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The Solubility of $AmOHCO_3(c)$ and the Aqueous Thermodynamics of the System Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O

By Andrew R. Felmy, Dhanpat Rai and Robert W. Fulton
Battelle, Pacific Northwest Laboratories, Richland, Washington 99352

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Americium / Carbonate / Complexation / Ion-interaction / Solubility

Abstract

The solubility of $AmOHCO_3$ was investigated as a function of time and over wide ranges of CO_3^{2-}/HCO_3^- concentrations and pH values. Experiments were conducted at pH values from 5.5 to 9.3 at a fixed P_{CO_2} at 10^{-3} atmospheres, at pH values from 10.6 to 11.3 in 0.003 to 0.1 *M* Na_2CO_3, and at pH values from 11.7 to 13.0 in 0.07 *M* Na_2CO_3.

Long-term equilibrations from both oversaturation and undersaturation show that $AmOHCO_3(c)$ is the thermodynamically stable solid phase in equilibrium with solutions in which the total carbonate concentration is <0.1 *M* and the pH is between 5.5 and 13.1.

The solubility of $AmOHCO_3(c)$ shows a complex behavior as a function of both pH and CO_3^{2-} ion concentration. However, this behavior can be explained by the existence of relatively few Am species [Am^{3+}, $AmCO_3^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{3-}$]. Our thermodynamic model does not require the myriad of aqueous complexes proposed by previous investigators, yet it accurately reproduces, or is consistent with, all of the existing experimental data we are aware of, including solubility and solvent extraction data for the system Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O. In this study, the log *K* value for $AmOHCO_3(c) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-}$ was found to be −22.5. The log *K* values for association reactions [$Am^{3+} + xCO_3^{2-} \rightleftharpoons Am(CO_3)_x^{3-2x}$], involving $AmCO_3^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{3-}$ were found to be 7.6, 12.3, and 15.2, respectively. Pitzer ion-interaction parameters were also evaluated for Am^{3+} with ClO_4^- and for Na^+ with $Am(CO_3)_3^{3-}$, to explain the solvent extraction coefficient data in $NaClO_4$ media. A revised maximum log *K* value of 13.4 for the $Am(OH)_3(aq)$ association reaction was also calculated from the experimental data.

Introduction

Experimental data for the Am^{3+}-CO_3^{2-}-HCO_3^--H_2O aqueous system indicates that Am^{3+} and CO_3^{2-}/HCO_3^- interact strongly in the aqueous phase [1–4]. However, considerable confusion exists regarding the form of these interactions. Shiloh *et al.* [1] interpreted their spectrophotometric data at high concentrations of K_2CO_3 (0.1 to 0.6 *M*) in terms of only one $AmOH(CO_3)_3^{4-}$ aqueous species. Lundqvist [2] interpreted his solvent extraction and electromigration data in terms of both $AmCO_3^+$ and $Am(CO_3)_2^-$. Bidoglio [3] represented his solvent extraction data for 0.2 *M* $NaClO_4$ in terms of four aqueous complexes: $AmHCO_3^{2+}$, $Am(HCO_3)_2^+$, $Am(CO_3)_2^-$, and $AmOH(CO_3)_2^{2-}$. Bernkopf and Kim [4] interpreted their solubility data in 0.1 *M* $NaClO_4$ in terms of six aqueous complexes: $AmCO_3^+$, $Am(CO_3)_2^-$, $Am(CO_3)_3^{3-}$, $AmOHCO_3(aq)$, $AmOH(CO_3)_2^{2-}$, and $Am(OH)_2CO_3^-$.

Which solid phase(s) in the Am^{3+}-CO_3^{2-}-HCO_3^--H_2O system is (are) thermodynamically stable is also unclear. Silva and Nitsche [5] determined that $AmOHCO_3(c)$ was the stable phase in their solubility measurements at pH ~6. Bernkopf and Kim [4] also indicated that $AmOHCO_3(c)$ was the thermodynamically stable solid phase in their CO_3^{2-}/HCO_3^- solutions, at least in solutions up to 0.1 *M* total carbonate. However, Shiloh *et al.* [1] found $Am_2(CO_3)_2(s)$ to be the stable phase in 0.1 to 0.6 *M* K_2CO_3. Clearly, there is a need to understand and clarify the thermodynamic equilibrium relations in the Am^{3+}-HCO_3^--CO_3^{2-}-H_2O system.

The objectives of this study were 1) to determine the thermodynamically stable solid phases in the Am^{3+}-HCO_3^--CO_3^{2-}-H_2O system at low total carbonate concentrations (<0.1 *M*), and 2) to develop thermodynamic data necessary to unravel the confusion regarding the aqueous Am carbonato complexes. Both objectives can be achieved by solubility studies.

In our first series of experiments, we began with two different amorphous Am-CO_3 precipitates and monitored the solution compositions and crystallinity of the solid phases as the precipitates aged. These experiments were conducted at a fixed P_{CO_2} (10^{-3} atm) and at a pH <9.3. Conducting experiments with solutions that are in equilibrium with $CO_2(g)$ controls the pH and CO_3^{2-}/HCO_3^- ratios. By beginning these experiments with amorphous materials, we effectively approached equilibrium from oversaturation with respect to the crystalline materials that later formed.

After analyzing the results of these experiments, we conducted a second series of experiments by resuspending the crystallized precipitates obtained from the first series of experiments in different concentrations of Na_2CO_3 and in Na_2CO_3 plus NaOH. In these experiments, we effectively approached equilibrium from undersaturation.

Experimental approach

In the first series of experiments, we examined the solubility of two amorphous Am-CO_3 materials. The first material, designated $AmCO_3$(SB), was prepared by direct introduction of Am^{3+} into $NaHCO_3$ solutions at pH 7. This precipitate is believed to represent the type of material that would be most likely to form in a natural system. The Am-CO_3(SB) precipitate was initially slightly pink.

The second material, designated Am-CO_3(TCA), was prepared by the trichloroacetic acid (TCA) method described by Charles [6] and used for preparing rare-earth carbonates. This preparation method is very sensitive to temperature, CO_2 pressure, and the washing procedure. The material was heated to 50°C for 6 hours. The Am-CO_3(TCA) precipitate was amorphous to X-rays, but its appearance was distinctively different from the Am-CO_3(SB) precipitate. The Am-CO_3(TCA) precipitate was finer grained than the Am-CO_3(SB) precipitate and deeper pink in color. Although the Am-CO_3(TCA) precipitate is not one that would be expected to precipitate in a natural system, we studied its solubility under the same conditions as those chosen for the Am-CO_3(SB) precipitate to determine whether the same thermodynamic equilibrium would be reached and whether the same final stable solid phase would be identified.

The Am-CO_3(SB) precipitates were prepared by adding 0.1 ml ($\sim$4.5 mg Am) of a 43-g/L ^{243}Am stock solution to 30 ml of 0.01 M $NaHCO_3$ at pH 7 in a 50-ml polypropylene centrifuge tube. This pH was chosen to prevent the formation of $Am(OH)_3$, which is very soluble at pH <7 [7]. The precipitate was washed twice with about 20 ml of 0.0004 M $NaHCO_3$ at pH 8.

The Am-CO_3(TCA) precipitates were prepared by following, as closely as possible, the procedure used by Charles [6] to prepare rare-earth carbonates. Solutions were heated for approximately 6 hours at 50°C and then allowed to cool overnight. The precipitates were then washed with 0.0004 M $NaHCO_3$ at pH 8.

