Waste Isolation Pilot Plant

Compliance Certification Application

Reference 249

Felmy, A.R., D. Rai, S.M. Sterner, M.J. Mason, N.J. Hess, and S.D. Conradson. 1996. Thermodynamic Models for Highly Charged Aqueous Species: The Solubility of ThIV Hydrous Oxide in Concentrated NaHCO$_3$ and Na$_2$Co$_3$ Solutions. In preparation. (Copy on file in the Sandia WIPP Central Files. A:1.1.10.1.1: TO: QA: Inorganic (+IV) Actinide Thermodynaimc Data)

Thermodynamic Models for Highly Charged Aqueous Species: Solubility of Th(IV) Hydrous Oxide in Concentrated NaHCO₃ and Na₂CO₃ Solutions

Andrew R. Felmy,[1] Dhanpat Rai,[1] S. Michael Sterner,[1] Marvin J. Mason,[1] and Nancy J. Hess[1]
Pacific Northwest National Laboratory, Richland, Washington 99352

Stephen D. Conradson
Los Alamos National Laboratory, Los Alamos, New Mexico

An aqueous thermodynamic model is proposed to describe the solubility of Th(IV) hydrous oxide in the aqueous Na⁺-HCO₃-CO₃²⁻-OH⁻-ClO₄-H₂O system extending to high concentration at 25°C. This model is relatively simple in that only two aqueous species are included: Th(OH)₃CO₃ and Th(CO₃)₅⁶⁻. Pitzer ion-interaction parameters, β⁽⁰⁾ and β⁽¹⁾ for Na⁺ with Th(CO₃)₅⁶⁻, are also determined (1.31 and 30, respectively) and represent the first published values for this 1:6 electrolyte type. Reconciliation of all of the experimental solubility data for Th(IV) hydrous oxide in NaClO₄ media required the introduction of a large mixing parameter for the highly charged Th(CO₃)₅⁶⁻ species with ClO₄. The relatively large values required for the ion-interaction parameters β⁽⁰⁾ and β⁽¹⁾, together with commensurately large mixing terms with the bulk anionic species, resulted in considerable uncertainty in determining standard state equilibrium constants for the formation of the highly charged Th(CO₃)₅⁶⁻ species. This uncertainty is a result of the large contributions from β⁽⁰⁾ and β⁽¹⁾ to the excess solution free energy at the concentrations (0.1 m) where this species becomes important. The magnitude of the mixing term implies that formation of this species depends strongly upon the bulk ionic media. X-ray absorption results, confirming the presence of the thorium pentacarbonate species in concentrated bicarbonate and carbonate solutions, are also included.

1. Introduction

The aqueous complexation of tetravalent actinide species, including species of Th(IV), U(IV), Np(IV), and Pu(IV) with carbonate, has been the subject of intense research efforts because 1) carbonate is a ubiquitous ligand in groundwater systems, 2) carbonate can form strong aqueous complexes with tetravalent actinide species, and 3) these complexes can increase the solubility of compounds, such as the tetravalent hydrous oxides, that may be present in nuclear wastes (Rai et al. 1995;[1] Clark et al. 1995;[2] Tait et al. 1995;[3] Joao et al. 1995;[4] Osthols et al. 1994).[5] All of these studies clearly demonstrate the potential importance of carbonate complexation of the tetravalent actinides, including Th(IV). However, extreme disagreement exists about the magnitude of the complexation, and definitive evidence of the species in the solutions is often lacking. For example, the logarithm of the equilibrium constant for the formation of the Th(CO₃)₅⁶⁻ species differs by over 10 orders of magnitude, from 31 (Osthols et al. 1994)[5] to 22 (Joao et al. 1995).[4] Such large discrepancies in reported thermodynamic values make the accurate use of such information in equilibrium thermodynamic calculations problematic. In this study, to develop a more reliable thermodynamic model for the Th(IV) carbonate system, we re-examine recent solubility data (Rai et al. 1995;[1] Osthols et al. 1994)[5] from studies conducted in

[1]Battelle, Pacific Northwest Laboratories, Richland, Washington 99352.

