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ARTICLE INFORMATION

0033-8230
RADIOCHIMICA ACTA
52-3():29 34 1991

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Radiochimica Acta 52/53, 29 – 34 (1991)
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The Carbonate Complexation of the Am(III) Ion

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(Received November 6, 1989; revised February 26, 1990)

Americium / Carbonate complexation / Spectroscopy / Solubility / Stability constant / Solubility product

Abstract

Am(III) carbonate complexation has been investigated in 0.1 *M* $NaClO_4$ (or 0.3 *M* $NaClO_4$) under Ar + 1% CO_2 atmosphere at pH = 6.0 – 9.2. Under these conditions the Am^{3+} ion precipitated is found to be $Am_2(CO_3)_3(s)$. Solubility and spectroscopic experiments are carried out in parallel. The contribution of hydrolysis reactions to total reactions is found to be small at $P_{CO_2} = 10^{-2}$ but considerable at $P_{CO_2} = 10^{-3.5}$. The probability of formation of hydroxocarbonate species of Am(III) is discussed. The average constants determined by the two separate experiments are: $\log K_{sp}$ $(Am_2(CO_3)_3)$ = -29.80 ± 0.10, $\log \beta_1 = 6.22 \pm 0.08$ and $\log \beta_2 = 9.76 \pm 0.17$.

1. Introduction

The carbonate complexation of the Am^{3+} ion has been investigated by spectrophotometry [1], solubility experiment combined with pH titration [2] and solvent extraction [3, 4]. In the solubility experiment, the $Am(OH)CO_3(s)$ precipitate is postulated under 0.031% CO_2 partial pressure at 0.1 *M* or 0.3 *M* $NaClO_4$ [2] and its solubility product is determined. The formation of such a mixed hydroxocarbonate precipitate is later confirmed by powder X-ray diffraction method [5]. The stability constants of mono-, di- and tricarbonate complexation [1 – 4] as well as of hydroxocarbonates [2] have been reported. The formation of hydrogencarbonate complexes is also considered for the interpretation of solvent extraction results [3] but cannot be corroborated by spectroscopic experiment [1].

Since the hitherto known stability constants of Am(III) carbonate complexation [1 – 4] and hydrolysis reactions [6] indicate a strong competition of the two reactions, the formation of either carbonates or hydroxocarbonates is possible depending on the CO_2 partial pressure of a given system. For this reason, the present experiment is conducted under somewhat higher CO_2 partial pressure (1%) in 0.1 *M* $NaClO_4$ (or for some cases 0.3 *M* $NaClO_4$) in order to verify the Am(III) carbonate species produced in both solid and liquid phases and hence to evaluate their solubility product and stability constants. Further aim is to clarify conditions that produce Am(III) carbonates and/or hydroxocarbonates.

2. Experimental

A solubility experiment in combination with radiometric pH titration has been carried out in a thermostated titration vessel (100 ml) in the pH range from 6.0 to 9.2 under Argon plus 1% CO_2 atmosphere. The gas mixture with a precise CO_2 concentration is supplied by Linde Co. The ionic strength of the solution is adjusted by 0.1 *M* $NaClO_4$ at pH = 6 – 8 and 0.3 *M* $NaClO_4$ at pH = 8 – 9 so as to attain the desired carbonate ion concentrations in the pH range under the given CO_2 atmosphere. The Am^{3+} ion in 0.1 *M* $HClO_4$ is introduced into the reaction vessel to make a concentration of 5×10^{-4} mol l^{-1}, and precipitated at pH = 8 by addition of 0.05 *M* Na_2CO_3 solution. The solution with precipitate is left to stand under Ar + 1% CO_2 atmosphere for 14 days. During this time pH changes spontaneously to 6.4. The titration is made by addition of either 0.1 *M* $HClO_4$ or 0.05 *M* Na_2CO_3 for the pH region of 6 – 8, and 0.3 *M* $HClO_4$ or 0.1 *M* Na_2CO_3 for the pH region of 8 – 9. pH is measured by a combination glass electrode (type-ROSS, Orion Co.) which is calibrated with standard buffer solutions conditioned to desired ionic strengths. The electrode potentials (mV) are calibrated for different buffer solutions by a linear iteration before each pH measurement. The accuracy of the pH measurement in the region of pH = 2 – 11 is better than 0.03 pH unit.