The first series of experiments (those at fixed P_{CO_2}) was conducted in a glovebox maintained with 10^{-3} atm CO_2 in ultrapure argon. All CO_3^{2-}/HCO_3^- solutions were initially equilibrated with the chamber gas for 2 to 3 days before these solutions were added to the precipitated materials. The centrifuge tubes containing the solutions were kept lightly capped to allow exchange of CO_2(g) with the glovebox atmosphere. All centrifuge tubes were placed on an orbital shaker and shaken.

In the second series of experiments (those in Na_2CO_3), the solutions in selected centrifuge tubes containing either Am-CO_3(SB) or Am-CO_3(TCA) suspensions were removed and the precipitates washed with deionized water. These precipitates were then resuspended either in Na_2CO_3 solutions that ranged in concentration from 0.003 M to 0.1 M and had initial pH values from 10.6 to 11.3 or in 0.07 M Na_2CO_3 solutions that were pH-adjusted upward with CO_2-free NaOH. The pH values in these 0.07 M suspensions ranged between 11.7 and 13.0. All suspensions were then placed onto the orbital shaker and shaken. The tubes were kept capped to minimize introduction of CO_2(g) from the controlled-atmosphere chamber. However, total inorganic carbon analyses indicate that CO_2(g) was slowly adsorbed by these solutions over the 2.5-month aging period (Table 1).

In the first series of experiments, each of the Am-CO_3(SB) suspensions was sampled after 2, 10, 21, 36, and 66 days of aging. The Am-CO_3(TCA) suspensions were sampled after 12, 21, and 36 days of aging. In the second series of experiments, the eight tubes with the Na_2CO_3 solutions were sampled after 30, 44, and 78 days of aging and the four tubes containing pH-adjusted Na_2CO_3 solutions were sampled after 14, 28, and 62 days of aging. For both series of experiments, the pH of each suspension was measured and the samples were centrifuged at 2000 g for 7 – 10 minutes. Aliquots of the supernatants were filtered through Amicon type F-25 Centriflo®[1] membrane cones with effective 2500-molecular-weight cutoffs and approximately 0.0018-µm pore sizes. Rai and others [7, 8] have shown that these membranes are effective in separating solids from solutions when pretreated by 1) washing and equilibrating the filters with deionized water and 2) passing a small aliquot of the samples through the filters to saturate any adsorption sites on the filters and filter containers and then discarding the aliquot.

Filtrates used for Am and total chemical composition were acidified and stored until analyzed. Before Am analysis, samples were stored for approximately 30 days to allow the ^{239}Np decay product, which was produced from the total ^{243}Am solid in the original suspensions, to decay to near secular equilibrium with the ^{243}Am present in each vial. A waiting period was necessary to distinguish between the 74.67 keV gamma of ^{243}Am and the large Compton edge of the PuK X-rays arising from the ^{239}Np decay. Samples were counted using high-purity germanium planar detectors. Total chemical analyses were determined by inductively coupled plasma spectroscopy (ICP). The pH was measured with a combination glass electrode (Orion-Ross)®[2] calibrated with pH buffers. Total inorganic carbon was determined by using a Coulometrics Inc. model 5020 total carbon analyzer. Samples of the solid phase for X-ray diffraction (XRD) analysis were taken at various times after the 36-day sampling period in the first series of experiments and at the end of the sampling period for the second series of experiments. X-ray diffraction patterns of Am solids that had not been air-dried were obtained with a Gandolfi camera using CuK_α radiation.

Results and discussion

The first series of experiments was conducted at a fixed partial pressure of CO_2(g) of 10^{-3} atm. Therefore, although the dissolved carbonate concentrations

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[1] Centriflo is a trademark of the Amicon Corporation, Lexington, Massachusetts.

[2] Orion-Ross is a trademark of Orion Research, Cambridge, Massachusetts.

Table 1. Measured pH values and total inorganic carbon concentrations in Na$_2$CO$_3$ solutions

Na$_2$CO$_3$ (*M*)	pH 30 days	44 days	78 days	Total inorganic carbon (78 days) (*M*)
0.1	11.27	10.79	10.35	0.115
0.07	11.26	11.18	10.98	0.0736
0.05	10.47	10.26	9.67	0.0754
0.02	10.31	10.13	9.36	0.0353
0.01	10.42	10.28	9.71	0.0123
0.008	9.04	9.04	8.96	0.0143
0.005	9.42	8.84	8.68	0.0078
0.003	8.94	8.65	8.52	0.0043

Table 2. Measured and calculated pH values from AmCO$_3$(SB) suspensions in NaHCO$_3$ solutions equilibrated with 0.001 atm CO$_2$(g)

NaHCO (*M*)[a]	Measurd pH 2-day	10-day	21-day	36-day	66 day	Calculated pH[b]
0.04	9.09	9.28	9.27	9.30	9.30	9.23
0.03	8.93	9.19	9.16	9.17	9.11	9.14
0.02	8.93	9.03	8.94	9.05	9.09	9.01
0.01	8.65	8.81	8.74	8.79	8.83	8.75
0.008	8.45	8.70	8.63	8.63	8.66	8.67
0.006	8.25	8.51	8.51	8.54	8.57	8.56
0.004	8.14	8.37	8.24	8.39	8.22	8.39
0.002	7.77	7.92	7.93	7.96	7.63[c]	8.11
0.001	7.35	7.65	7.53	7.56	7.21[c]	7.81
0.0008	7.20	7.54	7.49	7.48	7.08[c]	7.72
0.0006	7.09	7.48	7.47	7.47	6.89[c]	7.60
0.0005	7.10	7.17	7.49	7.50	6.80[c]	7.52
0.0004	—	7.12	7.50	7.45	7.32[c]	7.42

[a] Initial concentration before equilibration.

[b] Calculated using Pitzer's ion-interaction model with zero liquid junction potential assumed.

[c] Acidification from radiolysis effects is suspected.

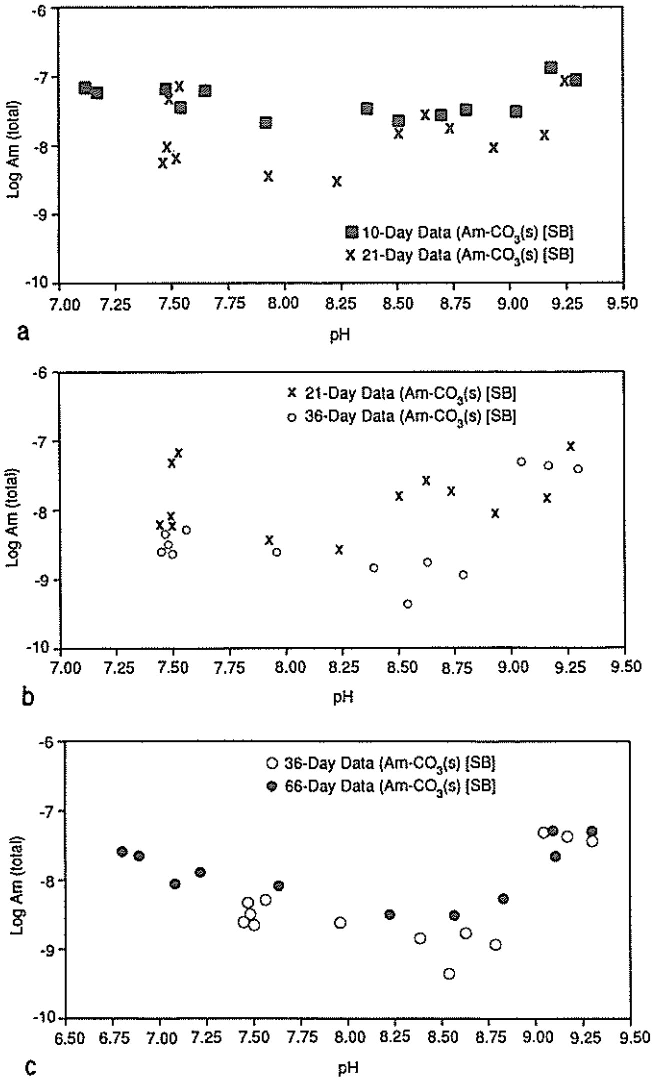

Fig. 1. Solubility data for Am-CO$_3$(SB) precipitates after aging a) 10 and 21 days, b) 21 and 36 days, and c) 36 and 66 days.