different ionic media. These two studies were selected for analysis because together they cover the entire ranges from very dilute to essentially saturated with $NaHCO_3$ and Na_2CO_3 and from relatively low pH (5) to 1.0 M in NaOH. Additional data considered in the development of our model include the results of recent x-ray absorption spectroscopy (XAS) analysis of speciation in the high bicarbonate and carbonate solutions. The thermodynamic analysis included primary experimental data covering the following ranges of carbonate and bicarbonate concentration:

- $NaHCO_3$ solutions, 0.005 to 0.25 M
- Na_2CO_3 solutions, 0.1 to 2.0 M
- Na_2CO_3 solutions, 0.1 to 2.0 M with 0.1 M NaOH
- NaOH solutions, 0.01 to 0.50 M with 1.0 M Na_2CO_3
- $NaClO_4$ (0.5 M) fixed total carbonate and variable pH (c_0 total ~ 0.1m)
- $NaClO_4$ (0.5 M) fixed partial pressure of $CO_2(g)$ P_{CO_2} = 0.1 atm and variable pH.

(The data for $NaClO_4$ are from Osthols et al. 1994;[5] all other data from Rai et al. 1995.)[1]

2. Thermodynamic Model

The aqueous thermodynamic model used in this study to interpret the solubility data is the ion-interaction model of Pitzer and co-workers (Pitzer 1973,[6] 1991).[7] This model emphasizes a detailed description of the specific ion interactions in the solution. The effects of the specific ion interactions on the excess solution free energy are contained in the expressions for the activity coefficients. The activity coefficients can be expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j \beta_{ij}(I)m_j + \sum_j \sum_k C_{ijk}m_j m_k + \cdots \qquad (1)$$

where m is the molality and γ_i^{DH} is a modified Debye-Hückel activity coefficient that is a universal function of ionic strength. $\beta_{ij}(I)$ and C_{ijk} are specific for each ion interaction and are functions of ionic strength. Pitzer [1973,[6] 1991][7] gives explicit phenomenological expressions for the ionic-strength dependence of β. The third virial coefficient, C, is understood to be independent of ionic strength. The form of β is different for like, unlike, and neutral ion interactions. A detailed description of the exact form of Eq. (1) is published in Felmy and Weare (1986)[8] and Felmy et al. (1989).[9] The Pitzer thermodynamic model is applicable from zero to high concentration, and our solubility data in carbonate and bicarbonate solutions extend to high ionic strength.

Using any model of excess solution free energy to describe the activity relations for highly charged aqueous species, such as $Th(CO_3)_5^{6-}$, is extremely difficult because activity coefficients vary widely with changes in solution composition. These large changes in activity coefficients result from the Debye-Hückel activity coefficient term, which contains a minus charge squared factor (-36, in this case). Such large variations in the Debye-Hückel terms can readily lead to non-convex free energy models. That is, the determinate of the second derivative matrix of the excess free energy (Hessian matrix) is negative as a result of the negative contribution from the Debye-Hückel term. Therefore, if such highly charged species remain stable across broad ranges of solution composition, the activity relations must be stabilized by other specific ion-interactions with the bulk electrolyte ions (Na^+, ClO_4^-). In the case of the Pitzer thermodynamic

model, these specific ion-interactions are included in the ion-interaction parameters, the most important of which are those describing the interactions of ions of like sign (β and C). The development of a realistic set of such parameters for the $Th(CO_3)_5^{6-}$ species is one of the major objectives of this paper, because no values for such a 1:6 electrolyte type have been published.
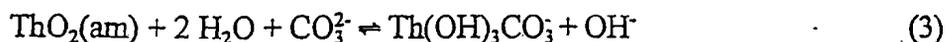
The thermodynamic analyses described in this paper were conducted with the FiTiT_ aq program developed by S.M. Sterner and colleagues (unpublished) at the Pacific Northwest National Laboratory (PNNL). The FiTiT_aq code evaluates the parameters of equations-of-state (EOS) for chemical systems of aqueous solutions by performing a comprehensive thermo-dynamic analysis of a wide variety of different types of primary experimental data. The algorithm is based on a constrained minimization of the Gibbs free energy approach (Greenberg et al. 1985;[10] Harvie et al. 1987)[11] as implemented in the computational code GMIN (Felmy 1995)[12] and the precursor parameter optimization routine NONLIN.[2] FiTiT_aq calculates chemical equilibria involving multiple solid and aqueous species, including the formation of aqueous complexes. In the present application of FiTiT_aq to evaluate parameters for the Pitzer ion-interaction electrolyte model, various types of solubility data were augmented by spectroscopic information. The coupling of free energy minimization (and corresponding introduction of ion pairs) with global optimization of EOS parameters, using a diverse database, yields considerable flexibility within the Pitzer formalism, thereby permitting accurate description of thermophysical properties of complex, multi-component aqueous fluids to extreme ionic strengths.

