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Solubility of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ in Concentrated Na_2CO_3 and $NaHCO_3$ Solutions

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Neodymium / Sodium carbonate / Sodium bicarbonate / Solubility / Ion-interaction

Abstract

$NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ was identified to be the final equilibrium solid phase in suspensions containing concentrated sodium carbonate (0.1 to 2.0 M) and sodium bicarbonate (0.1 to 1.0 M), with either $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ or $Nd_2(CO_3)_3 \cdot xH_2O(s)$ as initial solids. A thermodynamic model, based on Pitzer's specific ion-interaction approach, was developed to interpret the solubility of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ as functions of sodium carbonate and sodium bicarbonate concentrations. In this model, the solubility data of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ were explained by assuming the formation of $NdCO_3^+$, $Nd(CO_3)_2^-$ and $Nd(CO_3)_3^{3-}$ species and invoking the specific ion interactions between Na^+ and $Nd(CO_3)_3^{3-}$. Ion interaction parameters for Na^+-$Nd(CO_3)_3^{3-}$ were developed to fit the solubility data. Based on the model calculations, $Nd(CO_3)_3^{3-}$ was the predominant aqueous neodymium species in 0.1 to 2 M sodium carbonate and 0.1 to 1 M sodium bicarbonate solutions. The logarithm of the $NaNd(CO_3)_2 \cdot 6\,H_2O$ solubility product ($NaNd(CO_3)_2 \cdot 6\,H_2O(c) = Na^+ + Nd^{3+} + 2\,CO_3^{2-} + 6\,H_2O$) was calculated to be −21.39. This model also provided satisfactory interpretation of the solubility data of the analogous Am(III) system in less concentrated carbonate and bicarbonate solutions.

1. Introduction

Thermodynamic data on stable solid phases, solubility limits, and aqueous speciation are essential in understanding and predicting the transport of radionuclides in aqueous systems. In recent years, the solid-liquid phase equilibria of trivalent actinides and lanthanides in carbonate-bicarbonate systems have been the subject of several studies because of the following concerns: 1) some natural aqueous systems have high CO_2 partial pressures (0.03 to 10%) [1, 2], which results in high aqueous concentrations of carbonate and bicarbonate, and 2) actinide and lanthanide cations form strong aqueous carbonato complexes under certain conditions [3–6], which could increase the aqueous concentrations of these cations and significantly enhance their mobility.

Unfortunately, the available thermodynamic data for carbonate systems involving trivalent actinides and lanthanides are highly diverse and complex. Several different carbonate compounds of trivalent actinides/lanthanides were reported under various conditions. For example, Silva and Nitsche [7] determined $AmOH(CO_3)(c)$ to be the stable solid phase in suspensions equilibrated with 0.03% CO_2 (pH about 6). Bernkopf and Kim [5] reported that $AmOH(CO_3)(c)$ was the thermodynamically stable solid phase in solutions with total carbonate concentrations of at least 0.1 M. However, Shiloh *et al.* [6] found $Am_2(CO_3)_3(s)$ to be the stable phase in 0.1 to 0.6 M K_2CO_3. More recently, Runde and Kim [8] reported $NaAm(CO_3)_2(s)$ to be the stable solid phase in 5 M NaCl solution of neutral pH under 0.01 atm CO_2 partial pressure and Kim *et al.* [9] used time-resolved laser-induced fluorescence spectroscopy to characterize europium(III) and curium(III) carbonate solids and their aqueous carbonato complexes in 0.1 M $NaClO_4$ solutions, with pH from 4 to 10 and under 1 to 100% CO_2 partial pressure. In most of these studies, values of conditional solubility products were reported for the identified solid compounds and high uncertainties in those values were observed. For example, Firsching and Mohammadzadel [10] determined the solubility of rare earth carbonates ($Ln_2(CO_3)_3$, Ln = lanthanides) in H_2O with a pH range of 4.6 to 6.2 and reported pK_{sp} values ranging from 28.25 to 35.45. Their data showed an abnormally high solubility for $Er_2(CO_3)_3$ relative to its neighboring rare earth analogs. This abnormality remains unexplained and questionable. Recently, Meinrath and co-workers [11–13] and Runde *et al.* [14] determined conditional solubility products of different Am(III) and Nd(III) carbonates in 0.1 and 0.3 M $NaClO_4$ solutions maintained at different CO_2 partial pressures (0.03 to 100%) and pH values (4 to 9). In these systems, either $MOH(CO_3)(s)$ or $M_2(CO_3)_3(s)$ (where M is Am or Nd) was found to be the stable solid. In an attempt to summarize literature data on the solubility of three different solids ($Am(OH)_3$, $AmOHCO_3$ and $Am_2(CO_3)_3$), Vitorge [15] discussed the utilization of the specific ion interaction (SIT) method to extrapolate the conditional K_{sp} values to zero ionic strength, in which some difficulties and uncertainties were involved because of insufficient experimental data.

