefficients. The activity coefficients can be expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{DH}} + \sum_j B_{ij}(I) m_j + \sum_j \sum_k C_{ijk} m_j m_k + \ldots \tag{6}$$

where m is the molality, and γ_i^{DH} is a modified Debye-Hückel activity coefficient that is a universal function of ionic strength. $B_{ij}(I)$ and C_{ijk} are specific for each ion interaction and are a function of ionic strength. Pitzer [9] gives explicit phenomenological expressions for the ionic-strength dependence of B. The third virial coefficient, C, is taken to be independent of ionic strength. The form of B is different for like, unlike, and neutral ion interactions. A detailed description of the exact form of eq. (6) is given in the Appendix.

In PBB1 brine, the most important ion interactions affecting the solubility of $Pu(OH)_3$ are the Pu^{3+}-Cl^-, Pu^{3+}-Na^+, and Pu^{3+}-Na^+-Cl^- interactions, and the corresponding terms for hydroxide ion (i.e., OH^--Cl^-, Na^+-OH^-, Na^+-Cl^--OH^-). The hydroxide ion-interaction parameters [$\Theta_{OH^--Cl^-}$, $\beta°$, β^1, C^ϕ (Na^+-OH^-), etc.; see Appendix] were taken from Harvie *et al.* [12]. However, no information exists on the Pu^{3+} interaction parameters.

The strongest of the Pu^{3+} ion interactions is expected to be the interaction of Pu^{3+} with Cl^-. The important parameters for the binary Pu^{3+}-Cl^- interactions are therefore expected to be $\beta°$, β^1, and C^ϕ. Ideally, the interaction parameters for Pu^{3+}-Cl^- could be obtained from isopiestic experiments on $PuCl_3$ solutions. Unfortunately, such data do not exist in the literature. However, osmotic data do exist for several 3:1 chloride salts, including $LaCl_3$, $CeCl_3$, $PrCl_3$, $SmCl_3$, $EuCl_3$, and $NdCl_3$. The osmotic coefficients for all of these 3:1 electrolytes have very similar values (see the tabulation in Appendix 8.10 of ref. [24]). Using these data, Pitzer and Mayorga [25] calculated the binary ion-interaction parameters ($\beta°$, β^1 and C^ϕ) for these 3:1 electrolytes. As expected from the osmotic coefficient data, all the calculated parameters are very similar for all the 3:1 electrolytes. Because of these results, we have elected to use the binary parameters for isostructural $NdCl_3$ given by Pitzer and Mayorga to represent the corresponding $PuCl_3$ parameters, [i.e., $\beta^{\circ}_{Pu^{3+},Cl^-} = .6117$, $\beta^{1}_{Pu^{3+},Cl^-} = 5.403$, $C^{\phi}_{Pu^{3+},Cl^-} = -.0284$].

Figure 3 shows the $Pu(OH)_3$ solubilities in PBB1 brine calculated using only these binary parameters for Pu^{3+}-Cl^- in the ion-interaction model of Pitzer and coworkers. Similar calculations without the inclusion of the $NdCl_3$ parameters are also shown in Figure 3. The model without the $NdCl_3$ parameters (which uses only the extended Debye-Hückel equation for the activity coefficient of Pu^{3+}) gives results that

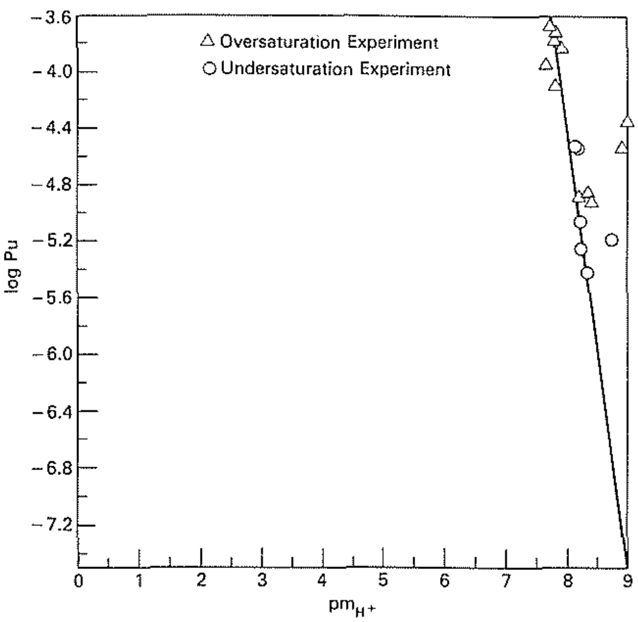

Fig. 4. Calculated and experimental solubilities in PBB3 brine as a function of the negative logarithm of the molality of hydrogen ion pm_{H^+}). Calculated solubilities use ion-interaction models with only binary parameters for Pu^3-Cl^- interactions.

are approximately 5 orders of magnitude too high. However, with the $NdCl_3$ parameters included, the agreement between model calculations and experimental data is quite good. This result has two implications. First, the binary parameters for $NdCl_3$ are a good approximation of the corresponding $PuCl_3$ values. Second, the interaction of highly charged Pu^{3+} with Cl^- appears to dominate the aqueous solution chemistry of Pu^{3+} in this NaCl-dominated brine.