3. Results and Discussion

Previous studies have identified the large increases in solubility of ThO_2(am) that can occur in the presence of carbonate solutions (Figure 1). The increases are hypothesized to result primarily from the formation of the $Th(CO_3)_5^{6-}$ species at higher carbonate concentration and, also under lower pH and carbonate conditions, the formation of a mixed carbonate hydroxide species ($Th(OH)_3CO_3^-$) by means of the following reactions with the hydrous oxide (Osthols et al. 1994).[5]

$$ThO_2(am) + 2\ H_2O + 5\ CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 4\ OH^- \tag{2}$$

and

$$ThO_2(am) + 2\ H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- + OH^- \tag{3}$$

Definitive spectroscopic evidence for the formation of these species has never been presented. To address this issue, we used XAS to analyze several solutions containing high carbonate and bicarbonate concentrations (used in Rai et al. 1995)[1] for aqueous thorium species (see the appendix). The pentacarbonato thorate complex was clearly present at high concentrations of bicarbonate (1.0 M to approximately 0.15 M) and carbonate (1.0 M Na_2CO_3 in 0.1 M NaOH). Further, XAS clearly shows a change in speciation at low bicarbonate concentrations (e.g., the 0.1 M solution), but the total thorium concentration was too low to allow definitive identification of the species. In agreement with this change in speciation, we were unable to develop a satisfactory thermodynamic model for the entire chemical system by assuming the formation of

---

[2]This program, NONLIN, developed by A. R. Felmy, utilizes the MINPACK non-linear least-squares programs in combination with a chemical equilibrium program based on the Gibbs free energy minimization procedure of Harvie et al.[13] The mathematical development has been outlined by Harvie.[14]

only the $Th(CO_3)_5^{6-}$ species, regardless of the ion interaction parameters used in the Pitzer model. As expected, the disparities were most pronounced in the lower pH and fixed P_{CO_2} data of Osthols et al. (1994)[5] and in the bicarbonate data of Rai et al.[3] (1995)[1] where, at least in the data of Rai et al., a clear change exists in the XAS spectra. In agreement with Osthols et al. (1994), these data were most satisfactorily explained by the introduction of a mixed thorium-hydroxide-carbonate species, $Th(OH)_3CO_3^-$ species. By using only these two species and including a mixing term (θ ClO_4^- $Th(CO_3)_5^{6-}$), we obtained a satisfactory fit to all of the solubility data in this chemical system. The inclusion of the mixing term was necessary because the solubility of hydrous thorium (IV) oxide in the region where the $Th(CO_3)_5^{6-}$ species is dominant is highly dependent on the $NaClO_4$ concentration. Interestingly, such large changes in solubility are not predicted for lower carbonate concentrations where monovalent $Th(OH)_3CO_3^-$ is calculated to be the dominant species in solution.

The parameters for this proposed model are summarized in Table 1. The agreement of this model with all of the solubility data in the $Na-Th-CO_3-HCO_3-OH-ClO_4-H2O$ system at 25°C is depicted in Figures 1 and 2. The model provides a satisfactory representation of all the solubility data. Calculations made with the $ClO_4^- Th(CO_3)_5^{6-}$ mixing parameter set to zero are also shown in Figure 2. In this case, the model over predicts the solubility data of Osthols et al. (1994)[5] by approximately one order of magnitude in regions where the $Th(CO_3)_5^{6-}$ species is dominant, again emphasizing the importance of this mixing term and the possible differences in solubility that can be expected in different electrolyte solutions.