varied as a function of pH, the dissolved carbonate at any given pH was constant. To conduct a meaningful thermodynamic analysis, it must be established that the data were obtained from suspensions that were in equilibrium with the chamber gases. The measured and calculated pH[3] of these solutions (Table 2) after 10, 21, and 36 days of equilibration, along with those of samples aged for 66 days in solutions that contained >0.004 *M* NaHCO$_3$, were similar, indicating that the solutions had already reached equilibrium with the chamber gases in ≤ 10 days. In solutions with initial NaHCO$_3$ concentrations <0.004 *M* that were equilibrated for 66 days, there was a significant decrease in pH. This decrease in pH was probably the result of radiolysis-produced acidification of the samples. Such effects have been reported previously by Rai *et al.* [7, 11]. Results similar to those reported in Table 2 for Am-CO$_3$(SB) suspensions were also obtained for the Am-CO$_3$(TCA) suspensions.

The Am concentrations in solutions from Am-CO$_3$(SB) suspensions (Fig. 1) decreased progressively as the equilibration period increased. The concentrations at 36 and 66 days are similar, indicating that steady-state Am concentrations had been reached in ≤ 36 days. Similarly, steady-state Am concentrations in solutions from Am-CO$_3$(TCA) suspensions were also obtained in ≤ 36 days (Fig. 2). Because the P_{CO_2} is constant, the decrease in Am concentrations (Fig. 1) with time at a given pH can result from a change in the solid phase, such as the conversion of an amorphous phase to a more crystalline phase of the same composition or the conversion of a more soluble phase to a less soluble phase of different composition. The initial precipitates were amorphous to X-rays and could not be characterized. However, at the end of the equilibration period (36 to 66 days), the equilibrated solid

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[3] These values were calculated with Pitzer's [9] ion-interaction model, which in these solutions is reduced principally to Pitzer's form of the extended Debye-Hückel equation. All necessary thermodynamic data for this model were taken from the compilation of Harvie *et al.* [10]. A liquid junction potential of zero was assumed.

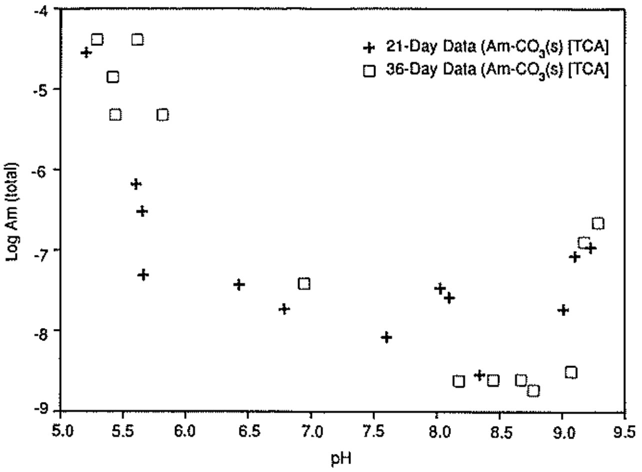

Fig. 2. Solubility data for Am-CO_3(TCA) precipitates after 21 and 36 days of aging.

Table 3. X-ray diffraction patterns of selected samples after 2 months of aging. All observed peaks are reported. Relative intensities (on a scale from 1 to 10) are in parentheses

Interplenar spacings, *d*(A^0) (from samples equilibrated at different pH values)			
pH = 7.96[a]	pH = 8.57	pH = 9.07[a]	Standard[b]
			5.50 (w)
4.23 (5)	4.23 (9)		4.28 (s)
3.66 (7)	3.67 (7)	3.65 (9)	3.67 (m)
3.31 (5)	3.29 (5)	3.30 (6)	3.31 (w)
	2.93 (7)		2.94 (w)
2.91 (7)		2.92 (8)	2.92 (m)
2.63 (4)	2.63 (3)	2.63 (4)	2.64 (w)
2.47 (4)	2.48 (6)	2.49 (4)	2.48 (w)
			2.40 (w)
	2.34 (6)	2.33 (7)	2.34 (m)
2.32 (6)			2.32 (w)
2.16 (5)		2.14 (4)	2.13 (w)
2.04 (4)	2.02 (5)	2.04 (6)	2.05 (m)
	1.99 (6)	1.98 (4)	1.99 (w)
1.93 (7)	1.93 (4)	1.90 (4)	1.93 (w)

[a] Higher *d* spacings may have been obscured by sample radiation.

[b] The most complete pattern reported by Silva and Nitsche [5]. Relative intensities (given in parentheses) were visually estimated as s = strong, m = medium, and w = weak.

phases in both the Am-CO_3(SB) and the Am-CO_3(TCA) suspensions were identified as $AmOHCO_3$(c) (Table 3). Therefore, the steady-state Am concentrations observed in the Am-CO_3(SB) (Fig. 1) and the Am-CO_3(TCA) (Fig. 2) suspensions represent the equilibrium solubility of $AmOHCO_3$(c). Because all experiments were conducted at a fixed P_{CO_2} and because $AmOHCO_3$(c) was the final equilibrium solid, it is not surprising that Am concentrations in solutions at any given pH are similar in the experiments involving Am-CO_3(SB) and those involving Am-CO_3(TCA) (Fig. 3).

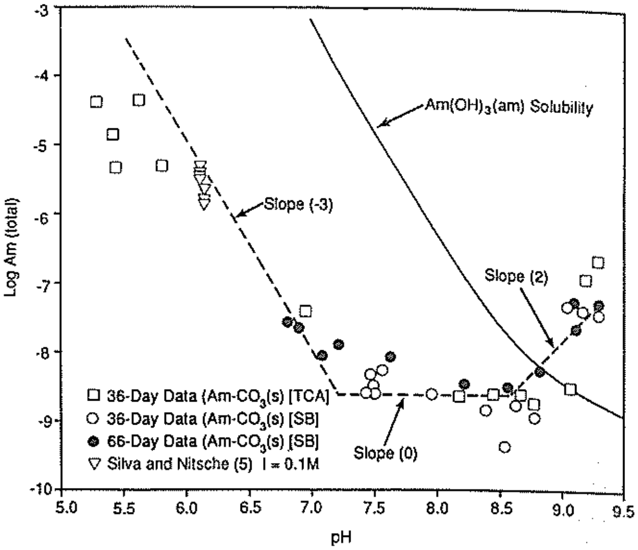

Fig. 3. Combined solubility data for all Am-CO_3(SB) precipitates and Am-CO_3(TCA) precipitates after 36 or more days of aging. The solid line represents the solubility of $Am(OH)_3$(am) [7] in the absence of complexes other than Am-hydroxo species. Dashed lines of different slopes are for reference only.