In summary, a literature survey indicates that 1) several different solid compounds may form, depending on the system conditions such as pH, partial

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pressure of CO_2, concentrations of total carbonate and other species (e.g. Na^+); 2) a large variability exists in values of data on solubility products and stability constants for aqueous complexes; 3) most of the studies provided only the conditional solubility products in particular electrolyte media and at specific ionic strengths. The validity of extrapolation of those conditional constants to the reference state (zero ionic strength) remains uncertain.

To provide reliable thermodynamic information on the solid-liquid equilibria in the Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system, Felmy *et al.* [16] determined the solubility of $AmOH(CO_3)(c)$ at low total carbonate concentrations (<0.1 M) over a wide pH range and reinterpreted the available solvent extraction data of Bidoglio [4] for americium-carbonate complexes. A thermodynamic model including ion interaction parameters for $Na^+/Am(CO_3)_3^{3-}$ was developed. Although it provided a good fit to the experimental results, a review of the model indicated that $Am(CO_3)_3^{3-}$ was not a predominant solution species of americium under the conditions in Felmy's work, except for a few points in the vicinity of the highest carbonate concentration (0.1 M). Consequently, the applicability of the ion interaction parameters thus developed for $Na^+/Am(CO_3)_3^{3-}$ remains questionable. Evidently, it is necessary to conduct solubility experiments in more concentrated carbonate and bicarbonate solutions, in which $Am(CO_3)_3^{3-}$ is most likely to be predominant, so that those parameters can be tested and modified if necessary. In the present work, neodymium was studied as the chemical analog for Am(III) and the concentrations of sodium carbonate and sodium bicarbonate were extended from 0.1 M to near saturation. Our objectives were to 1) identify the thermodynamically stable solid phases in the Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system of high sodium carbonate and sodium bicarbonate concentrations; 2) obtain the thermodynamic data on the stable solid phase and aqueous complexes; and 3) test and develop the necessary ion interaction parameters to describe the solubility data in both dilute and concentrated carbonate/bicarbonate solutions.

2. Materials and procedures

2.1 Stock solutions and reagents

All chemical reagents used in this work were A. R. grade or higher. Double-distilled acids (HNO_3 and HCl) were used when needed. Distilled and deionized water was used to prepare all solutions.

2.2 Characterization of $Nd_2(CO_3)_3 \cdot xH_2O(s)$

Neodymium carbonate ($Nd_2(CO_3)_3 \cdot xH_2O$, 99.99% purity) was purchased from Aldrich Chemical Company. X-ray diffraction (XRD) patterns of this solid indicated that 60% (by weight) of this solid was $Nd_2(CO_3)_3 \cdot 2.5\ H_2O$ while the rest was unidentified neodymium carbonate compounds, possibly $Nd_2(CO_3)_3$ with different numbers of H_2O molecules. This material was used without further purification as the initial solid in one series of the solubility experiments.

2.3 Preparation and characterization of $NaNd(CO_3)_2 \cdot 6\ H_2O(c)$

$NaNd(CO_3)_2 \cdot 6\ H_2O(c)$ was prepared by the following procedure based on the paper by Mochizuki *et al.* [17]. Into 30 mL of 0.3 M $NdCl_3$ solution (pH about 3.2), 30 mL of 1.0 M sodium acetate/1.0 M acetic acid buffer (pH about 5) was added and mixed thoroughly. Then, about 240 mL of 1 M Na_2CO_3 solution was slowly added into this buffered $NdCl_3$ solution with vigorous stirring. The final pH of the suspension was about 7. The polyethylene bottle containing the suspension was shaken on an orbital shaker for 4 to 7 days. The suspension was then centrifuged and the precipitate was washed twice with deionized water before it was analyzed by XRD. The XRD patterns of the prepared compound were in good agreement with those for $NaNd(CO_3)_2 \cdot 6\ H_2O$ reported by Mochizuki *et al.* [17]. To avoid any phase changes, the washed "wet" $NaNd(CO_3)_2 \cdot 6\ H_2O(c)$ was directly transferred into the centrifuge tubes for solubility experiments.