As a preliminary test of the importance of including the ternary interaction parameters (i.e., $\Theta_{Pu^{3+}-Na^+}$ and $\varphi_{Pu^{3+}-Na^+-Cl^-}$), we have estimated these parameters from the only available data for a ternary system for a triply charged positive ion, the $AlCl_3$-HCl system [26]. Although this system is not expected to be a good analog for the $PuCl_3$-NaCl system, the magnitude of the $AlCl_3$-HCl parameters is quite large [$\Theta_{Al^{3+},H^+} = .185$, $\Psi_{Al^{3+},H^+,Cl^-} = 0.13$] and will give an indication of the potential importance of including the ternary $PuCl_3$-NaCl parameters. The solubilities calculated using the Pitzer model with these estimated ternary parameters in PBB1 brine are shown as the dashed line in Figure 3, with the corresponding solubilities calculated with only the binary $NdCl_3$ parameters. The data in Figure 3 indicate that, although the inclusion of ternary parameters would affect the calculated solubility of $Pu(OH)_3$, the magnitude of this effect is less than the experimental error in the $Pu(OH)_3$-solubility experiments. Thus, although the exact values of these ternary parameters cannot be defined from these experimental data, the parameters do appear to be of secondary importance in predicting the solubility of $Pu(OH)_3$ in this brine.

Because the use of an ion-interaction model with only binary Pu^{3+}-Cl^- terms gave good agreement with the experimental $Pu(OH)_3$ solubility in the NaCl-dominated PBB1 brine, we chose to do similar calculations for the PBB3 brine, which contains significant amounts of $MgCl_2$ and $CaCl_2$. The presence of these salts as well as NaCl represents a more stringent test of the model. The calculated and experimental solubilities for PBB3 brine are shown in Figure 4. Again, the agreement between model and experiment is quite good. Apparently the Pu^{3+}-Cl^- interactions are still the most important Pu^{3+} ion interactions, despite the replacement of significant amounts of Na^+ with Ca^{2+} and Mg^{2+}.

In summary, the model we propose for the solubility of $Pu(OH)_3$ in high-ionic-strength chloride-dominated brines is quite simple. It does not require ion pairs between Pu^{3+} and OH^- or Cl^-, and requires only binary interaction parameters between the Pu^{3+} ion and Cl^-. These results indicate that for chloride-dominated brines, it may be possible to predict the aqueous solution chemistry of highly charged trace species, such as Pu^{3+}, using only binary interaction parameters for the highly charged species.

Acknowledgments

We gratefully acknowledge the assistance of Chuck Nelsen in our analytical determinations, R. Jeff Serne for a technical review of the document, and Laurel Grove for editorial assistance.

This paper is being submitted in advance of DOE technical review because of Congressional shutdown of the Salt Repository Project. Because of project termination, DOE has expedited the report clearance process to ensure availability of project data, waiving the requirement for formal review by the Salt Repository Project (SRP) and the Salt Repository Project Office (SRPO). This report has received internal PNL clearance.

APPENDIX

Phenomenological equations

It is convenient to describe the activities of the species a_i in electrolyte solutions by the following equation:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n} = \mu_i = \mu_i^\circ + RT\ln a_i \qquad (A.1)$$

where μ_i° is the standard chemical potential for species i. The activity coefficient (a_i), and osmotic coefficient (ϕ) are defined by

$$a_i = \gamma_i m_i \qquad (A.2)$$

for each solute species i and

$$\ln a_{H_2O} = \frac{-W}{1000}\left(\sum_i m_i\right)\phi \qquad (A.3)$$

for the solvent, γ_i and m_i are the activity coefficient and molality of solute species. The osmotic coefficient, ϕ, is related to the activity of the solvent by eq. (A.3) where W is the molecular weight of water (18.016). [The sum over i in eq. (A.3) represents the sum over all solutes: cations, anions, and neutrals.]

The chemical potentials for pure phases, such as minerals, are constants at fixed temperature and pressure.

The remaining variables lacking explicit definition in the theory are the excess functions γ_i and $(\phi - 1)$. We use the semiempirical equations of Pitzer [9] and coworkers to model these functions. These functions have been rewritten in eq. (A.4) and are the same as those of Felmy and Weare [11]. They have been reproduced here for the convenience of the reader.