In the second series of experiments, the $AmOHCO_3$(c) precipitates obtained in the first series of experiments were resuspended in Na_2CO_3 and in Na_2CO_3-plus-NaOH solutions and equilibrated for up to 61 days. At the end of the equilibration period, $AmOHCO_3$(c), as determined by XRD analysis, was still found to be the only crystalline Am solid phase present. The Am concentrations measured in the Na_2CO_3 solutions increased with the increase in pH (Fig. 4a), but there is a lot of scatter in the data, indicating perhaps that pH is not the most important variable in these solutions. However, when the carbonate ion concentration is calculated from the pH and total inorganic carbon and when the measured Am concentrations are plotted against log[CO_3^{2-}] (Fig. 4b), a more consistent trend appears. Americium concentrations increase almost linearly with log[CO_3^{2-}] when [CO_3^{2-}] is greater than 0.003 *M* CO_3^{2-}. However, almost the opposite trend is seen in the measured Am concentrations in the 0.07 *M* Na_2CO_3 solutions with added NaOH (Fig. 5). For these solutions, there is a very clear trend of decreasing Am concentration with increasing pH. Therefore, it appears that both pH and carbonate ion concentration must be important variables in these experiments. In this second series of experiments, equilibrium was approached from undersaturation, but the results are consistent with those from the first series of experiments, in which equilibrium was approached from oversaturation (Fig. 6). The data in Fig. 6 are for the pH range from 8.5 to 9.3, where the oversaturation and undersaturation experiments overlap. As noted previously, the scatter in the data is principally caused by the fact that both pH and carbonate ion concentration are important variables. Our results are also similar to the limited data set reported by Silva and Nitsche [5] and shown in Fig. 3 for the solubility of $AmOHCO_3$(c) at fixed P_{CO_2}; Silva and Nitsche approached the solu-

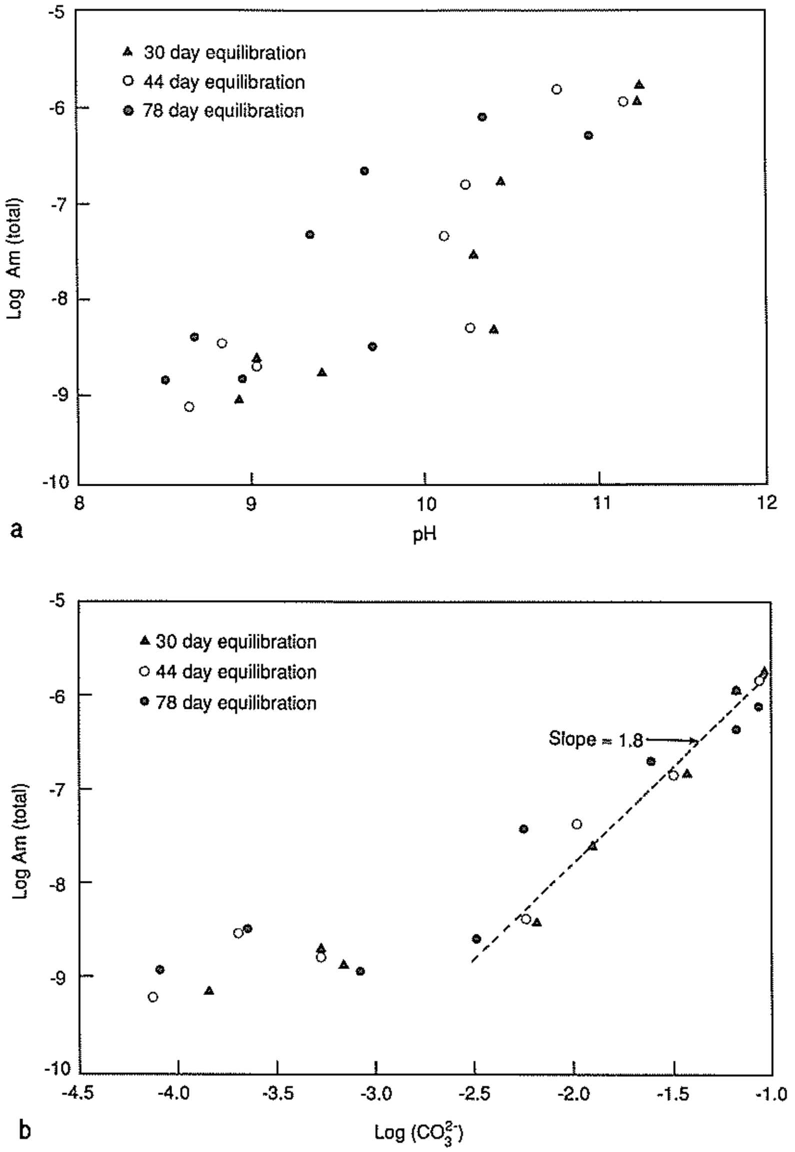

Fig. 4. Solubility of AmOHCO$_3$(c) in Na$_2$CO$_3$ versus a) measured pH; b) calculated carbonate ion concentrations. The dashed line is a best-fit line through data points at log $CO_3^{2-} > -2.5$.

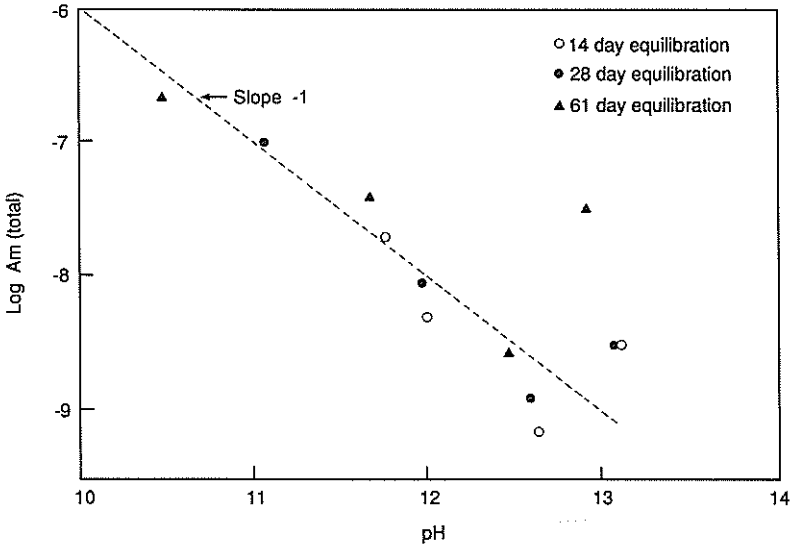

Fig. 5. Solubility of AmOHCO$_3$(c) in 0.07 *M* Na$_2$CO$_3$ with added NaOH. The dashed line is a best-fit line with −1 slope.