In all of these calculations, the thermodynamic equilibrium constants for reactions (2) and (3) (see Table 1) satisfactorily represented the data sets of Rai et al. (1995)[1] and Osthols et al. (1994).[5] Such an analysis implicitly assumes the solid $ThO_2(s)$ present in both studies has the same solubility behavior. There is no reason to assume *a priori* that this is the case. The two investigators reported different solubility products for their material,[4] and differences in crystallinity could affect the observed solubilities (Rai et al. 1987).[16] Therefore, the differences in solubility with and without $NaClO_4$ could be related to differences in crystallinity of the two sets of precipitates, rather than differences in aqueous free energies. However, as previously discussed, the observed differences in solubility are noted only when $Th(CO_3)_5^{6-}$ is dominant, and not when the monovalent $Th(OH)_3CO_3^-$ is present in significant quantity. These observations are difficult to reconcile with differences in hydrous oxide crystallinity/solubility. The calculations are also supported by the calculated logK values for reactions (2) and (3), shown in Table 1. Our calculated value for reaction (3), assuming equilibrium with $ThO_2(am)$ and $Th(OH)_3CO_3^-$, was so close to the value calculated by Osthols et al. 1994[5] using the S.I.T. activity coefficient model, that we adopted their published value of 6.78. Such similarities would be expected only for lower-charged species with smaller variations in activity coefficient and only if the solubilities of the solid phases were similar.

---

[3] In modeling the data of Osthols et al. (1994),[5] the analytically determined hydrogen ion concentration was used directly. In modeling the solubility data of Rai et al. (1995)[1] in bicarbonate solutions ranging in concentration from 0.01 M to 0.25 M, the hydrogen ion concentration was calculated using their measured pH. As described previously by Felmy et al. (1989;[9] 1991),[15] use of measured pH values in such calculations should be treated as only qualitative owing to unknown single ion activity coefficients and liquid junction corrections, especially at molality as high as 0.25 M.

[4] The differences in reported solubility products appear to be related mainly to the differences in assumptions about the presence or absence of hydrolyzed species in their model calculations, not to actual observed differences in solubility.

It is also worthwhile to examine the magnitude of the calculated values for $\beta^{(0)}$ and $\beta^{(1)}$ for $(Na^+- Th(CO_3)_5^{6-})$ relative to the values expected for a 1:6 electrolyte type. Unfortunately, there are no previously published values for $\beta^{(0)}$ and $\beta^{(1)}$ for a 1:6 electrolyte. However, data are published for a series of sodium phosphate electrolytes extending from 1:1 (i.e., $Na^+-H_2PO_4$) to 1:5 ($Na^+- P_3O_{10}^{5-}$) (Pitzer [1991]).[7] As a way of estimating reasonable values for a 1:6 electrolyte, we fit the results for the sodium phosphate series for both $\beta^{(0)}$ and $\beta^{(1)}$ to a second degree polynomial and plotted our calculated values for these parameters for $Na^+-Th(CO_3)_5^{6-}$ on these graphs (Figure 3a and b). Our calculated values for $\beta^{(0)}$ and $\beta^{(1)}$ appear to be reasonable for this electrolyte type.

Finally, it is interesting to discuss the implications of the need for the use of large values for ion-interaction parameters, such as those between Na^+ and $Th(CO_3)_5^{6-}$ and possibly between $Th(CO_3)_5^{6-}$ and ClO_4^-. Even in the most dilute carbonate/bicarbonate solutions (0.01 to 0.1 m) where $Th(CO_3)_5^{6-}$ dominates, the specific ion-interactions with the bulk cation (e.g., Na^+) are sufficiently strong to contribute significantly to the magnitude of the activity coefficients. In addition, if true, the corresponding specific interactions with the other bulk ions (e.g., ClO_4^-) means that activity coefficients for these species will also vary considerably with ionic media. That variation may account for the large differences in stability constants obtained by different investigators. Such observations suggest that it is currently impossible to extrapolate unambiguous standard state thermodynamic quantities for such highly charged species from solution data in different electrolyte media.

