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Nd^{3+} and Am^{3+} Ion Interactions with Sulfate Ion and Their Influence on $NdPO_4(c)$ Solubility

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The effects of Nd(III)/Am(III) complexation with sulfate were studied by 1) re-examining existing data for the Am-SO_4 system using more advanced aqueous electrolyte models valid to high concentration to obtain reliable thermodynamic data for SO_4^{2-} complexes or ion interactions with Nd^{3+} and Am^{3+} and 2) conducting experimental solubility studies of $NdPO_4(c)$, an analog phase of $AmPO_4(c)$, a possibly important phase in high level nuclear wastes, in the presence of SO_4^{2-} to test the newly developed thermodynamic model and show the possible influence of sulfate in a repository environment. The data showed that the increase in the solubility of $NdPO_4(c)$ resulted primarily from the increase in ionic strength. Slightly higher observed Nd concentrations in the presence of sulfate, as compared with concentrations predicted at the experimental ionic strengths, resulted from the weak complexes or ion interactions involving Nd^{3+}-SO_4^{2-}. The Pitzer ion interaction parameters, applicable to 0.5m sulfate, were obtained for Am^{3+}-SO_4^{2-} from a reinterpretation of known solvent extraction data. These parameters are also consistent with literature data for Am^{3+}/Na^+ exchange and solvent extraction in the presence of sulfate. When used for the analogous Nd^{3+}-SO_4^{2-} system to predict $NdPO_4(c)$ solubility in the presence of sulfate, they provided excellent agreement between the predicted and the observed solubilities, indicating that they can be reliably used to determine Nd^{3+} or Am^{3+} ion interactions with SO_4^{2-} in all ground waters where SO_4^{2-} is less than 0.5m.

KEY WORDS: Solubility; crystalline $NdPO_4$; sulfate complexes; Nd; Am; Pitzer parameters; solubility product.

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1. INTRODUCTION

Nd(III) is isostructural with trivalent actinide elements, such as Am(III), and studies of the chemistry of Nd(III) can have direct relevance to the chemical behavior of actinide species which are important components of high level nuclear wastes. Sulfate is an important anion in natural ground- waters and sulfate could potentially form strong aqueous complexes with Nd(III)/Am(III) and thereby mobilize trivalent actinide species in groundwater systems. To predict the effects of such complexation reactions in multi- component groundwater systems requires accurate thermodynamic data for sulfate complexes/ion-interactions.

The aqueous Nd and Am complexation reactions with SO_4^{2-} have been studied extensively, principally for Am^{3+}, in perchlorate media, and by solvent extraction(1-5) and ion-exchange methods(2,6-9) (Table I). Most of these studies were conducted at relatively high and constant ionic strengths (0.5-2.0 mol-kg^{-1}) to avoid variations in aqueous phase ionic activity coefficients that would complicate the thermodynamic analysis.

Unfortunately, extrapolating thermodynamic data to zero ionic strength from studies conducted at only one ionic strength is difficult because information is not given on the electrolyte concentration dependence of the apparent equilibrium constants. To overcome these difficulties, some authors, McDowell and Coleman(3) in particular, conducted their solvent extraction studies in the absence of a constant ionic-strength medium but over a range of Na_2SO_4 concentrations extending to $0.5m$. They extrapolated their thermodynamic data to zero ionic strength using the extended Debye-Hückel equation. The values of equilibrium constants thus obtained by McDowell and Coleman(3) are significantly different from previous results that were not extrapolated to zero ionic strength.

The extended Debye-Hückel equation does not provide reliable interpretations of data involving such high-ionic-strength solutions as some of the samples reported by McDowell and Coleman.(3) Therefore, those data, which are based on very well done experiments, have been reinterpreted (fit) using more appropriate electrolyte models to obtain revised thermodynamic data describing Am^{3+}-SO_4^{2-} interactions. In addition, some of the ion-exchange and solvent- extraction data based on experiments in constant ionic-strength solutions maintained by $NaClO_4$ could be reinterpreted if appropriate ion-interaction parameters were available. However, such data specifically for Am^{3+}-ClO_4^- do not exist. Making the reasonable assumptions that 1) binary interactions between

Table I. Equilibrium Constants for Formation of Aqueous Am^{3+} and Nd^{3+} Complexes with SO_4^{2-} [a]

$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	I	Medium	Ref.
		Americium			
1.49	2.47	-	1.0-1.3	$NaClO_4$	8
1.78	-	-	0.75	$NaClO_4$	6
1.76	2.11	-	1.5	NH_4ClO_4	7
1.57	2.66	-	1.0	$NaClO_4$	1
1.49	2.36	-	1.0	$NaClO_4$-Na_2SO_4	9
1.86	2.79	-	0.5	$NaClO_4$(IE)[b]	2
1.85	2.83	-	0.5	$NaClO_4$(SE)[b]	2
1.43	1.85	-	2.0	$NaClO_4$	10
3.76	5.64	5.29	0, ext.[c]	Na_2SO_4-H_2SO_4	3
1.71	2.89	-	1.0	$HClO_4$-H_2SO_4	4
1.72	-	-	1.0	NH_4ClO_4-$(NH)_2SO_4$	5
		Neodymium			
1.26	1.79	-	2.0	$NaClO_4$	10
3.64	-	-	0, ext.[d]	$Nd_2(SO_4)_3$	11
2.92	-	-	0, corrected	-	12

[a] Equilibrium constants β_n for reactions $M^{3+} + nSO_4^{2-} \rightleftarrows M(SO_4)_n^{3-2n}$, where M is Am^{3+} or Nd^{3+}. [b] IE = ion-exchange and SE = solvent-extraction methods. [c] Extrapolated from data for solutions with ionic strengths varying up to 1.5 mol-L^{-1}. [d] Extrapolated from solutions with ionic strengths varying up to 1.2.