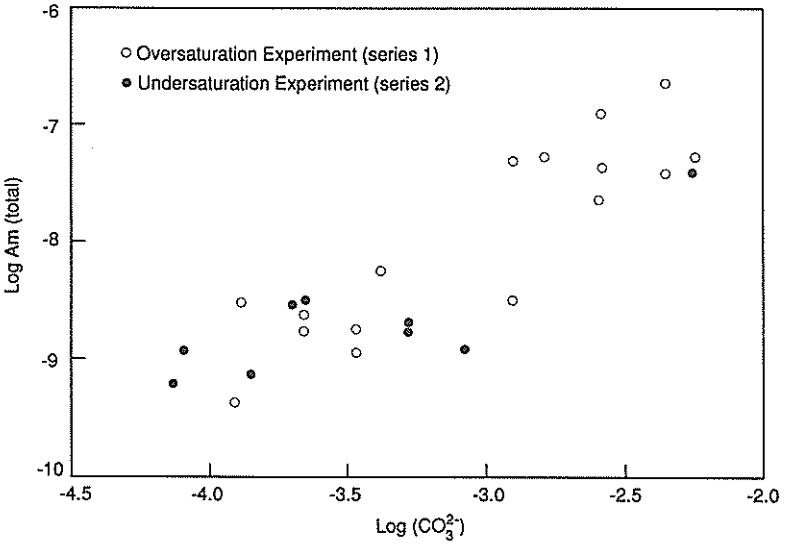

Fig. 6. Comparison of $AmOHCO_3(c)$ solubilities approached from oversaturation and undersaturation.

bility from both oversaturation and undersaturation in 0.1 *M* $NaClO_4$ solutions.

Thermodynamic analysis

In developing our thermodynamic model, we have utilized the ion-interaction model of Pitzer [9] and coworkers. The thermodynamic formulations of Pitzer were chosen because they are applicable from zero to high ionic strengths. This broad applicability makes it easier to consistently analyze not only our data but also the data of other investigators who conducted their experiments at higher ionic strengths [2–5].

Because previous experiments were conducted in $NaClO_4$ [2–5], it was necessary to have ion-interaction parameters for Na^+-HCO_3^-, Na^+-CO_3^{2-}, Na^+-ClO_4^-, H^+-ClO_4^-, and Am^{3+}-ClO_4^-, and possibly for the aqueous Am-CO_3 complexes with Na^+ or ClO_4^-. The necessary standard chemical potentials for Am hydrolysis species were calculated from the equilibrium constants given by Rai *et al.* [7]. The necessary standard chemical potentials and ion-interaction parameters for carbonate were obtained from the paper by Harvie *et al.* [10]. The H^+ and Na^+ perchlorate values were taken from the paper by Pitzer and Mayorga [12]. Interaction parameters for Am^{3+}-ClO_4^- were determined from the osmotic data of Rard *et al.* [13], using $Nd(ClO_4)_3$ as an analog for $Am(ClO_4)_3$. Felmy *et al.* [14] and Silva and Nitsche [5] have previously demonstrated that Nd^{3+} is a good analog for trivalent actinide species. The calculated Pitzer ion-interaction parameters for Nd^{3+}-ClO_4^- are $\beta^0 = 0.80$, $\beta^1 = 5.35$, and $C^\phi = -0.0048$, with a small standard deviation (0.027) in the calculated and experimental osmotic coefficients for $Nd(ClO_4)_3$ molalities extending to 5.4 *M*. The Pitzer ion-interaction parameters are summarized in Table 4.

Table 4. Pitzer ion-interaction parameters used in this study

Cation	Anion	β^0	β^1	C^ϕ	Reference
Na^+	ClO_4^-	0.0554	0.2755	−0.00118	12
Na^+	HCO_3^-	0.0277	0.0411	–	10
Na^+	CO_3^{2-}	0.0399	1.389	0.0044	10
H^+	ClO_4^-	0.1747	0.2931	0.00819	12
Am^{3+}	ClO_4^-	0.80	5.35	−0.0048	this study

Our experiments can be grouped into three distinct pH and carbonate concentration regions. The first is a lower-pH region (5–9.3) maintained at fixed P_{CO_2}, and the hydroxide and carbonate concentrations are relatively low. In the second region, the pH is higher, ~9–11, and the carbonate concentration changes rapidly; and in the third region, the pH is high, 11–13, and the carbonate concentration is fixed at a high value of 0.07 *M*. Since carbonate and hydroxide concentrations (directly related to pH) are the most important variables in our system, we began our analysis by examining the data for region 3, where pH and carbonate concentration are expected to have the largest effect.

In these solutions, the important Am^{3+} ligands are OH^- and CO_3^{2-}. The solubility reactions for $AmOHCO_3(c)$ can be written in terms of these ligands and the Am-CO_3 complexes that have been proposed in the literature as

$$AmOHCO_3(c) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-} \tag{1}$$

$$AmOHCO_3(c) + H_2O \rightleftharpoons AmHCO_3^{2+} + 2\,OH^- \tag{2}$$

$$AmOHCO_3(c) + 2\,H_2O + CO_3^{2-} \rightleftharpoons Am(HCO_3)_2^+ + 3\,OH^- \tag{3}$$

$$AmOHCO_3(c) \rightleftharpoons AmCO_3^+ + OH^- \tag{4}$$

$$AmOHCO_3(c) + CO_3^{2-} \rightleftharpoons Am(CO_3)_2^- + OH^- \tag{5}$$

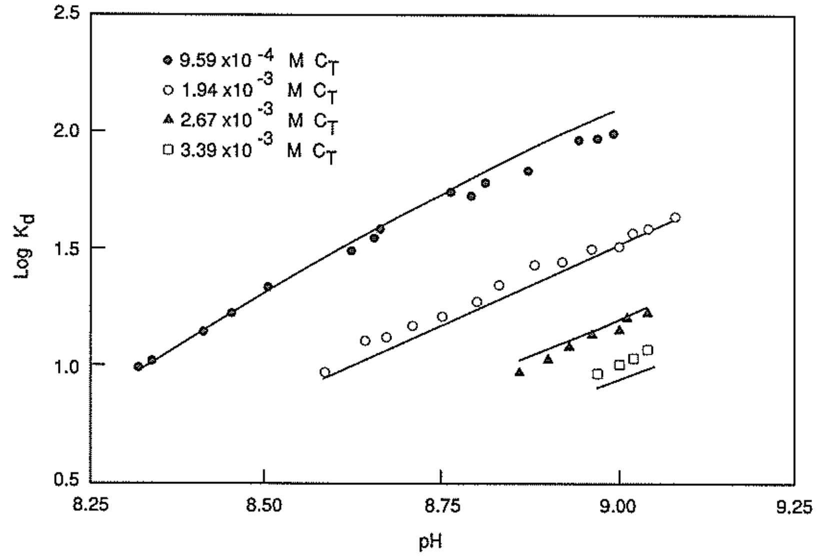

Fig. 7. Experimental data (points in Figure 3) from Bidoglio [3] and calculated (solid lines) Am distribution coefficients at different total soluble inorganic carbon concentrations.