2.4 Solubility experiments

Two series of solubility experiments were performed, with $Nd_2(CO_3)_3 \cdot xH_2O(s)$ and $NaNd(CO_3)_2 \cdot 6\ H_2O(c)$ as the initial solids, respectively. In each series, two sets of experiments were conducted: one set contained sodium carbonate in a concentration range of 0.1 to 2.0 M, the other set contained sodium bicarbonate in a concentration range of 0.1 to 1.06 M. As a result, the pH of the solutions in the first set was around 11, while that in the second set was around 8. The solubility experiments were carried out in 50 mL polypropylene centrifuge tubes, each containing enough initial solid to guarantee excess solid phase materials remaining after the system reached equilibrium. After the initial pH was measured, these centrifuge tubes were sealed and continuously shaken on an orbital shaker until the scheduled sampling and analysis. No particular measures were taken to control the atmosphere under which the suspensions were equilibrated. However, the pH and total carbonate concentrations were measured after each sampling to ascertain no significant changes in the carbonate concentration occurred.

The equilibration periods for the first series ($Nd_2(CO_3)_3 \cdot xH_2O$ as the initial solid) were 15, 48, 78 and 110 days, while the equilibration periods for the second series ($NaNd(CO_3)_2 \cdot 6\ H_2O$ as the initial solid) were 14, 46, 76 and 111 days.

2.5 Analyses

At the end of each equilibration period, the pH of the suspensions was measured with a combination glass

electrode calibrated against standard pH buffers to determine the relative acid-base properties of the solutions. The suspensions were then centrifuged at about 2,000 g for 7 to 10 minutes. Samples of the supernatants were filtered through membranes (approximate pore size = 0.0018 μm, effective molecular-weight cutoff = 25,000) based on the procedure developed by Rai *et al.* [18, 19]. The procedure is as follows: 1) the filters were washed with deionized water; 2) 2.0 mL of the supernatant was passed through the filters to saturate any possible adsorption sites on the filters and filtration containers (this filtrate was discarded); 3) 6.0 mL of the supernatant was filtered. Of the 6.0 mL of final filtrate, 1.0 mL was used for analysis of total inorganic carbon with a coulometric CO_2 analyzer. The remaining 5.0 mL of filtrate was acidified with concentrated nitric acid and used for analysis of sodium and neodymium. Sodium was determined by inductively coupled plasma spectroscopy (ICP), while neodymium was analyzed by the inductively coupled plasma spectroscopy − mass spectrometry (ICPMS) technique, with indium-115 as the internal standard. The analytical errors in [Nd] (at the 95% confidence level) are estimated to be less than 10% in all cases, based on the standard deviations of the tests using NBS certified Nd standard solutions.

At the end of the sampling periods (110 and 111 days for the two series of experiments, respectively), wet samples of the solid phases were taken and analyzed by XRD.

3. Results and discussion

The change in aqueous neodymium concentrations as a function of equilibration periods ranging from 14 to 111 days indicates that neodymium concentrations reached steady states in about 15 days in the sodium carbonate systems (Figs. 1 a and 1 b) and in 46 to 48 days in the sodium bicarbonate systems (Figs. 1 c and 1 d). As a result, the data obtained from 14- and 15-day samplings of the sodium bicarbonate systems were not included in the subsequent development of the thermodynamic model.

In the bicarbonate systems containing $Nd_2(CO_3)_3 \cdot xH_2O$ as the initial solid (Fig. 1 c), the neodymium concentrations at the 15-day sampling were lower than the steady state concentrations. This is understandable because the equilibrium was approached from undersaturation. However, when $NaNd(CO_3)_2 \cdot 6\,H_2O$ was used as the initial solid, the neodymium concentrations at the 14-day sampling were much higher than the steady state concentrations (Fig. 1 d). This is most likely because the $NaNd(CO_3)_2 \cdot 6\,H_2O$ was added in the "wet" form after washing with deionized water (pH about 6). The solubility of $NaNd(CO_3)_2 \cdot 6\,H_2O$ at pH 6 is expected to be significantly higher than the final equilibrium concentrations in these sodium bicarbonate systems at a pH of about 8. In other words, the solid-liquid equilibrium was approached from oversaturation when "wet" $NaNd(CO_3)_2 \cdot 6\,H_2O$ was used as the initial solid.

All the solid samples from the systems using $Nd_2(CO_3)_3 \cdot xH_2O$ as the initial solid and several representative solid samples from the systems using $NaNd(CO_3)_2 \cdot 6\,H_2O$ as the initial solid were analyzed by XRD. The XRD patterns of all the samples are consistent with those for $NaNd(CO_3)_2 \cdot 6\,H_2O$ [17].

The observations can be summarized as follows: 1) steady state concentrations were reached in 15 to 48 days, 2) final steady-state concentrations were similar when approached from undersaturation or oversaturation, and when obtained from $Nd_2(CO_3)_3 \cdot xH_2O$ or $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ as the initial solid, 3) the final solid at the steady state was found to be $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$. Based on these observations, we concluded that the steady-state neodymium concentrations represent the equilibrium solubility of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ under the experimental conditions. Therefore, only the steady state data were used in the thermodynamic analysis.