Am^{3+} and ClO_4^- are the most important at the ionic strengths of these experiments (Table I), and 2) Nd^{3+}-ClO_4^- binary parameters(13) are applicable to Am^{3+}-ClO_4^-, the older data in $NaClO_4$ media can be used to verify the Am^{3+}-SO_4^{2-} parameters obtained from simple systems.(3)

With these facts in mind, this study had two objectives: 1) to reanalyze the solvent-extraction data of McDowell and Coleman(3) and other data in perchlorate media(1,9) using more advanced electrolyte models such as those of Pitzer,(13,14) which are valid to high electrolyte concentration, and 2) to test the validity of this new thermodynamic model both on data from previous perchlorate media studies and with independent experimental data that we developed on the solubility of $NdPO_4$(c) in Na_2SO_4 solutions. The $NdPO_4$(c) studies are needed to clearly demonstrate the ability of aqueous SO_4^{2-} to solubilize such compounds of trivalent rare earths and actinides as $AmPO_4$(15) that may be present or form in the radioactive waste repository environment, possibly resulting in these elements moving out of the waste package and into the surrounding environment.

2. METHODS AND MATERIALS

2.1. Stock Solutions and Reagents

The Nd stock solution was prepared from Nd_2O_3 in the following manner: Nd_2O_3 was heated briefly to about 850°C to remove adsorbed water and CO_2 and thus to convert back to stoichiometric Nd_2O_3. A 50.5-g quantity of Nd_2O_3 was weighed, placed in about 250 ml of H_2O, and brought to boiling. Concentrated (12*M*) HCl was added to the boiling suspension. As the stoichiometric amount needed to dissolve the Nd_2O_3 was approached, HCl was gradually added in small increments. The container was intermittently placed in an ultrasonic bath to break up larger particles or lumps of Nd_2O_3 and to produce fine turbidity throughout the solution once all the HCl had been added. Very little excess HCl was used in the dissolution. The final clear solution was boiled down until significant crystallization occurred. At this point the solution was diluted with 250 ml of H_2O and brought back to boiling, which produced a very fine (milky) turbidity caused by NdOCl. The solution was stirred rapidly on a hot plate, and 0.3*M* HCl was added by drops until the addition of one drop took the solution from a slightly turbid state to one showing only a Tyndall effect. At this point 0.100 ml of 12*M* HCl was added, and the solution was diluted to 1 L. The resulting solution was expected to be 0.30 $NdCl_3$ and 0.001*M* free H^+. No Tyndall effect could be observed. Stock solutions of desired Nd molality were prepared from this solution for use in the studies reported here.

A stock solution of phosphate was prepared from reagent-grade $NaH_2PO_4 \cdot H_2O$ and deaerated water. Ultrapure HCl was used to prepare stock solutions of varying molarity and to adjust the pc_{H^+} values of experimental solutions. Stock solutions containing Na_2SO_4 were prepared using the deaerated water, and the solutions were kept in a controlled-atmosphere glovebox until they were used.

2.2. Precipitation of $NdPO_4$(c)

A 0.1*M* $NdCl_3$ stock solution was slowly mixed with the 0.1*M* NaH_2PO_4 H_2O stock solution in equal volume ratios, using the multihead peristaltic pump, to form the $NdPO_4$ precipitate. The pH value of the suspension was adjusted to about 2.5, at which point most of the Nd

Table II. Concentration of HCl Used in Different Experiments and the Calculated pc_{H^+} Values of Solutions

	$10^{-3.06}m\ SO_4$[b]		$10^{-1.12}m\ SO_4$[b]
-log HCl[a]	pc_{H^+}	$pH_{meas.}$	pc_{H^+}
1.60	1.61	1.63	1.95
1.70	1.71	1.75	2.08
1.80	1.81	1.83	2.17
1.89	1.90	1.93	2.26
2.00	2.02	2.03	2.38
2.10	2.12	2.13	2.50
2.22	2.25	2.26	2.62
2.30	2.33	2.36	2.70
2.40	2.43	2.44	2.80
2.49	2.53	2.54	2.90
2.52	2.56	2.56	2.93
2.70	2.73	2.75	3.11
2.80	2.83	2.85	3.21
2.89	2.92	2.94	3.29
3.00	3.04	3.06	3.41
3.22	3.27	3.28	3.63

[a] Initial added concentration. [b] pc_{H^+} was calculated from input molalities of HCl, NaH_2PO_4, and Na_2SO_4 using the GMIN Code (Ref.16), which contains appropriate ion-interaction terms for various species. $pH_{meas.}$ = pH measured with glass electrode.

precipitated as $NdPO_4$. The precipitate was aged for one week in the parent liquor. The aged precipitate was washed twice with deionized water at pH 4.5 to prevent the secondary precipitation of $NdOHCO_3$ or $Nd(OH)_3$ that could result at higher pH values. The x-ray diffraction patterns obtained from smear mounts showed this precipitate to be crystallized $NdPO_4$. The washed precipitate was apportioned to different sampling tubes.