The solubility equilibrium at a given pH is established in two or three days. The Am concentration is measured, when the adjusted pH is stabilized for a certain period of time (2 – 3 days), after filtration of the solution at 450 nm pore size. A known volume of the filtrate is acidified and the activity is counted by a liquid scintillation counter (Beckman LS 6800) at the α-energy region. A number of sample solutions collected at different pH are speciated by either UV-spectroscopy for the higher concentration ([Am] $> 10^{-5}$ mol l^{-1}) or laser-induced photoacoustic spectroscopy (LPAS) for the lower concentration ([Am] $< 10^{-6}$ mol l^{-1}).

To further our understanding of the chemical state of the Am precipitate under the given experimental conditions, the experiment is performed with the chemically analogous Nd in place of Am thus avoiding the difficulties involved in handling the α-radiating substance. The Nd precipitate is prepared in a similar way to the Am precipitation described above. The Nd precipitates are prepared at pH = 6.7, 8.0 and 8.3 and characterized by Gunier X-ray diffraction measurement, differential thermal analysis (from 20°C to 1500°C) and IR spectroscopy.

3. Result and discussion

3.1. Chemical state of Am precipitate

Since, in the experimental solution, concentrations of OH^- and CO_3^{2-} vary simultaneously with separate functions as pH changes, the chemical state of the Am precipitate may also vary with pH change. The experiment is carried out in the pH range of 6–9.2 and the Am precipitates in equilibrium at different pH are indirectly characterized. In place of Am(III), Nd(III) is used for the characterization. Use of Nd(III) as a reference to Am(III) is already tested in the literature [5]. The chemical analogy of these elements derives from their common trivalent oxidation state in solution and similar ionic radii: 111.5 pm (CN6) for Am^{3+} and 112.3 pm (CN6) for Nd^{3+} [7]. The Nd^{3+} ion is precipitated under the same conditions as the experiment with the Am^{3+} ion. The violet-blue gelatinous precipitate produced at first is changed overnight to a microcrystalline structure. The precipitates sampled by filtration at pH = 6.7, 8.0 and 8.3 are dried at room temperature and characterized by X-ray diffraction measurement, differential thermal analysis (DTA) combined with thermogravimetry and IR spectroscopy.

The X-ray diffraction measurements indicate that the Nd precipitate produced in 0.1 *M* $NaClO_4$ under 1% CO_2 partial pressure is comparable to the diffraction data of $Nd_2(CO_3)_3 \cdot 8H_2O$ in the literature [8] as shown in Table 1. The diffraction data given in this table are quite different from the data known for $Nd(OH)_3$, $NdOHCO_3$ and $NaNd(CO_3)_2$ [5, 9–12]. The precipitates sampled at three different pH are found to be the same, suggesting only one solid state is involved in the present experiment.

The Nd precipitate is further analysed by thermogravimetry and differential thermal analysis. The results are given in Fig. 1. The gravimetric change indicates the following structural change:

$$\begin{array}{lll} \text{at } 80^\circ C & Nd_2(CO_3)_3 \cdot 5H_2O \rightarrow & Nd_2(CO_3)_3 \cdot 2H_2O \\ \text{at } 115^\circ C & Nd_2(CO_3)_3 \cdot 2H_2O \rightarrow & Nd_2(CO_3)_3 \\ \text{at } 400^\circ C & Nd_2(CO_3)_3 \rightarrow & Nd_2O_2CO_3 \\ \text{at } 620^\circ C & Nd_2O_2CO_3 \rightarrow & Nd_2O_3. \end{array}$$