3.1 Thermodynamic analysis and the solubility product of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$

In the Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system, the equilibrium neodymium concentrations, i.e., the observed total $[Nd]_{aq}$, were the sum of the concentrations of all aqueous neodymium species, which were in simultaneous equilibria with the solid phase. The aqueous species included Nd^{3+}, neodymium hydroxy species, and various neodymium carbonato species. The observed changes in $[Nd]_{aq}$ as functions of $[NaHCO_3]$ or $[Na_2CO_3]$ were the overall effect of changes in ligand concentration and changes in the activity coefficients of various species in those equilibria. The dissolution of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ can be expressed by the following reaction:

$$NaNd(CO_3)_2 \cdot 6\,H_2O(c) = Na^+ + Nd^{3+} + 2\,CO_3^{2-} + 6\,H_2O \quad (1)$$

where Nd^{3+} is in simultaneous equilibria with other species such as

$$Nd^{3+} + i\,OH^- = Nd(OH)_i^{(3-i)+} \quad (2)$$

probable values of $i = 1, 2, 3$

$$Nd^{3+} + j\,CO_3^{2-} = Nd(CO_3)_j^{(2j-3)-} \quad (3)$$

probable values of $j = 1, 2, 3$

To evaluate these equilibria simultaneously based on the experimental data, a nonlinear least-squares program (NONLIN) was used in combination with a chemical equilibrium program (GMIN) [16]. The NONLIN is based upon the algorithm of Harvie and associates [20, 21]. Details of the minimization procedure have been outlined in previous publications [22, 23]. In the current system, the quantity minimized