$$AmOHCO_3(c) + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-} + OH^- \quad (6)$$

$$AmOHCO_3(c) \rightleftharpoons AmOHCO_3(aq) \quad (7)$$

$$AmOHCO_3(c) + OH^- \rightleftharpoons Am(OH)_2CO_3^- \quad (8)$$

$$AmOHCO_3(c) + CO_3^{2-} \rightleftharpoons AmOH(CO_3)_2^{2-} \quad (9)$$

$$AmOHCO_3(c) + 2\,CO_3^{2-} \rightleftharpoons AmOH(CO_3)_3^{4-} \quad (10)$$

The analysis of the $AmOHCO_3(c)$ solubility data in terms of these reactions is presented in the following sequence: solubility in high pH and 0.07 M Na_2CO_3 (Fig. 5), solubility in high pH and 0.003 to 0.1 M Na_2CO_3 (Fig. 4), and solubility in a fixed P_{CO_2} atmosphere (Fig. 3). In the region with high pH and constant Na_2CO_3 (Fig. 5), the solubility of $AmOHCO_3(c)$ decreases with increasing OH^-. The only reactions that satisfy this criterion are reactions (1)–(6). The straight line that best approximates the solubility data in Fig. 5 has a slope of -1, indicating, as would be expected given the stoichiometry of $AmOHCO_3(c)$, that only the hydroxide from $AmOHCO_3(c)$ is involved in the reaction. Thus only reactions (1) and (4)–(6) are possible. None of the aqueous species in these reactions contains OH^-. Therefore the aqueous Am-CO_3 complexes in this high-pH region do not contain OH^-, and given that this high-pH region is the region in which OH^- would be most likely to be included in these complexes, it can be concluded that OH^- would not be involved in any of the aqueous Am-CO_3 complexes. This finding at least partially invalidates the conclusions of all previous investigators except Lundqvist [2], because they all included OH^- in their aqueous Am-CO_3 complexes, based primarily on the results of statistical fitting procedures. Our experimental results indicate that these complexes either are not important or do not even exist.

We now turn to our solubility data for different concentrations of Na_2CO_3 (Fig. 4). In these solutions, CO_3^{2-} and OH^- are the dominant ligands. The best-fit straight line through the data (Fig. 4b) at $CO_3 > 10^{-3}$ M has a slope of almost 2. The only reaction that can satisfactorily explain both these results and the higher-pH data is reaction (6), which involves $Am(CO_3)_3^{3-}$. Thus, it appears that $Am(CO_3)_3^{3-}$ is the dominant aqueous species in > 0.003 M CO_3 solutions. Because the solubility of $AmOHCO_3(s)$ changes quite differently with changes in CO_3 concentration at < 0.003 M CO_3 concentrations, $Am(CO_3)_3^{3-}$ cannot be the dominant Am-CO_3 complex at lower carbonate ion concentrations.

To determine the dominant species at CO_3 concentrations < 0.003 M and pH values < 9, we examined the solubility of $AmOHCO_3(c)$ at fixed P_{CO_2}. In these experiments (Fig. 3), P_{CO_2} and pH were the principal experimental variables. Since our higher-pH data show that OH^- is not involved in the Am carbonato complexes, we need examine only reactions (1)–(6), which involve CO_3^{2-} and HCO_3^- as ligands. Reactions (1)–(6) can be written in terms of the variables pH and P_{CO_2} as

$$AmOHCO_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + CO_2(g) + 2\,H_2O \quad (11)$$

$$AmOHCO_3(c) + 2\,H^+ \rightleftharpoons AmHCO_3^{2+} + H_2O \quad (12)$$

$$AmOHCO_3(c) + H^+ + CO_2(g) \rightleftharpoons Am(HCO_3)_2^+ \quad (13)$$

$$AmOHCO_3(s) + H^+ \rightleftharpoons AmCO_3^+ + H_2O \quad (14)$$

$$AmOHCO_3(s) + CO_2(g) \rightleftharpoons Am(CO_3)_2^- + H^+ \quad (15)$$

$$AmOHCO_3(s) + 2\,CO_2(g) + H_2O \rightleftharpoons Am(CO_3)_3^{3-} + 3\,H^+. \quad (16)$$

At fixed P_{CO_2}, the solubility of $AmOHCO_3(s)$ changes with pH in three pH regions (Fig. 3). Where pH <7, a reference line of slope −3 gives a good approximation of the overall trend in the solubility data. In the pH range from 7 to 8.5, a reference line that is independent of pH (i.e., slope 0) gives a good approximation. Where pH >8.5, the trend is less obvious. Nonlinear least-squares analysis[4] indicates that a slope of +2 gives the best overall agreement.

In the lower pH region, <7, the slope of −3 is an indication that the uncomplexed Am^{3+} ion is the dominant species (reaction 11). However, none of the possible reactions (11)−(16) would result in predicted graphs of slope 0 or +2. Therefore, in the >7 pH regions, it appears that a combination of species must be contributing to the solubility of $AmOHCO_3(c)$. Because of the increase in CO_3 concentration with the increase in pH, the most likely combinations of dominant species are $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ in the >8.5 pH region and $AmCO_3^+$ and $Am(CO_3)_2^-$ in the region between pH 7 and 8.5. Approximately equal concentrations of these species will give slopes of +2 and 0 in their respective pH regions of importance. There does not appear to be any need to assume the existence of the bicarbonate complexes $AmHCO_3^{2+}$ and $Am(HCO_3)_2^+$.

To satisfactorily explain the $AmOHCO_3(c)$ solubility data obtained in this study, as well as the data obtained by Silva and Nitsche [5] for 0.1 *M* $NaClO_4$ (Fig. 3), a preliminary statistical analysis required the inclusion of three Am-CO_3 complexes: $AmCO_3^+$, $Am(CO_3)_2^-$, and $Am(CO_3)_3^{3-}$, the species mentioned above. In this preliminary analysis, the standard chemical potentials for these species, as well as the standard chemical potential for $AmOHCO_3(c)$, were calculated with Pitzer ion-interaction parameters for the Am-CO_3 complexes set to zero. When this preliminary model was applied to the solvent extraction data of Bidoglio[5], the agreement was fair. The model agreed reasonably well with Bidoglio's results at lower carbonate concentrations, but it deviated significantly as the carbonate ion concentration increased. This deviation corresponded to solution composition regions where the $Am(CO_3)_3^{3-}$ began to predominate. Species with a −3 charge can interact strongly with the bulk electrolyte, particularly with the bulk cation. Bidoglio's solvent-extraction study was performed in 0.2 *M* $NaClO_4$, and specific ion interactions between Na^+ and −3 charged species could be important in such solutions. There are no Pitzer ion-interaction parameters for Na^+ with $Am(CO_3)_3^{3-}$ in the literature; however, there are values for Na^+ with other −3 charged anions (PO_4^{3-} and AsO_4^{3-}) [12, 18]. The parameters for PO_4^{3-} and AsO_4^{3-} are similar. We therefore decided to include ion-interaction parameters for Na^+-AsO_4^{3-} in our thermodynamic model for Na^+-$Am(CO_3)_3^{3-}$, to test whether such parameters could be important. The revised model showed significant improvement over the model without these ion-interaction parameters. It appears that such specific ion interactions cannot be ignored, at least in 0.2 *M* $NaClO_4$. The solvent-extraction data of Bidoglio can be accurately fit by adjusting either of the binary Pitzer ion-interaction parameters (β^0 or β^1) for Na^+-$Am(CO_3)_3^{3-}$ but not adjusting both simultaneously, since they are redundant in these solutions. We elected to fix β^0 at the Na^+-AsO_4^{3-} value and adjust only β^1. This decision has important consequences for higher ionic strengths, because β^1 is less important at higher ionic strengths than β^0. By including most of the specific ion-interaction effects in β^1, any error introduced will become progressively less important with increasing ionic strength.