2.3. General Procedure

The solubility of $NdPO_4(c)$ was determined as a function of H^+ concentration, at two different SO_4 concentrations, and at a fixed concentration of NaH_2PO_4.

Two sets of experiments were conducted. Each set contained $NdPO_4$ precipitates suspended in 30 ml of $10^{-3.5}M$ NaH_2PO_4 in 16 different centrifuge tubes containing varying amounts of standard HCl (Table II). These sets also contained $10^{-3.06}$ or $10^{-1.12}M$ Na_2SO_4. All experiments were conducted on the bench top. The samples were continuously shaken until analyzed. Previous studies with $NdPO_4$ showed that equilibrium is reached in less than 6 days.(17) Therefore, the samples were equilibrated for at least 7 days. At the end of an equilibration period, 7 days for the low sulfate set and 14 and 28 days for the high sulfate set, the pH values of the suspensions were measured with a combination glass electrode calibrated against pH buffers. For accurate thermodynamic interpretations of the solubility data, accurate values of H^+ activity or concentration are required. The ionic strength of the low sulfate set was low and the measured pH should have reasonably represented the H^+ activity and approximated the H^+ concentration, because convention-dependent single-ion activity coefficients and differences in liquid junction potentials between standards and solutions can be neglected for these dilute solutions. To conclusively demonstrate this fact, we calculated the H^+ concentration in all our solutions using the starting molalities (it was assumed that the molarities equal molalities in these dilute solutions) of HCl, NaH_2PO_4, and Na_2SO_4 in the GMIN computer program,(16) which performs the chemical equilibrium speciation calculations. These results (Table II), in dilute solution, are extremely close to our measured pH values. However, in $10^{-1.12}M$ SO_4, the differences in single ion activity coefficients and liquid junction potentials between standards and solutions cannot be ignored, and the measured pH may not be an accurate estimate of the H^+ activity or concentration. Therefore, the equilibrium H^+ concentrations pc_{H^+} were calculated from the input molalities using GMIN as described above. For consistency, these calculated pc_{H^+} values for all sets were used to interpret and represent the data.

After the pH was measured, the suspensions were centrifuged at about 2000 g for 7-10 min. Aliquots of the supernatants were withdrawn and filtered through Amicon Type F-25 Centriflo membrane cones (Amicon Corp., Lexington, Massachusetts) with effective 25,000-molecular-weight cutoffs and approximately 0.0018-µm pore sizes. To increase the efficacy of the filters, they were pretreated as described by Rai(18) according to the following steps: 1) the filters were washed and equilibrated with deionized water, adjusted to the pc_{H^+} values of the samples to prevent precipitation of the solid phase caused by changes in the pc_{H^+} values during filtration, and 2) a small aliquot of the sample was passed through the filters to saturate any possible adsorption sites on the filters and filtration containers; this filtrate was then discarded. Filters treated this way have been successfully used in studies involving several elements, including Am,(19,20) which is a chemical analog of Nd.

The filtrates were acidified and stored until analyzed. Neodymium concentrations in filtrates were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS). The concentrations of P, Na, and S were analyzed by inductively coupled plasma spectroscopy (ICP).

2.4. Reinterpretation of Literature Data for Am^{3+}-SO_4^{2-} Interactions

A literature review of the data for Am^{3+} and Nd^{3+} complexes with SO_4^{2-} (Table I) shows that extensive data exist only for Am^{3+} and that all of the Am studies except the study done by McDowell and Coleman(3) used $NaClO_4$ as the ionic medium for maintaining a constant ionic strength. Therefore, McDowell and Coleman's(3) data are ideally suited for determining the values of Am^{3+}-SO_4^{2-} ion interactions where effects due to $NaClO_4$ specific ion interactions are absent. McDowell and Coleman(3) interpreted their data using the Debye-Hückel equation to correct for the ionic-strength differences in solutions. The use of this equation for interpreting their high-ionic-strength solutions, reaching as high as 1.5, is very questionable. Therefore, we decided to reinterpret their data in terms of the Pitzer model that is applicable to high ionic strength solutions and where specific ion interactions for all of the species except Am are available. Details of these reinterpretations are given in the results and discussion section. The reliability of the values obtained from the reinterpretation of McDowell and Coleman's(3) data were checked against the data reported by Nair(9) and Sekine.(1)