4. Summary

An aqueous thermodynamic model is proposed to describe the solubility of Th(IV) hydrous oxide in the aqueous $Na^+-HCO_3^--CO_3^{2-}-OH^--ClO_4^--H_2O$ system extending to high concentration at 25°C. This model gives a satisfactory representation of all of the solubility data in this chemical system, although a large mixing parameter for $Th(CO_3)_5^{6-}$ with ClO_4^- is required to explain the differences in solubility observed in the presence and absence of $NaClO_4$ in regions where $Th(CO_3)_5^{6-}$ is dominant. The large calculated values for the ion-interaction parameters $\beta^{(0)}$ and $\beta^{(1)}$ appear to be reasonable for this electrolyte type, and they are the first published values for a 1:6 electrolyte. These observations suggest that it is currently impossible to unambiguously determine standard state equilibrium constants for the formation of the highly charged $Th(CO_3)_5^{6-}$ species from solution data in different electrolyte media. X-ray absorption spectroscopy results supporting the formation of the thorium pentacarbonato thorate complex are also included.

Appendix

XAS Analysis Procedures and Results

X-ray absorption spectroscopy (XAS) was conducted to determine directly the speciation of the Th carbonato species of seven solutions covering a range of bicarbonate and carbonate concentrations (Table A.1). All absorption measurements were performed at the thorium L_{III} edge. Spectra were collected simultaneously in transmission and fluorescence modes to photoelectron wavevector of 13 Å^{-1}. Energy calibration was based on assigning the first inflection point in the absorption edge of either a zirconium metal foil to 17999.35 eV or a thorium metal foil at 16300 eV.

The extended x-ray absorpton fine structure and the Fourier transforms for selected samples are shown in Figure A.1. For the lowest concentration sample, 5 mg/l Th, only the x-ray absorption near edge spectroscopy portion of the absorption spectrum was collected. At high carbonate concentrations, the Fourier transforms reveal two clearly resolved peaks centered at 1.9 Å and 3.6 Å. The peak at 1.9 Å corresponds to the first coordination shell around the thorium cation and consists of oxygen. Using the guanidinium pentacarbonato thorate tetrahydrate structure (Voliotis and Rimsky 1975)[18] as a qualitative model, the identity of the atoms of the second shell can be assigned to distal oxygens. The coordination shell due to the five carbons is not resolved from the first shell oxygens. Its existence can be determined only by quantitative analysis using the multiple scattering code, FEFF6 (Zabinsky et al. 1995;[19] Rehr et al. 1992).[20] At lower carbonate concentrations, the signal to noise ratio is lower and the amplitude of the first oxygen and distal oxygen coordination shells is reduced.

The FEFF6 code was used to calculate the phase and amplitude for the individual scattering paths Th-O, Th--C, and Th--O_d and for multiple scattering paths that have the same effective distance as the Th--O_d path. The parameterized scattering paths were used to fit the EXAFS over the photoelectron wavevector region 1.88 to 12.09 Å^{-1}, except for sample Th71, which was fit over 1.88 to 10.01 Å^{-1}. To the contribution from the Th--C scattering path, the EXAFS were first fit with only Th-O and Th--O_d scattering paths. The remaining Th--C scattering path is clearly evident in a Fourier transform of the residual as shown in Figure A.2. A filtered fit of the back Fourier transform of this shell was performed to further isolate the carbon shell from the remaining residual signals. The resulting fits to the EXAFS are shown in Figure A.2; Table A.2 contains the resulting metrical parameters for the individual scattering paths.

At high carbonate concentrations, the thorium cation is coordinated by 10 oxygens at 2.49 Å. A carbon shell is identified at 3.00 Å and a distal oxygen shell at 4.23 Å. The calculated bond distances for Th--C and Th--O_d are a few hundredths of an Å longer than those reported for the solid structure (Voliotis and Rimsky 1975)[18] and are in good agreement with other actinide bidentate carbonato complexes, such as the Np(V)mono-, bis-, tri- carbonato species (Clark et al. 1996).[2] However, determination of the number of carbonate groups involved in the complextion is hindered because (1) the carbon shell resides within Th-O, (2) photoelectron scattering off low z elements is intrinsically weak, and (3) the EXAFS originating from second and third coordination shells are dampened by increased disorder contributions. These effects are evident in the greater uncertainty in the metrical parameters for Th--C and Th--O_d given in Table A.3.