In developing our final thermodynamic model, we adjusted β^1 for Na^+-$Am(CO_3)_2^{3-}$ in Bidoglio's solvent-extraction data, with β^0 fixed at the Na^+-AsO_4^{3-} value, and then refit the standard chemical potentials for the Am-CO_3 complexes in our solubility data, with all Pitzer ion-interaction parameters fixed. Our final thermodynamic model has μ^0/RT $(AmOHCO_3(c)) = -569.98$, μ^0/RT $(AmCO_3^+) = -472.06$, μ^0/RT $(Am(CO_3)_2^-) = -695.88$, μ^0/RT $(Am(CO_3)_3^{3-}) = -915.46$, β^0 $(Na^+\text{-}Am(CO_3)_3^{3-}) = 0.24$, and β^1 $(Na^+\text{-}Am(CO_3)_3^{3-}) = 8.1$, assuming $\mu^0/RT\,(Am^{3+}) = -241.694$ (calculated from ΔG_f^0 given by Ref. [19]). The value used for β^1 compares with 3.9 and 5.5 for Na^+-AsO_4^{3-} given by Pitzer and Mayorga [12] and Kim and Frederick [18], respectively. The calculated standard chemical potentials yield log *K* values of −22.5, 7.6, 12.3, and 15.2, respectively, for the reactions

$$AmOHCO_3(c) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-} \qquad (1)$$

$$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+ \qquad (17)$$

$$Am^{3+} + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_2^- \qquad (18)$$

$$Am^{3+} + 3\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}. \qquad (19)$$

A comparison of our model calculations with the solvent-extraction data of Bidoglio [3] (Fig. 7) shows very good agreement, in terms of variability in both total inorganic carbon and pH. This agreement has been achieved without involving the Am-HCO_3 complexes proposed by Bidoglio [3].

The agreement of our calculated data with our experimental data at fixed P_{CO_2} and with the data of Silva and Nitsche [5] is shown in Fig. 8. The agreement

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[4] The nonlinear least-squares program that we used, NONLIN, was developed by A. R. Felmy and combines the MINPACK nonlinear least-squares programs with a chemical equilibrium program that is based upon the Gibbs free energy minimization procedure of Harvie *et al.* [15]. The mathematical development has been outlined by Harvie [16].

[5] In the case of Bidoglio's solvent extraction data, we have digitized and refit all of the high-distribution-coefficient, >9, data. High distribution coefficients ensure that the activity of the extracted Am(III) organic complex is constant in the organic phase. The Am(III) organic complex must be assumed to be at constant activity in the organic phase, because activity data for such complexes in the organic phase are entirely lacking. The necessity for such assumptions has been discussed by Allen and McDowell [17].

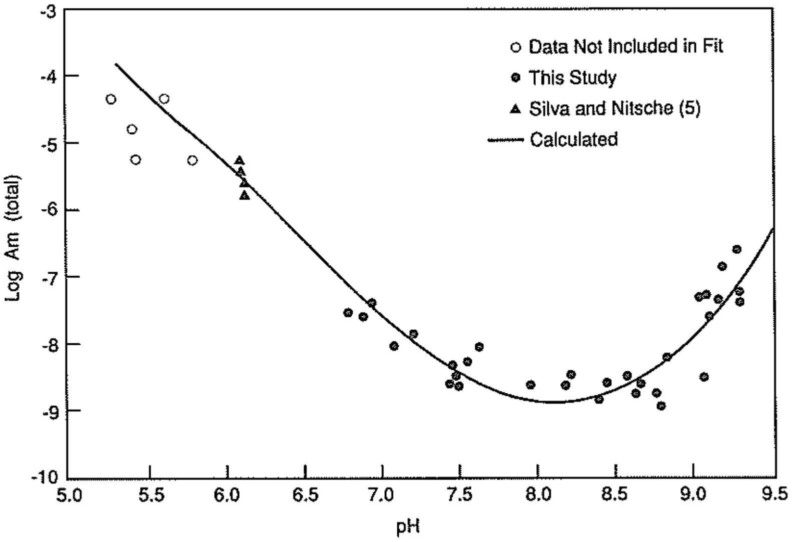

Fig. 8. Experimental and calculated solubilities of AmOHCO$_3$(c) at a fixed P_{CO_2} of 10^{-3} atm. The points not included in the fit represent samples in which the presence of the solid phase could not be positively ascertained.

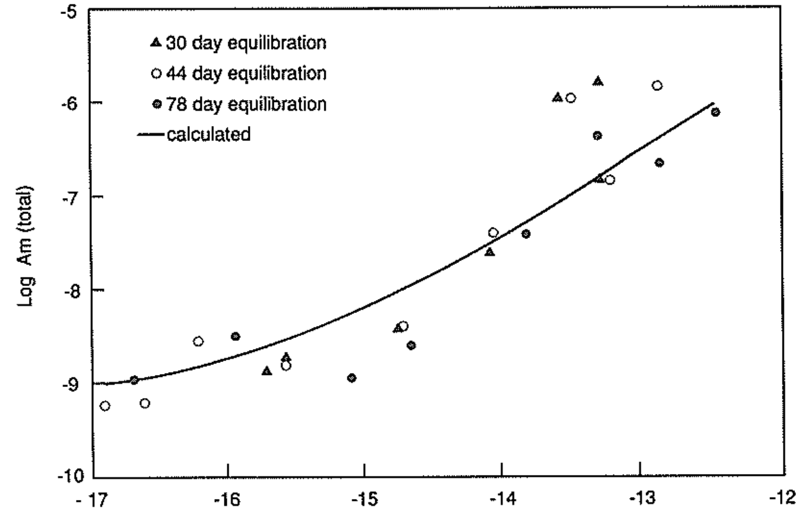

Fig. 9. Experimental and calculated AmOHCO$_3$(c) solubilities in Na$_2$CO$_3$ solutions.

between model and experiment is reasonably good, given that the ranges in Am concentration, pH, and total carbonate concentration covered by the experimental data are large. It should be noted that the points represented as open circles in Fig. 8 were not part of the overall statistical fit, because the presence of the solid phase could not be determined with certainty. However, these points are also in reasonable agreement with our final thermodynamic model.

In the case of our AmOHCO$_3$(c) solubility data in Na$_2$CO$_3$ (Fig. 4), a direct comparison on a two-dimensional figure is complicated by the fact that both pH and carbonate ion concentrations are important variables. To properly demonstrate the agreement between our model calculations and the experimental data, we must find an appropriate combination of these two important variables. The most important solubility reaction in these Na$_2$CO$_3$ solutions can be written as

$$\mathrm{AmOHCO_3(c)} + \mathrm{H^+} + 2\,\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Am(CO_3)_3^{3-}} + \mathrm{H_2O} \tag{20}$$

or, at equilibrium, as the equation

$$\log\{\mathrm{Am(CO_3)_3^{3-}}\} = \log K + 2\log\{\mathrm{CO_3^{2-}}\} - \mathrm{pH}\,. \tag{21}$$

Thus, if $\mathrm{Am(CO_3)_3^{3-}}$ is the only important complex, a plot of the quantity $2\log\{\mathrm{CO_3^{2-}}\} - \mathrm{pH}$ versus $\log \mathrm{Am^T}$ would be a straight line. This is not the case for all of the Na$_2$CO$_3$ solutions, given that $\mathrm{Am(CO_3)_2^-}$ is also important in the lower-pH samples. Nevertheless, using the quantity $2\log \mathrm{CO_3^{2-}}$-pH should normalize the solubility data. The comparison between our measured and our calculated data in Na$_2$CO$_3$