$$\begin{aligned}(\phi - 1) = \frac{2}{(\sum_i m_i)}\Bigg[& -\frac{A^\phi I^{3/2}}{1 + bI^{1/2}} + \sum_c\sum_a m_c m_a (B^\phi_{ca} + ZC_{ca}) \\ & + \sum_{c<}\sum_{c'} m_c m_{c'} (\Phi^\phi_{cc'} + \sum_a m_a \Psi_{cc'a}) \\ & + \sum_{a<a'}\sum m_a m_{a'} (\Phi^\phi_{aa'} + \sum_c m_c \Psi_{aa'c}) + \sum_n\sum_c m_n m_c \lambda_{nc} \\ & + \sum_n\sum_a m_n m_a \lambda_{na} + \sum_n\sum_c\sum_a m_n m_c m_a \xi_{nca}\Bigg] \end{aligned} \qquad (A.4a)$$

$$\begin{aligned}\ln\gamma_M = {} & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) \\ & + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \Psi_{Mca}) + \sum\sum_{a<a'} m_a m_{a'} \Phi_{aa'M} \\ & + |z_M| \sum_c\sum_a m_c m_a C_{ca} + \sum_n m_n (2\lambda_{nM}) + \sum_n\sum_a m_n m_a \xi_{naM} \end{aligned} \qquad (A.4b)$$

$$\begin{aligned}\ln\gamma_X = {} & z_X^2 F + \sum_c m_c (2B_{Xc} + ZC_{Xc}) \\ & + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \varphi_{Xca}) + \sum_{c<}\sum_{c'} m_c m_{c'} \Phi_{cc'X} \\ & + |z_X| \sum_c\sum_a m_c m_a C_{ca} + \sum_n m_n (2\lambda_{nX}) + \sum_n\sum_c m_n m_c \xi_{ncX} \end{aligned} \qquad (A.4c)$$

$$\ln\gamma_N = \sum_c m_c (2\lambda_{Nc}) + \sum_a m_a (2\lambda_{Na}) + \sum_c\sum_a m_c m_a \xi_{Nca} \qquad (A.4d)$$

where

$$\begin{aligned}F = {} & -A^\phi\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] + \sum_c\sum_a m_c m_a B'_{ca} \\ & + \sum_{c<}\sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<}\sum_{a'} m_a m_{a'} \Phi'_{aa'} \end{aligned} \qquad (A.5)$$

$$C_{MX} = \frac{C^\phi_{MX}}{2|Z_M Z_X|^{1/2}} \qquad (A.6)$$

$$Z = \sum_i |z_i| m_i \qquad (A.7)$$

A^ϕ is one-third the Debye-Hückel limiting slope and equal to 0.39 at 25°C. The subscripts c and a represent cations and anions, respectively. The second virial coefficients, B_{MX}, are given the following ionic-strength dependence [9].

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha_1\sqrt{I}} + \beta^{(2)}_{MX} e^{-\alpha_2\sqrt{I}} \qquad (A.8)$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha_1\sqrt{I}) + \beta^{(2)}_{MX} g(\alpha_2\sqrt{I}) \qquad (A.9)$$

$$B'_{MX} = \beta^{(1)}_{MX}\frac{g'(\alpha_1\sqrt{I})}{I} + \beta^{(2)}_{MX}\frac{g'(\alpha_2\sqrt{I})}{I} \qquad (A.10)$$

The functions g and g' are defined by

$$g(\chi) = 2\,\frac{[1-(1+\chi)e^{-\chi}]}{\chi^2} \tag{A.11}$$

$$g'(\chi) = -2\,\frac{\left[1-\left(1+\chi+\frac{\chi^2}{2}\right)e^{-\chi}\right]}{\chi^2} \tag{A.12}$$

with $\chi = \alpha_1\sqrt{I}$ or $\alpha_2\sqrt{I}$. When either cation M or anion X is univalent, $\alpha_1 = 2.0$. For 2-2 of higher valence pairs, $\alpha_1 = 1.4$. For all electrolytes, $\alpha_2 = 12$, and $b = 1.2$. The dimensions of α_1 and α_2 are $kg^{1/2}\,mol^{-1/2}$. The second virial coefficients, Φ, which depend upon ionic strength, are given the following form [26].

$$\Phi^{\phi}_{ij} = \Theta_{ij} + {}^{E}\Theta_{ij}(I) + I^{E}\Theta'_{ij}(I) \tag{A.13}$$

$$\Phi_{ij} = \Theta_{ij} + {}^{E}\Theta_{ij}(I) \tag{A.14}$$

$$\Phi'_{ij} = {}^{E}\Theta'_{ij}(I) \tag{A.15}$$

The functions ${}^{E}\Theta_{ij}(I)$ and ${}^{E}\Theta'_{ij}(I)$ are functions only of ionic strength and the electrolyte pair type.

The second and third virial coefficients, λ_{ni} and ζ_{nij}, representing the interactions between ions and neutral species, are assumed to be constant. The third virial coefficients C^{ϕ}_{MX} and Ψ_{ijk}, are also assumed to be independent of ionic strength.

The following are the complete set of parameters defining the model for nonideal behavior of electrolyte solutions:

$\beta^0_{MX}, \beta^1_{MX}, \beta^2_{MX}$, and C^{ϕ}_{MX} for each cation-anion pair

Θ_{ij} for each cation-cation and anion-anion pair

Ψ_{ijk} for each cation-cation-anion and anion-anion-cation triplet

λ_{ni} and ζ_{nij} for ion-neutral and ion-ion-neutral interactions. Harvie *et al.* discuss these equations more completely [12, Appendix].

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