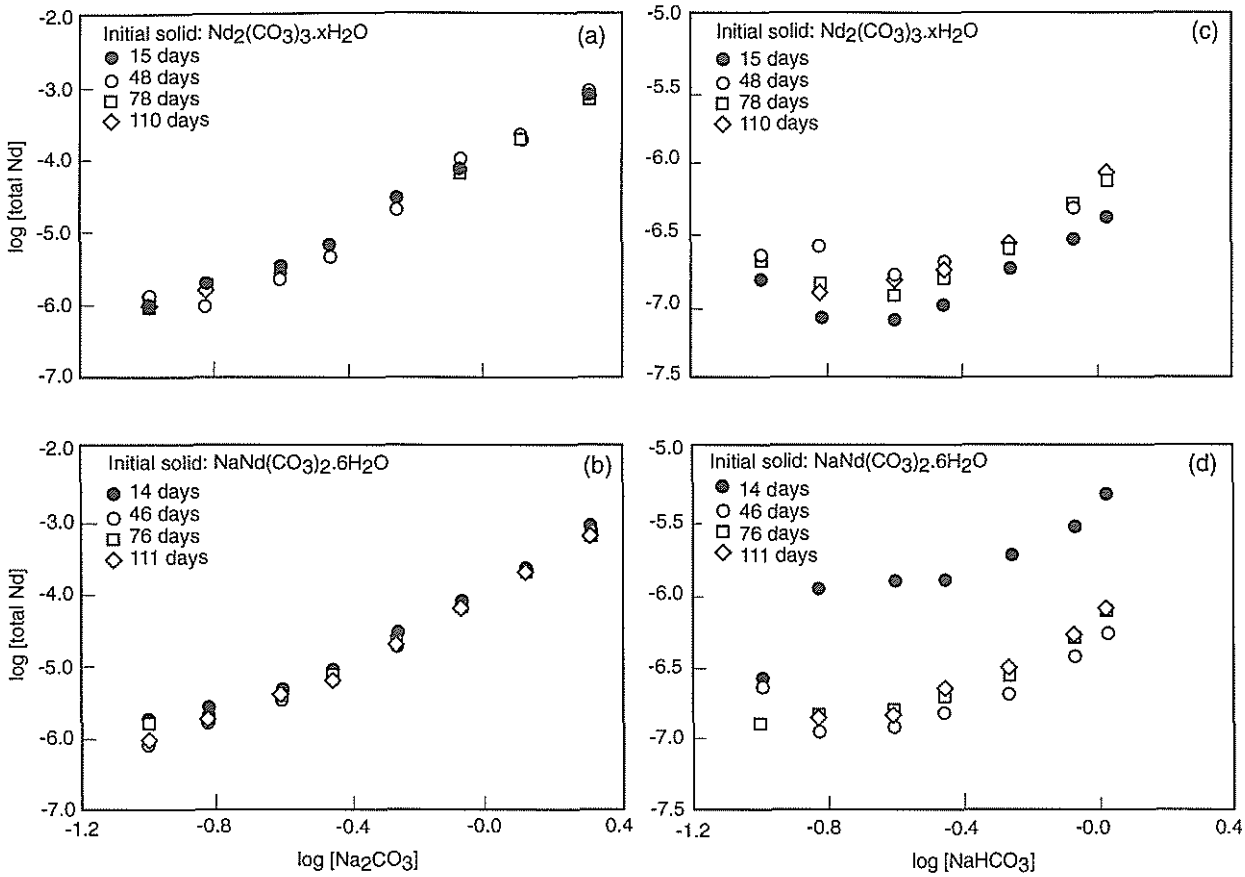

Fig. 1. Measured neodymium concentrations as functions of equilibration time and concentrations of sodium carbonate or sodium bicarbonate. (a) and (b) for sodium carbonate. (c) and (d) for sodium bicarbonate.

was the statistical summation of $f(\chi)$ over all experimental points, where $f(\chi)$ was defined as

$$\begin{aligned} f(\chi) &= (\mu/RT)_{\text{solid}} - (\mu/RT)_{\text{solution}} \\ &= (\mu^{\circ}/RT)_{NaNd(CO_3)_2\cdot 6H_2O} - \{(\mu^{\circ}/RT)_{Na^+} \\ &+ (\mu^{\circ}/RT)_{Nd^{3+}} + 2(\mu^{\circ}/RT)_{CO_3^{2-}} \\ &+ 6(\mu^{\circ}/RT)_{H_2O} + \ln(m_{Na^+}\gamma_{Na^+}) \\ &+ \ln(m_{Nd^{3+}}\gamma_{Nd^{3+}}) + 2\ln(m_{CO_3^{2-}}\gamma_{CO_3^{2-}})\} \end{aligned} \quad (4)$$

where μ° is the standard chemical potential, R is the gas constant, T is temperature in degrees Kelvin, m denotes the molality of the subscripted species, and γ refers to the activity coefficient of the subscripted species.

In Eq. (4), all μ°/RT values were from literature except for $(\mu^{\circ}/RT)_{NaNd(CO_3)_2\cdot 6H_2O}$. The molalities of Na^+, Nd^{3+} and CO_3^{2-} were obtained from corresponding molarities and the density of carbonate and bicarbonate solutions. The $[Na^+]$ was determined by ICP analysis. The $[Nd^{3+}]$ and $[CO_3^{2-}]$ were calculated using the NONLIN program with the μ°/RT values for various aqueous species involved in the aqueous equilibria. The μ°/RT values used in the evaluation are listed in Table 1. Preliminary calculations that included the neodymium hydroxy species $(Nd(OH)_i^{(3-i)^+}$, $i = 1, 2, 3)$ indicated that these species were not significant in the concentrated carbonate or bicarbonate solutions. As a result, the μ°/RT values for $Nd(OH)_i^{(3-i)^+}$ were not included in Table 1.

Table 1. Chemical species and their μ°/RT values used in this study

Species	μ°/RT	Reference
H_2O	− 95.663	[24]
Na^+	− 105.651	[24]
OH^-	− 63.435	[24]
CO_3^{2-}	− 212.944	[24]
HCO_3^-	− 236.751	[24]
CO_2(aq)	− 155.680	[24]
Nd^{3+}	− 270.926	[25]
$NdCO_3^+$	− 501.292	[22]
$Nd(CO_3)_2^-$	− 725.112	[22]
$Nd(CO_3)_3^{3-}$	− 944.692	[22]
$NaNd(CO_3)_2\cdot 6H_2O$(c)	−1425.70	this work

Besides the necessary μ°/RT values, the activity coefficients in Eq. (4) had to be calculated to evaluate the experimental data. In this study, the ion-interaction model of Pitzer *et al.* [26, 27] was used to calculate the activity coefficients because of its broad applicability to solutions with zero to high ionic strengths. Based on Pitzer's model, the effects of the specific ion interactions on the excess solution free energy are represented within the activity coefficient expressions.

Table 2. Pitzer ion-interaction parameters used in this study

Species	Ion-interaction parameters		
	Binary system interactions		
	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^+-HCO_3^-	0.0277	0.0411	0
Na^+-CO_3^{2-}	0.0399	1.389	0.0044
Na^+-OH^-	0.0864	0.253	0.0044
Na^+-$Nd(CO_3)_3^{3-}$	−0.256	5.0	0.0443
	Common ion ternary system interactions		
H^+-Na^+	0.036		
OH^--CO_3^{2-}	0.10		
OH^--CO_3^{2-}-Na^+	−0.017		
CO_3^{2-}-HCO_3^-	−0.04		
CO_3^{2-}-HCO_3^--Na^+	0.002		

All the parameters were taken from Ref. [24], except those for Na^+-$Nd(CO_3)_3^{3-}$ developed in this work.