Therefore, efforts to determine the number of carbonate groups were focused on the distal oxygen, which is more distant but well-isolated from other contributions. In addition, filtered fits of the back Fourier transform of the Th--O_d shell were performed over the photoelectron region of 3.10 to 4.20 Å^{-1} while fixing sigma, the disorder term, at an average value of 0.07; the metrical parameters are shown in Table A.3.

These data clearly show that five carbonate groups are involved in the solution complexation of thorium, except in the lowest 0.1 M bicarbonate solution (sample Th71). At a concentration of 0.10 NaHCO$_3$, the thorium speciation changes dramatically. The distance to the Th-O shell decreases from 2.50 Å to 2.46 Å and the number of oxygens changes from 10 to 8; an indication of a small number (no more than three) of distal oxygens is present at 4.21 Å. No residual corresponding to a Th--C path could be identified. Several models of bidentate and monodentate carbonate coordination were evaluated, but the lower signal to noise ratio of this low concentration sample frustrated further attempts to quantify the number of atoms constituting it and distance to the Th--C and Th--O_d shells. Nonetheless, some general conclusions can be drawn. The contraction of the Th-O shell is consistent with a decrease in the number of carbonate groups that coordinate thorium. In analogy with other actinides, if thorium is coordinated by hydroxyl groups it would likely have an even shorter Th-O distance. This result and the indication of some Th--O_d amplitude suggest that thorium exists as a mixed carbonate hydroxide species.