Table 1. Comparison of X-ray diffraction data of the Nd carbonate precipitate with the literature data of $Nd_2(CO_3)_3 \cdot 8H_2O$ [8]

d (Å)			
Nd carbonate ppt (This work)	$Nd_2(CO_3)_3 \cdot 8H_2O$ [8]	Nd carbonate ppt (This work)	$Nd_2(CO_3)_3 \cdot 8H_2O$ [8]
8.45	8.410	2.42	2.412
4.72	4.710	2.417	–
4.45	4.430	2.378	–
4.22	4.150	2.360	–
4.12	4.110	2.305	2.305
3.94	3.910	2.272	2.266
3.85	3.840	2.221	–
3.82	–	2.203	–
3.63	–	2.195	–
3.53	–	2.156	–
3.23	3.230	2.149	2.142
3.17	–	2.126	2.118
3.15	3.150	2.097	–
3.06	–	2.086	2.082
3.02	3.020	2.062	2.055
2.99	–	2.042	–
2.97	2.979	2.024	–
2.91	2.909	2.009	2.005
2.81	2.811	1.957	1.953
2.68	2.681	1.926	–
2.57	2.565	1.870	1.868
2.52	–	1.816	1.815

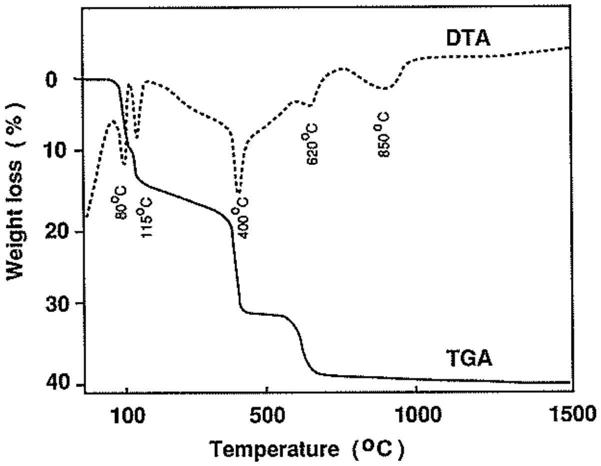

Fig. 1. Thermographimetric (TGA) and differential thermal analysis (DTA) of $Nd_2(CO_3)_3 \cdot 5H_2O$ (air dried). Temperature increase: 5°C min^{-1}.

The differential thermal analysis displays a structural change taking place also at 840°C. According to the literature [13], the structure of Nd_2O_3 changes at this temperature from cubic to hexagonal form. The final hexagonal product Nd_2O_3 obtained at the maximum temperature is in accordance with the result of other experiments [13]. The reconstruction of gravimetric changes given in Fig. 1 leads to the conclusion that the Nd precipitate dried at room temperature is $Nd_2(CO_3)_3 \cdot 5H_2O$, although the X-ray diffraction data were comparable with the literature values of $Nd_2(CO_3)_3 \cdot 8H_2O$ [8]. A few water molecules seem to be loosely associated with the product and thus the number of crystalline water molecules changes easily in handling [14].

The Nd precipitate is further analysed by FT-IR spectroscopy. The result is shown in Fig. 2 and the observed characteristic absorption bands are compared with the literature data [15] in Table 2. The wave numbers of characteristic absorption bands measured in this experiment by FT-IR spectrometer are slightly different from the numbers of corresponding bands determined by normal IR spectrometer in the litera-

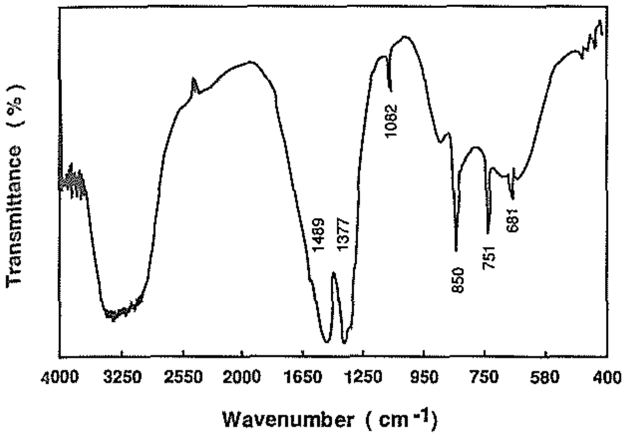

Fig. 2. FTIR spectrum of $Nd_2(CO_3)_3 \cdot 8H_2O$ in KBr pellet.