3. RESULTS AND DISCUSSION

Previous studies on the solubility of $NdPO_4(c)$ indicated that equilibrium between solids and solutions was reached in less than 6 days.(17) Therefore, the greater than 6-day equilibration period was selected for these studies involving the effect of sulfate on the solubility of $NdPO_4(c)$. As expected, the observed aqueous Nd concentrations in equilibrium with $NdPO_4(c)$ in the presence of both levels of sulfate (pSO_4 of about 3.06 and 1.12) decreased with the increase in pc_{H^+} (Fig. 1). However, a significant increase in the solubility of $NdPO_4(c)$ was observed at pSO_4 of 1.12, as compared with pSO_4 of 3.06. The observed increase in solubility with the increase in sulfate may result from the increase in ionic strength, aqueous complexation of Nd^{3+} with SO_4, or both. To determine the effect of ionic strength and the specific ionic media used in this study, the solubilities of $NdPO_4(c)$ at the measured phosphate, sulfate, sodium, and pc_{H^+} were calculated with the GMIN equilibrium code,(16) using $\Delta_f G^\circ/RT$ values (Table III) and Pitzer ion-

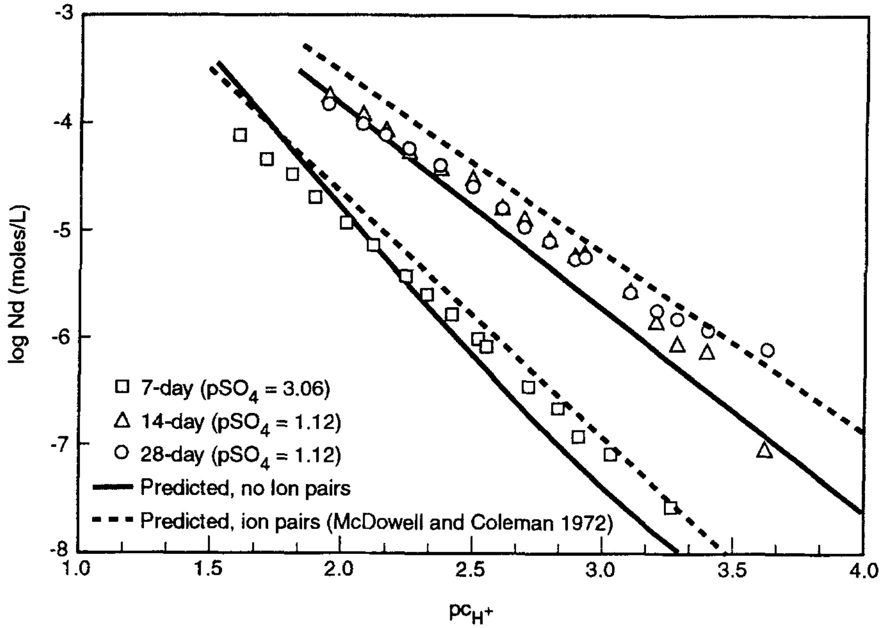

Fig. 1. Aqueous Nd concentrations in equilibrium with $NdPO_4(c)$ at NaH_2PO_4 = $10^{-3.5}M$ and as a function of pc_{H^+} and SO_4. Dashed lines represent predicted concentrations using the ion-interaction approach, which included values for $NdSO_4^+$, $Nd(SO_4)_2^-$, and $Nd(SO_4)_3^{3-}$, assuming equilibrium constants for the formation of these species are identical to those reported by McDowell and Coleman(3) for the corresponding Am-SO_4 species at zero ionic strength.

interaction parameters (Table IV) excluding Nd^{3+}-SO_4^{2-}. In these calculations and all of the other calculations that follow, the total sulfate was speciated into SO_4^{2-} and HSO_4^- and total phosphate was speciated into H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} using the $\Delta_f G°/RT$ values reported in Table III. A comparison of the calculated $NdPO_4(c)$ solubilities (solid lines, Fig 1) with those observed in the presence of SO_4 shows that they are similar, with the exception of slightly higher observed concentrations in the high pc_{H^+} region. These results indicate that the increase in solubility in the presence of sulfate is primarily caused by the increase in ionic strength, not by Nd^{3+}-SO_4^{2-} complexation, although some complexation or ion interaction between Nd^{3+} and SO_4^{2-} may be responsible for the higher observed solubilities in the pc_{H^+} region >2.2 (Fig. 1).

Since the calculated $NdPO_4$ solubilities (solid lines, Fig. 1) at higher sulfate concentrations were lower than our experimental results,

Table III. Dimensionless Standard Molar Gibbs Energies of Formation of Different Species Used in Calculations

Species	$\Delta_f G^\circ/RT$	Reference
Nd^{3+}	-270.926	21
Am^{3+}	-241.694	22
H_3PO_4	-460.90	23
$H_2PO_4^-$	-455.960	23
HPO_4^{2-}	-439.367	21
PO_4^{3-}	-410.947	21
SO_4^{2-}	-300.386	24
HSO_4^-	-304.942	24
$NdPO_4(c)$	-738.63	17
$NdH_2PO_4^{2+}$	-733.20	17[a]

[a] Either the $NdH_2PO_4^{2+}$ species or the binary interactions between the Nd^{3+} and $H_2PO_4^-$ must be included (see footnote to Table IV).

even at these relatively low dissolved sulfate concentrations, we suggest that Nd^{3+}-SO_4^{2-} complexes/interactions might be important. To evaluate the importance and obtain reliable values for these interactions, the existing experimental data on Am^{3+}-SO_4^{2-} complexes as an analog for Nd^{3+}-SO_4^{2-} complexes were reanalyzed using the aqueous thermodynamic model of Pitzer.