A detailed description of these expressions are given elsewhere [24, 28]. The complete set of parameters defining the non-ideal behavior of electrolytes include $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{ϕ} for each cation-anion pair, Θ_{ij} for each cation-cation or anion-anion pair, Ψ_{ijk} for each cation-cation-anion and anion-anion-cation triplet, and λ_{in} and δ_{ijn} for each ion-neutral and ion-ion-neutral interactions. Some of these interaction parameters for the Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system were available from the literature [24] and are summarized in Table 2.

Felmy *et al.* [16] previously developed a thermodynamic model that provided satisfactory interpretation of the solubility of $AmOH(CO_3)(c)$ in less concentrated sodium carbonate and bicarbonate solutions (<0.1 M). In that model, the interactions between Na^+ and $Am(CO_3)_3^{3-}$ were considered by including $\beta^{(1)}$ and $\beta^{(0)}$ parameters. The $\beta^{(1)}$ for Na^+-$Am(CO_3)_3^{3-}$ interaction was fixed at the literature $\beta^{(1)}$ value of 8.1 for Na^+-AsO_4^{3-} interaction, on the assumption that these two interactions were analogous. The $\beta^{(0)}$ was then adjusted to 0.24 to fit the solvent extraction data of Bidoglio [4]. Ideally, the same model might be applicable to the Nd(III) system, because Nd(III) has been demonstrated to be a good analog for trivalent actinide species [28, 29]. However, when the model was tested with the solubility data for Nd(III) in the concentrated carbonate and bicarbonate solutions, it was found that some adjustments of $\beta^{(0)}$ and/or $\beta^{(1)}$ for Na^+-$Nd(CO_3)_3^{3-}$ seemed to be necessary. Because $\beta^{(0)}$ and $\beta^{(1)}$ may be redundant in these solutions, improvements on the fitting could be achieved by adjusting either of them, but not both simultaneously. For the Na^+-$Nd(CO_3)_3^{3-}$ interaction, we decided to fix $\beta^{(1)}$ at the value of 5.0, which is typical of the ion interactions between a trivalent cation and monovalent anion, and adjust $\beta^{(0)}$ and C^{ϕ}. The standard chemical potentials for aqueous Nd(III)-carbonate species were fixed at the values calculated for the analogous Am(III) species by Felmy *et al.* [16].

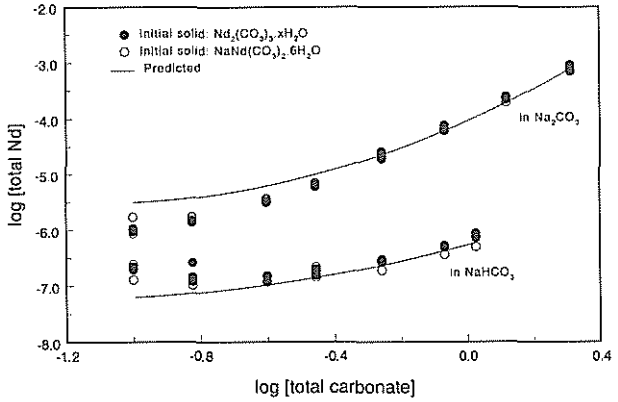

Fig. 2. Solubility of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ in sodium carbonate and sodium bicarbonate solutions.

Different models were tested, and the simplest model that was consistent with the solubility data in this study and those in Felmy *et al.* [16] is given in Table 2. The value of μ°/RT for $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ was calculated to be −1425.70 by this model, which corresponds to a K_{sp} value of $10^{-21.39}$ for the reaction

$$NaNd(CO_3)_2 \cdot 6\,H_2O(c) = Na^+ + Nd^{3+} + 2\,CO_3^{2-} + 6\,H_2O \quad (5)$$

The current model provides a satisfactory interpretation of the available solubility data of $NaNd(CO_3)_2 \cdot 6\,H_2O$ (c) in both the sodium carbonate and bicarbonate solutions over a wide range of concentrations (Fig. 2).

Whether or not trivalent lanthanides and actinides form bicarbonato complexes in these systems has been a controversial subject in the literature. Bidoglio [4] represented his solvent extraction data in terms of aqueous complexes including $Am(HCO_3)^{2+}$ and $Am(HCO_3)_2^+$. However, the spectrophotometric experiments of Nitsche and Silva [29] did not support the existence of such complexes. Felmy *et al.* [16] found that both their solubility data and Bidoglio's solvent extraction data [4] could be well interpreted without invoking the americium bicarbonato complexes. In this study for the Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system, the inclusion of $Nd(HCO_3)^{2+}$ and/or $Nd(HCO_3)_2^+$ complexes into the model did not provide satisfactory interpretation of the experimental data. As a result, these complexes were not invoked.