References

1. Dhanpat Rai, A. R. Felmy, D. A. Moore, and M. J. Mason, *The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaHCO$_3$ and Na$_2$CO$_3$ Solutions*. Materials Research Society Symposium, Vol. 353, pp. 1143-1150 (1995).
2. D. L. Clark, S. D. Conradson, S. A. Ekberg, N. J. Hess, D. R. Janeky, M. P. Neu, P. D. Palmer, and C. D. Tait. *New Journal of Chemistry*, 20:211-15 (1996).
3. C. D. Tait, S. A. Eckberg, P. D. Palmer, and ; D. E. Morris, *Plutonium Carbonate Speciation Changes as Measured in Dilute Solutions with Photoacoustic Spectroscopy* LA-12886-MS, (Los Alamos National Laboratory, Los Alamos, NM, 1995).
4. A. Joao, H. D. Burrows, L. Zikovsky, and M. Lipponen, *Radiochim. Acta* 68, 177-183 (1995).
5. E. Osthols, J. Bruno, and I. Grenthe, Geochimica et Cosmochim. Acta, 58(2), 613-623 (1994).
6. K. S. Pitzer, J. Phys. Chem. 77(2):268 (1973).
7. K. S. Pitzer, *Ion Interaction Approach: Theory and Data Correlation Activity*, Chapter 3 in: Coefficients in Electrolyte Solutions, 2nd edn, K. S. Pitzer Ed., CRC Press, Boca Raton, FL (1991).
8. A. R. Felmy and J. H. Weare, *Geochim. Cosmochim. Acta* 50:2771-2783 (1986).
9. A. R. Felmy, Dhanpat Rai, and R. W. Fulton, "Am(III) Carbonato Complexes and Solubility Product of AmOHCO$_3$(c)" in: *Performance Assessment Center for Engineered Barriers (PACE) Program, FY 1988 Summary Report* PNC SA0865 89-001. (Power Reactor and Nuclear Fuels Development Corporation of Japan 1989).
10. J. P. Greenberg, J. H. Weare, and C. E. Harvie, High Temp. Sci., 20:1045-1057 (1985).
11. C. E. Harvie, Ph.D. Dissertation #AAD82-03026, University Microfilms, Ann Arbor, MI, 1987.
12. A. R. Felmy, *GMIN, A Computerized Chemical Equilibrium Program Using a Constrained Minimization of the Gibbs Free Energy: Summary Report*, Chapter 18 in Chemical Equilibrium and Reaction Models, Soil Science Society of America Special Publication 42 (1995).
13. C. E. Harvie, J. P. Greenberg, and J. H. Weare, *Geochim. et Cosmochim.* Acta 51 1045 (1987).
14. C. E. Harvie, *Theoretical Investigations in Geochemistry and Atom Surface Scattering*, Ph.D. Dissertation, University of California, San Diego, CA, 1981.
15. A. R. Felmy, Dhanpat Rai, and M. J. Mason, *Radiochim. Acta* 55:177-185 (1991).
16. Dhanpat Rai, J. L. Swanson, and J. L. Ryan, *Radiochim. Acta* 42, 35-41 (1987).
17. C. E. Harvie, N. Moller, J. H. Weare, *Geochim. Cosmochim. Acta*, 48, 723-751 (1984).
18. P. S. Voliotis and A. Rimsky, Acta Cryst. B31:2612 (1975).
19. S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, Phys Rev B (1995).
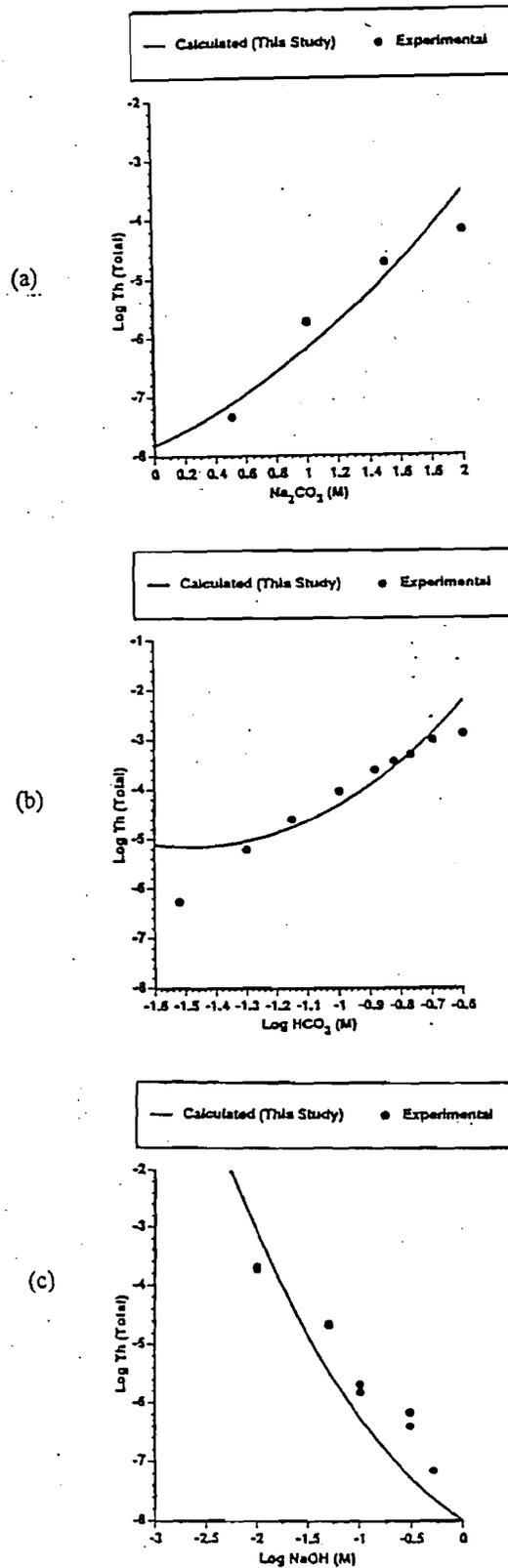20. J. J. Rehr, S. I. Zabinsky, and R. C. Albers, Phys Rev Let 69:3397 (1992).

Fig. 1. Experimental and calculated aqueous thorium concentrations in (a) Na_2CO_3 solutions at fixed NaOH (0.1 M), (b) $NaHCO_3$ solutions, and (c) NaOH solutions at fixed Na_2CO_3 (1 M). Experimental data of Rai et al. (1995).[1]