Am is an analog of Nd and reliable experimental data are available in simple systems(3) that provide values of $[Am(SO_4)_n^{3-2n}]$ complexation constants (Table I). Assuming that complexation constant values for $Nd(SO_4)_n^{3-2n}$ reactions are identical to the corresponding Am reactions at zero ionic strength reported by McDowell and Coleman,(3) chemical potentials for $Nd(SO_4)_n^{3-2n}$ were calculated and included in the GMIN model for predicting the influence of SO_4^{2-} on $NdPO_4(c)$ solubility. The calculations with the inclusion of complexed SO_4^{2-} species (dashed lines, Fig. 1) showed higher solubilities compared with those observed, especially for the $pSO_4 = 1.12$. These higher calculated solubilities most likely result from inaccurate values for sulfate complexes due to the use of the extended Debye-Hückel equation in the thermodynamic analysis of McDowell and Coleman.(3) We have therefore reanalyzed the experimental data of McDowell and Coleman(3) using the Pitzer ion-interaction approach, which is valid to high electrolyte concentration.

Table IV. Ion-Interaction Parameters Used in Calculating Activities with the Ion-Interaction Model

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Ref.
		Binary Interactions			
Nd^{3+}-Cl^-	0.6117	5.403	0.00	-0.0284	25
Na^+-$H_2PO_4^-$	-0.0533	0.0396	0.00	0.00795	25
Na^+-HPO_4^{2-}	-0.0583	1.4655	0.00	0.02938	25
Na^+-PO_4^{3-}	0.17813	3.8513	0.00	-0.05154	25
Nd^{3+}-$H_2PO_4^-$	0.00	0.00	-92.9	0.00	17[a]
H^+-Cl^-	0.1775	0.2945	0.00	0.0008	24
Na^+-Cl^-	0.0765	0.2664	0.00	0.00127	24
Na^+-SO_4^{2-}	0.01958	1.113	0.00	0.00497	24
Na^+-HSO_4^-	0.0454	0.398	0.00	0.00	24
Nd^{3+}-SO_4^{2-}	3.0398	0.00	-2500	0.00	This study
Am^{3+}-SO_4^{2-}	3.0398	0.00	-2500	0.00	This study
Am^{3+}-ClO_4^-	0.754	6.53	0.00	0.0075	This study[b]
Na^+-ClO_4^-	0.0554	0.2755	0.00	-0.00118	13
H^+-ClO_4^-	0.1747	0.2931	0.00	0.00819	13
H^+-SO_4^{2-}	0.0298	0.00	0.00	0.0438	24
H^+-HSO_4^-	0.2065	0.5556	0.00	0.00	24
		Neutral Ion Interactions			
$H_3PO_4^o$-$H_3PO_4^o$		0.0503			23
$H_3PO_4^o$-$H_3PO_4^o$-$H_3PO_4^o$		0.0109			23
$H_3PO_4^o$-$H_2PO_4^-$		-0.4			23
$H_3PO_4^o$-H^+		0.29			23
		Ternary Interactions			
H^+-Na^+		0.036			24
H^+-Na^+-Cl^-		-0.004			24
Cl^--$H_2PO_4^-$		0.10			23
H^+-Na^+-HSO_4^-		-0.0129			24
SO_4^{2-}-HSO_4^--Na^+		-0.0094			24
SO_4^{2-}-ClO_4^-		0.020			This Study[c]
SO_4^{2-}-ClO_4^--Na^+		0.0014			This Study[c]
SO_4^{2-}-Cl^-		0.0200			24
SO_4^{2-}-Cl^--Na^+		0.0014			24
HSO_4^--Cl^-		-0.0060			24
HSO_4^--Cl^--H^+		0.0130			24
HSO_4^--Cl^--Na^+		-0.006			24

[a] We represent Nd^{3+} interactions with $H_2PO_4^-$ by these binary interactions instead of with $(\Delta_f G^o/RT)(NdH_2PO_4^{2+})$. [b] Assuming Nd^{3+}-ClO_4^- parameters from Ref. 13 apply to Am^{3+}-ClO_4^-. [c] Assuming Cl^- parameters from Ref. 24 apply to the ClO_4^- system.