Table 2. Comparison of characteristic IR absorption bands of Nd carbonate precipitate with the literature values [15] of $Nd_2(CO_3)_3 \cdot 8H_2O$

Wave number (cm^{-1})	
This work	Literature [15]
1489 (s)	1470 (s)
1377 (s)	1370 (s)
1342 (m,sh)	1340 (m,sh)
1082 (w)	1880 (m)
850 (s)	847 (s)
751 (m)	748 (m)
681 (w)	675 (m)

(s): strong; (m): middle; (w): weak; (sh): shoulder

ture. The differences are only due to different instrumentations. The results of IR spectroscopy corroborates the above proposed formula: $Nd_2(CO_3)_3 \cdot 8H_2O$. This result provides further confirmation of the Am precipitate as $Am_2(CO_3)_3$ under the present experimental conditions. However, by lowering the CO_2 partial pressure to $10^{-3.5}$ atmosphere, the Nd precipitate is found as $NdOHCO_3$.

3.2. Carbonate complexation of Am(III) in solution

As discussed above, this experiment deals with solubility equilibria of $Am_2(CO_3)_3(s)$ in the carbonate solution under 1% CO_2 partial pressure. The equilibrium concentrations of Am(III) in the solution are then correlated with pH and CO_3^{2-} concentrations. The CO_3^{2-} concentration at a given pH is calculated by following the reactions:

$$CO_2(g) \overset{K_H}{\rightleftarrows} CO_2(aq) \overset{K^*}{\rightleftarrows} H_2CO_3 \overset{K_1}{\rightleftarrows} H^+ + HCO_3^- \overset{K_2}{\rightleftarrows} 2H^+ + CO_3^{2-}$$

and by the relationship:

$$\log[CO_3^{2-}] = \log K_H K^* K_1 K_2 + \log P_{CO_2} + 2\,pH \tag{1}$$

Table 3. Henry's constant (K_H) of CO_2 and the first and second dissociation constants of H_2CO_3 at different ionic strengths

Constant	Ionic strength (M)							Ref.
	0	0.1	0.2	0.5	1.0	2.0	3.0	
pK_H	1.46	–	1.48	1.51	1.56	1.65	1.73	[17]
$pK_1{}^a$	6.35	6.11	6.06	5.98	5.96	–	–	[18]
	6.35	6.33	6.31	–	–	–	–	[21]
pK_2	10.25	10.20	10.07	–	–	–	–	[19]
	10.33	–	–	–	–	–	–	[22]

a: Here given K_1 is a combined constant of K^*K_1 in Eq. (1).

where K_H is Henry's constant; K^*, K_1 and K_2 are constants for given reactions at the ionic strength of 0.1 M or 0.3 M. The constants known for different ionic strengths are summarized in Table 3. For each constant a number of different values are known in the literature [16], deviating from one another in some cases by tens of percents. For this reason the integrated constant in Eq. (1) is directly determined in the given experimental system and the result is found to be

$$\log K_H K^* K_1 K_2 = -17.62 \pm 0.10$$

which agrees closely with the sum of the selected literature data given in Table 3 for the ionic strength of 0.1 M: $\Sigma \log K_i = -17.78$ from $\log K_H = -1.47$ [17], $\log K^*K_1 = -6.11$ [18], $\log K_2 = -10.20$ [19]. For the ionic strength of 0.3 M, the interpolated or extrapolated values based on the data in Table 3 are used.

Solubility study

The total concentration of Am(III) in the carbonate solution in equilibrium with $Am_2(CO_3)_3(s)$ can be expressed by

$$[Am]_t = \sqrt{K_{sp}/[CO_3^{2-}]^3} \sum_{i=0} \beta_i [CO_3^{2-}]^i \tag{2}$$

which is a function of the CO_3^{2-} concentration (and pH cf. Eq. (1)). The solubility product is given by $K_{sp} = [Am^{3+}]^2[CO_3^{2-}]^3$ and the stability constant of a ligand number (i) by $\beta_i = [Am(CO_3)_i^{3-2i}]/[Am^{3+}][CO_3^{2-}]^i$.