3.2 Application of the present model in less concentrated carbonate and bicarbonate systems

Developing a model that is applicable to systems covering a wide concentration range is desirable. Because the interaction parameters in the present model (Table 3) were developed based on the data for concentrated sodium carbonate and sodium bicarbonate

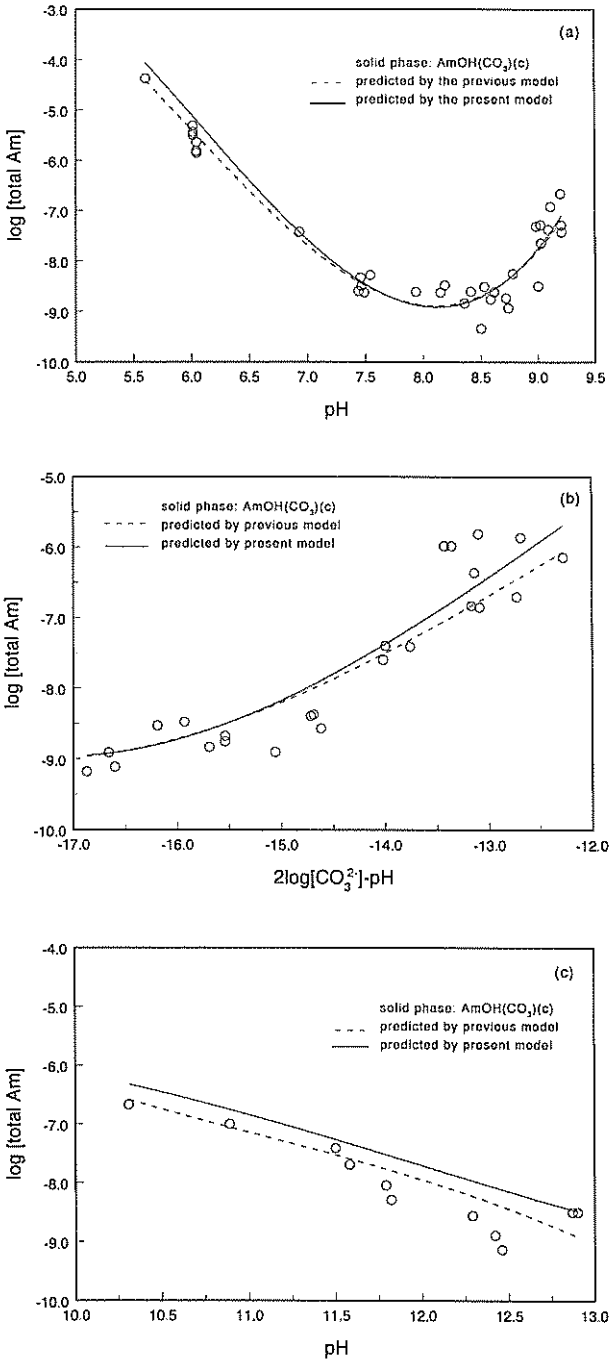

Fig. 3. Comparison of the predictions for the Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system by the previous [16] and the present models. (a) At fixed partial pressure of CO_2 ($P_{CO2} = 10^{-3.5}$ atm). (b) In Na_2CO_3 solutions of different concentrations. (c) At fixed [Na_2CO_3] (0.07 M).

solutions (0.1 M to near saturation), the applicability of this model needed to be tested in less concentrated solutions. Based on the assumption that Nd(III) is a good analog of Am(III), this model was tested with the experimental solubility data [16] for the Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system at lower carbonate and bicarbonate concentrations (<0.1 M) and over a wide pH range (Fig. 3). The tests for the data in the pH region below 9.5 indicated that the predictions made with the present model are in very good agreement with the original data and with the previous model proposed by Felmy *et al.* [16] (Figs. 3a and 3b). However, the predictions made with the two models deviate slightly from each other in the higher pH region. Nevertheless, even in the higher pH region (Fig. 3c), the present model provides satisfactory predictions.