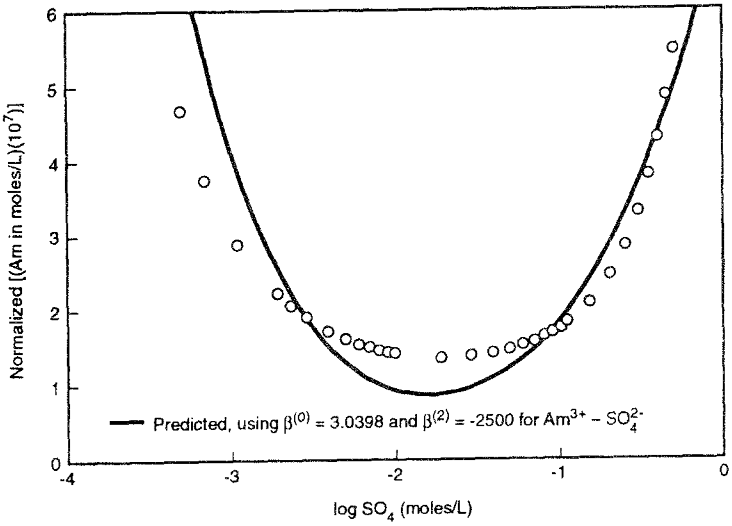

Fig. 2. Variation in normalized equilibrium aqueous phase Am concentrations as a function of sulfate ion concentrations at constant acid activity and constant organic-extractant-phase composition calculated for experimental data of McDowell and Coleman.(3) The solid line is the best-fit approach that included values of $\beta^{(0)} = 3.04$ and $\beta^{(2)} = -2500$ for Am^{3+}-SO_4^{2-}.

McDowell and Coleman(3) do not report actual experimental data. However, they do report the relative distribution of Am species as a function of aqueous sulfate. Using their data, we were able to calculate the relative aqueous Am concentrations as a function of aqueous sulfate concentrations (Fig. 2). These solvent extraction data were analyzed to obtain binary ion-interaction parameters for Am^{3+}-SO_4^{2-} using a nonlinear least-squares and chemical equilibrium program (NONLIN)[2] that included $\Delta_f G°/RT$ and ion-interaction parameter values reported in Tables III and IV. In this program, the actual quantity minimized was the standard deviation σ, defined by

$$\sigma^2 = \sum_{i=1}^{N} f(x)^2/N \tag{1}$$

where N is the total number of data points and $f(x)$ is given by the phase equilibrium condition as

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[2] NONLIN, developed by A. R. Felmy, uses the MINPACK nonlinear least-squares program in combination with a chemical equilibrium program based on the Gibbs energy minimization procedure of Weare *et al.*.(26) The mathematical development is outlined by Harvie.(27)

$$f(x) = (\Delta_f G)_{Am_2(SO_4)_3(org.)} - (\Delta_f G)_{solution}$$

In the case of the extraction in the organic phase of $Am_2(SO_4)_3$, the extractable species proposed by McDowell and Coleman,(3) this condition gives

$$f(x) = \left[(\Delta_f G^\circ/RT)_{Am_2(SO_4)_3(org)}\right]$$

$$- \left[2(\Delta_f G^\circ/RT)_{Am^{3+}} + 3(\Delta_f G^\circ/RT)_{SO_4^{2-}} + 2\ln(C\gamma)_{Am^{3+}} + 3\ln(C\gamma)_{SO_4^{2-}}\right] \quad (2)$$

where $\Delta_f G^\circ/RT$ is the dimensionless standard molar Gibbs energy of formation, C is the molar concentration and γ_i is the activity coefficient of the subscripted species. The unknown $(\Delta_f G^\circ/RT)_{Am_2(SO_4)_3(org.)}$ and the binary ion-interaction parameters for Am^{3+}-SO_4^{2-} were determined simultaneously.

Previous studies(28,29) have shown that 3:2 electrolytes exhibit marked association in extremely dilute solution, but at higher electrolyte concentration the decrease in ion-activity coefficients for bare ions results in a dissociation of such complexes. We found similar effects in the high valence Th^{4+}-SO_4^{2-} system.(30) Therefore, to determine definitive values for $\beta^{(2)}$ or the first ion-association constant requires data for extremely dilute solutions.(28) Unfortunately, McDowell and Coleman(3) do not present sufficient data in extremely dilute solution with which to unambiguously obtain the value of $\beta^{(2)}$ for Am^{3+} with SO_4^{2-}. Consequently, several different values of $\beta^{(2)}$ were tested on the solvent extraction data of McDowell and Coleman.(3) A value of -2500 best described the data. This selected value is similar to the recommended $\beta^{(2)}$ values(28) of -2085 for $La_2(SO_4)_3$. Using $\beta^{(2)} = -2500$, a reasonable value of $\beta^{(0)} = 3.04$ for Am^{3+}-SO_4^{2-} is obtained from the data of McDowell and Coleman.(3) The calculated Am concentrations with these parameters are in good agreement with the experimental values of McDowell and Coleman,(3) especially considering that Am data are plotted on a linear scale in almost the entire range of aqueous sulfate concentrations that were investigated (Fig. 2).