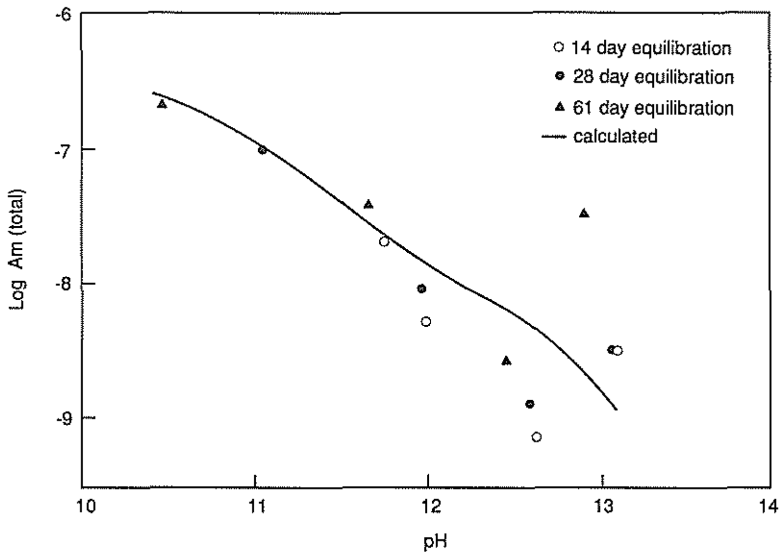

Fig. 10. Experimental and calculated solubilities of $AmOHCO_3(c)$ at fixed Na_2CO_3 concentration and variable pH.

solutions is shown in Fig. 9. The overall comparison is satisfactory, considering that pH, total inorganic carbon, and ionic strength all vary widely. The only significant discrepancy occurs for the two highest carbonate concentration solutions at 30 and 44 days of aging. This discrepancy may be due to an additional carbonate interaction in these solutions that has not been accounted for. It should be noted that, because the pH and carbonate ion concentration both decrease in these samples during the period from 44 to 78 days of equilibration (as a result of increased CO_2; Table 1), the calculated and experimental solubilities for even these two high-carbonate suspensions are in very good agreement after 78 days of equilibration.

Both our calculated and our measured $AmOHCO_3(c)$ solubilities at fixed total carbonate and variable pH are shown in Fig. 10. Again the agreement between model and experiment is good, considering that the data are somewhat scattered above pH 12.

The neutral $Am(OH)_3(aq)$ species must also be discussed in the context of our high-pH thermodynamic model. Rai *et al.* [7] proposed a maximum value for the equilibrium constant for this species, based on $Am(OH)_3(am)$ solubility data that were at or near the analytical detection limit. If this maximum equilibrium constant is used for the neutral $Am(OH)_3(aq)$ species, then the calculated $AmOHCO_3(c)$ solubilities increase sharply above pH 12.5, where this species becomes dominant. At pH 13.1, the calculated solubilities would be almost two orders of magnitude greater than the calculated values shown in Fig. 10. Fig. 10 does show one outlying point in this region. However, the five other points do not support the inclusion of this neutral species with so high an equilibrium constant. Therefore, we have assumed that the one high-Am-concentration point at pH 12.9 in Fig. 10 is not reflective of the true solubility of $AmOHCO_3(c)$, and we have calculated a new maximum value for the equilibrium constant for the $Am(OH)_3(aq)$ neutral species that is consistent with our thermodynamic model for the Am-CO_3 complexes. This new value is $\mu^0/RT = -462.95$ and gives a $\log K$ for the $Am(OH)_3(aq)$ association reaction of 13.4, close to the value of 15.0 proposed by Rai *et al.* [7]. No hydrolysis species other than $Am(OH)_3(aq)$ were calculated to be important in these carbonate-containing solutions.

Finally, our calculated equilibrium constants can be compared with those of Bernkopf and Kim [4] and of Lundqvist [2][6]. To conduct a meaningful comparison, we have extrapolated the equilibrium constants of Bernkopf and Kim [4] for 0.1 *M* $NaClO_4$ and those of Lundqvist [2] for 1 *M* $NaClO_4$ to zero ionic strength. The ion-interaction parameters for Am^{3+}-ClO_4^- and Na^+-$Am(CO_3)_3^{3-}$ generated in this study have improved our extrapolation of the equilibrium constants for these species. However, in the absence of ion-interaction parameters for $AmCO_3^+$ or $Am(CO_3)_2^-$, we have assumed that the activity coefficient for Na^+ equals that for $AmCO_3^+$ and that the activity coefficient for OH^- equals that for $Am(CO_3)_2^-$. These assumptions will be less accurate in 1 *M* $NaClO_4$ than in 0.1 *M* $NaClO_4$ because of specific ion interactions between the bulk electrolyte ions Na^+ and ClO_4^- and $AmCO_3^+$ and $Am(CO_3)_2^-$. Table 5 shows a complete comparison of experimental and calculated equilibrium constants. Our calculated solubility product for $AmOHCO_3(c)$ is essentially identical to the value we extrapolated from the data of Bernkopf and Kim [4]. However, our equilibrium constants for the Am-CO_3 complexes are slightly

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[6] A more detailed analysis of the data of Bernkopf and Kim [4] and of Lundqvist [2] is not possible, because these investigators either did not report their data in sufficient detail or conducted their studies at only one high concentration of background electrolyte, in which a large number of unknown specific ion interactions involving $AmCO_3^+$ and $Am(CO_3)_2^-$ may be important.

Table 5. Comparison of equilibrium constants for various Am-CO_3 complexes. All values are in terms of log K for the designated reaction

Reaction	Bernkopf and Kim [4]		Lundqvist [2]		This study $I=0$
	$I=0.1$	$I=0^0$	$I=1.0$	$I=0^a$	
$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$	5.08	6.5	5.81	8.2	7.6
$Am^{3+} + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$	9.27	11.2	9.72	13.2	12.3
$Am^{3+} + 3\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$	12.12	13.6	–	–	15.2
$AmOHCO_3(c) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-}$	−21.03	−22.7	–	–	−22.5

[a] Extrapolated.

higher than the values extrapolated from the data of Bernkopf and Kim [4]. This difference is probably due to Bernkopf and Kim's [4] inclusion of three additional Am-CO_3 complexes in their statistical fitting procedure. The inclusion of additional species can lower the calculated concentrations of individual species while the same total Am concentration is maintained. The lower concentrations for individual species in equilibrium with $AmOHCO_3$(c) lowers the calculated equilibrium constants. Table 5 also shows that our calculated equilibrium constants are in reasonably good agreement with the values extrapolated from the solvent-extraction and electromigration data of Lundqvist [2], considering that Lundqvist's experiments were in 1 M $NaClO_4$ and that we do not have ion-interaction parameters for either $AmCO_3^+$ or $Am(CO_3)_2^-$.

In summary, we believe the model we have developed is in good agreement with our extensive solubility data for $AmOHCO_3$(c), as well as with the experimental data in the literature. Our model is relatively simple in that it does not require the inclusion of complexes of Am^{3+} with HCO_3^-, and we have demonstrated that OH^- is not involved in the aqueous complexation reactions. In addition, we have demonstrated that $AmOHCO_3$(c) is the thermodynamically stable phase in equilibrium with solutions over the pH range 5.5 to 13 and in dilute <0.1 M carbonate solutions. We have also refined the equilibrium constant for the $Am(OH)_3$(aq) species to be consistent with our experimental findings. In addition, we have evaluated Pitzer ion-interaction parameters for Am^{3+} with ClO_4^- and for Na^+ with $Am(CO_3)_3^{3-}$.

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