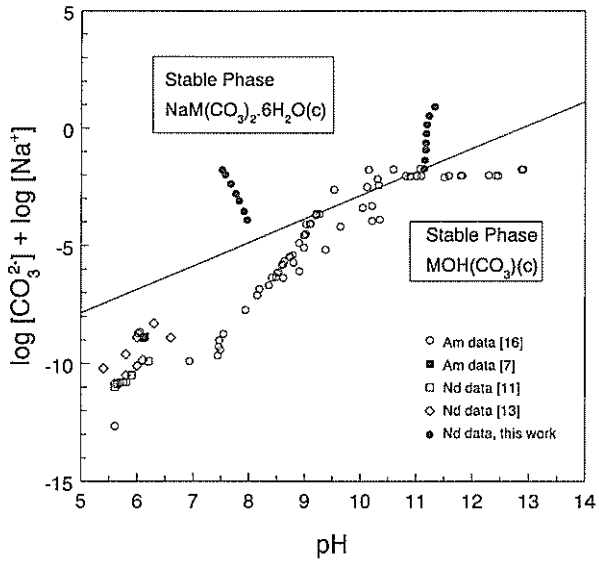

Fig. 4. Phase transition between $NaM(CO_3)_2 \cdot 6\,H_2O$ (c) and $MOH(CO_3)$ (c) (M represents Nd or Am).

3.3 Solution speciation and stable solid phases

Four aqueous Nd(III) species, i.e., Nd^{3+}, $Nd(CO_3)^+$, $Nd(CO_3)_2^-$ and $Nd(CO_3)_3^{3-}$, are invoked in this model. The model predicts that in both sodium carbonate and sodium bicarbonate solutions of 0.1 M or higher (up to 2 M for carbonate and 1 M for bicarbonate), $Nd(CO_3)_3^{3-}$ is the predominant species in the aqueous phase. Efforts were made to obtain experimental evidence for the existence of these neodymium species by the extended X-ray absorption fine structure (EXAFS) technique. However, due to the low neodymium concentration of these solutions and the limited sensitivity of the technique for solution analysis, no conclusive information regarding the structure of the neodymium carbonato species has been obtained at present.

In the previous work on the Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system at lower carbonate and bicarbonate concentrations (<0.1 M) [16], the stable solid phase was found to be the hydroxycarbonato compound of Am(III), $AmOH(CO_3)$(c) ($K_{sp} = 10^{-22.5}$). However, in this study on the Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system at higher carbonate and bicarbonate concentrations, the stable solid phase was found to be $NaNd(CO_3)_2 \cdot 6\,H_2O$(c), with a K_{sp} value of $10^{-21.39}$. It is interesting to use the available thermodynamic data and predict the stable regions for these two types of

solid phases, i.e., $NaM(CO_3)_2 \cdot 6\,H_2O(c)$ and $MOH(CO_3)(c)$ (M is Am or Nd). The phase transition between $NaM(CO_3)_2 \cdot 6\,H_2O(c)$ and $MOH(CO_3)(c)$ can be expressed by the following reaction:

$$NaM(CO_3)_2 \cdot 6\,H_2O(c) = MOH(CO_3)(c) + Na^+ + CO_3^{2-} + H^+ + 5\,H_2O\,. \quad (6)$$

This equilibrium depends on several factors such as pH and concentrations of carbonate and sodium ion. From the available chemical potential values for the species participating in this reaction, the equilibrium constant (K_{eq}) for Eq. (6) can be calculated. Based on this reaction, if $\{\log[Na^+] + \log[CO_3^{2-}]\}$ is plotted against pH, the equilibrium between these two solid phases will be represented by a straight line with a slope of +1 and an intercept of $\log K_{eq}$. Fig. 4 is such a plot, and it shows the equilibrium line dividing the two phases. Experimental points for $NaM(CO_3)_2 \cdot 6\,H_2O(c)$ from this work and those for $MOH(CO_3)(c)$ in literature are also included in the plot. As Fig. 4 indicates, most of the experimental points consistently fall in the phase region predicted for the identified solid phase, except that a few points corresponding to $AmOH(CO_3)$ (c) in the Na^+-Am^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system [16] fall in the phase region for $NaAm(CO_3)_2 \cdot 6\,H_2O(c)$. To investigate this discrepancy, data in Ref. [16] were revisited and it was found that the authors had noticed those few points significantly deviated from their model prediction (Fig. 9 in Felmy *et al.* [16]). Probably the uncertainty in identifying the solid phases for those few points is responsible for the discrepancy.

4. Summary

$NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ was identified to be the thermodynamically stable solid phase in sodium carbonate and sodium bicarbonate solutions (0.1 M to near saturation). The solubility product of $NaNd(CO_3)_2 \cdot 6\,H_2O(c)$ was calculated based on the thermodynamic model developed for the present Na^+-Nd^{3+}-HCO_3^--CO_3^{2-}-OH^--H_2O system. This model is in good agreement with the solubility data for the Am(III) and Nd(III) carbonate systems covering a wide range of carbonate concentrations (dilute to near saturation). Values of Pitzer parameters for the ion interactions of Na^+-$Nd(CO_3)_3^{3-}$ were developed. Further testing of this model is in progress in mixed electrolyte solutions of Na_2CO_3-NaCl and $NaHCO_3$-NaCl.

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