To check whether these ion-interaction parameters based on solvent extraction data in a simple system are applicable to such mixed systems as those involving ClO_4^--SO_4^{2-} and H_2PO_4-SO_4^{2-} and those involving ion exchange and solubility methods, predicted concentrations using these parameters were compared with the reliable experimental data amenable to these calculations reported in the literature(1,9) and data obtained in this study. Nair(9) and Sekine(1) studied the complexation behavior of Am^{3+} with SO_4^{2-} through ion- exchange and solvent-extraction

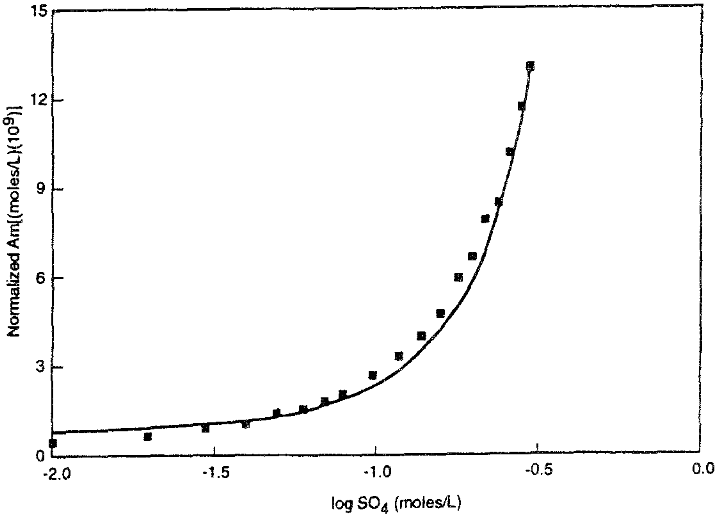

Fig. 3. Variation in normalized equilibrium aqueous phase Am concentrations as a function of sulfate ion concentrations at constant pH and constant ion-exchange-phase composition, calculated for experimental data of Nair.(9) The solid line is the predicted concentration using ion-interaction parameters reported in Table IV (for details see text).

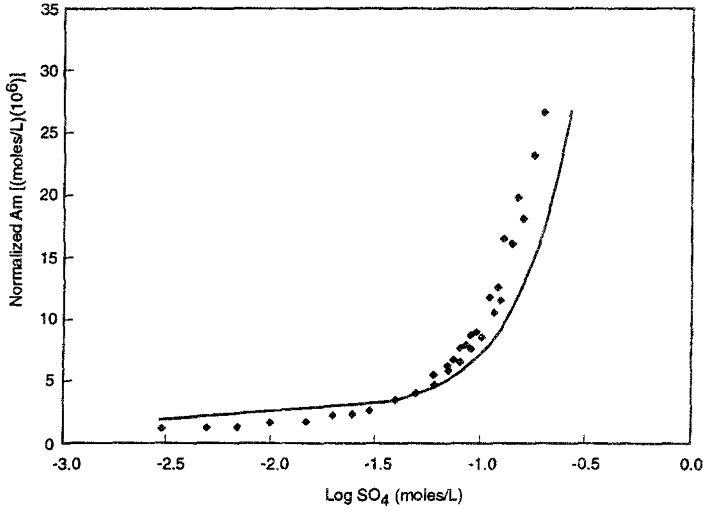

Fig. 4. Variation in normalized equilibrium aqueous phase Am concentrations as a function of sulfate ion concentrations at constant acid activity and constant organic-extractant-phase composition, calculated for experimental data of Sekine.(1) The solid line is the predicted concentration using ion-interaction parameters reported in Table IV (no ion-interaction parameters for 0.01*m* sulfanilic acid-sulfanilate, used in experiments, were included in the model; for details see text).

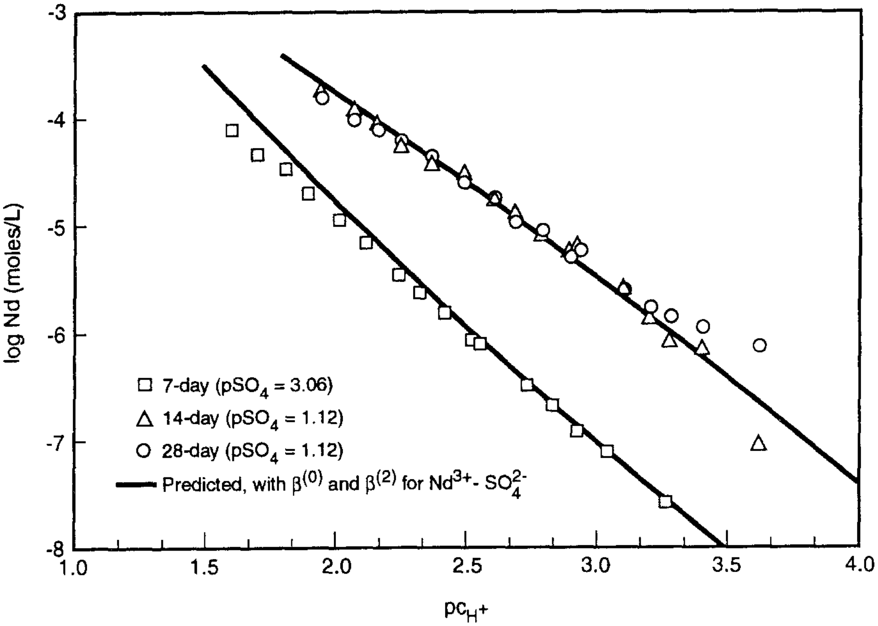

Fig. 5. Aqueous Nd concentrations in equilibrium with $NdPO_4(c)$ at $NaH_2PO_4 = 10^{-3.5}M$ and as a function of pc_{H^+} and SO_4. Solid lines represent predicted concentrations using the ion-interaction approach, which included values of $\beta^{(0)} = 3.0398$ and $\beta^{(2)} = -2500$ for Nd^{3+}-SO_4^{2-} obtained from McDowell and Coleman's(3) data for the analogous Am^{3+}-SO_4^{2-} system.

reactions, respectively, at a constant ionic strength of 1.0*M* maintained by $NaClO_4$. Values for all of the expected dominant ion interactions in these systems involving ClO_4^- except Am^{3+}-ClO_4^- are available (Table IV). Using these values, along with others discussed earlier, and assuming that binary Pitzer-model parameters for Nd^{3+}-ClO_4^- are applicable to the analogous Am^{3+}-ClO_4^- (a reasonable assumption), predictions were made of the Am concentrations in Am^{3+}/Na^+ exchange(9) and solvent extraction(1) reactions in the presence of SO_4^{2-}. Excellent agreement was found between the predicted and the experimental data of Nair(9) (Fig. 3). The agreement between the predicted and the experimental data of Sekine(1) (Fig. 4) is also good, considering that the Am concentrations are plotted on a linear scale, and that Sekine(1) used 0.01*M* sulfanilic acid-sulfanilate buffer in the experiments, and it was not possible to include its effects in the predicted concentrations. These results show that Am^{3+}-SO_4^{2-} ion interactions obtained from simple systems are applicable to mixed systems, and indirectly show that fitting solvent-extraction and ion-exchange data will result in identical values for the Am^{3+}-SO_4^{2-} binary ion-interaction parameters.

Because Nd and Am are chemical analogs, it is reasonable to assume that the binary ion-interaction parameters for Am^{3+}-SO_4^{2-} obtained in this study apply equally to the Nd^{3+}-SO_4^{2-} system. Using $\beta^{(0)} = 3.04$ and $\beta^{(2)} = -2500$ for $Nd^{3+}SO_4^{2-}$ and other parameters (including $\Delta_f G/RT$) shown in Tables III and IV, aqueous Nd concentrations in equilibrium with $NdPO_4$(c) in the presence of different concentrations of sulfate were predicted (Fig. 5). The excellent agreement between the predicted and the observed concentrations again indicates that the binary parameters obtained in this study are reliable.

In conclusion, Nd^{3+} and Am^{3+} complexes or ion interactions with SO_4^{2-} are either weak or important only in very dilute solution. Such interactions can be represented by Pitzer ion-interaction parameters $\beta^{(0)} = 3.04$ and $\beta^{(2)} = -2500$. These values are consistent with solvent-extraction and ion-exchange data reported in the literature(1,3,9) and have been verified with the $NdPO_4$(c) solubility in sulfate media. The assumption of strong Nd^{3+} and Am^{3+} complexation with SO_4^{2-} is not consistent with the experimental data when valid aqueous thermodynamic models are used to interpret the concentrated solution experimental data.

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APPENDIX

Analytical results from the solubility of $NdPO_4$(c) in Na_2SO_4, HCl, and NaH_2PO_4 solutions are graphed in the main body of the paper (Figures 1 and 5) and the corresponding data are reported in Table II and Appendix Table AI.

Table AI. Concentrations in 0.0018 μm Filtrates from $NdP0_4$(c) Suspensions Equilibrated for Different Periods from the Undersaturation Direction with $10^{-3.5}M$ of NaH_2PO_4 and Different Amounts of HCl and Na_2SO_4

	$10^{-3.06}$ *M* SO_4[b]		$10^{-1.12}$ *M* SO_4[b]			
	7 days		14 days		28 days	
$-\log C_{HCl}$	$-\log C_{Nd}$	$-\log C_p$	$-\log C_{Nd}$	$-\log C_p$	$-\log C_{Nd}$	$-\log C_p$
1.60	4.13	3.46	3.77	3.22	3.84	3.24
1.70	4.36	3.44	3.95	3.24	4.04	3.28
1.80	4.50	3.53	4.08	3.23	4.13	3.28
1.89	4.70	3.60	4.09	3.28	4.27	3.31
2.00	4.95	3.46	4.45	3.29	4.42	3.33
2.10	5.16	3.52	4.55	3.44	4.64	3.39
2.22	5.45	3.50	4.79	3.38	4.78	3.40
2.30	5.61	3.44	4.91	3.44	4.99	3.38
2.40	5.80	3.46	5.09	3.43	5.09	3.46
2.49	6.03	3.53	5.24	3.45	5.27	3.44
2.52	6.09	3.45	5.21	3.43	5.24	3.48
2.70	6.47	3.59	5.58	3.47	5.59	3.45
2.80	6.66	3.50	5.86	3.41	5.75	3.49
2.89	6.92	3.50	6.06	3.46	5.83	3.55
3.00	7.09	3.35	6.13	3.40	5.94	3.51
3.22	7.58	3.40	7.04	3.48	6.11	3.52

[a] Initial added concentration. [b] All concentrations in mol-L^{-1}.