The experimental results are given in Fig. 3. The solubility product and stability constants of the first and second carbonate complexes are calculated by Eq. (2) with the aid of a computer iteration procedure. The data obtained from this experiment are

$$\log K_{sp} = -29.89 \pm 0.18$$
$$\log \beta_1 = -5.97 \pm 0.15$$
$$\log \beta_2 = -9.58 \pm 0.24.$$

Fig. 3a shows the experimental results and calculated concentration lines of each Am species as a function of the pH. Fig. 3b presents the relative amounts of Am species, including hydrolysis products, in the experimental solution. For the species calculation the

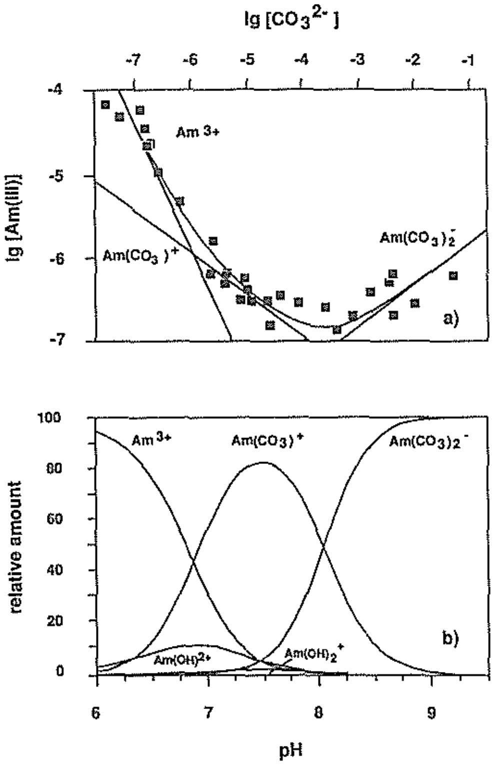

Fig. 3. Solubility of $Am_2(CO_3)_3(s)$ as a function of the pH and carbonate concentration (upper figure (a)) in 0.1 *M* $NaClO_4$ ($pH < 8$) and 0.3 *M* $NaClO_4$ ($pH > 8$). Relative amounts of Am species as a function of the pH and carbonate concentration (lower figure (b)).

known hydrolysis constants [6] are also included so as to illustrate all Am species given in the experimental solution. The amount of the Am monohydroxide is small but not insignificant, whereas the Am dihydroxide is given in negligible concentration. Whether or not the amount of the Am monohydroxide given in the solution may trigger the production of some hydroxocarbonate complexes of Am in the region of $pH = 7$ is difficult to verify. There is for the moment no straightforward method to verify the formation of such a small amount of mixed ligand complexes of Am. Since in the given experiment the M^{3+} ion is found to precipitate as $M_2(CO_3)_3(s)$, only the corroborating reactions are considered to take place in the solution.

Spectroscopic study

The complexation study has been also carried out by spectroscopic experiment. The spectroscopic changes of the Am carbonate solution at various pH are shown in Fig. 4. The spectra at $pH \leqq 6.7$ are measured by normal absorption spectroscopy with a multiscanning addition and the spectra at $pH \geqq 7.4$ are taken by LPAS because of the low Am concentration ($< 10^{-6}$ $mol\,l^{-1}$). The spectrum at $pH = 2.0$ represents the Am^{3+} ion. According to Fig. 3b, in the region of $pH = 6-7$ a mixture of Am species are given. At $pH = 7.4$ about 83% of the Am concentration is the $AmCO_3^+$ ion, whereas the $Am(CO_3)_2^-$ ion is the major species (96%) at $pH = 8.7$. Based on the molar absorbance (ε) of $410\ l\,mol^{-1}\,cm^{-1}$ for Am^{3+} and $334\ l\,mol^{-1}\,cm^{-1}$ for $Am(CO_3)_3^{3-}$ [20], and by analysing the spectra in Fig. 4, the molar absorbances of $AmCO_3^+$ and $Am(CO_3)_2^-$ are estimated to be $385\ l\,mol^{-1}\,cm^{-1}$ and $350\ l\,mol^{-1}\,cm^{-1}$, respectively. The spectra at $pH = 6.4$ and 6.7 are deconvoluted with the help of the two spectra at $pH = 2.0$ and $pH = 7.4$, and hence the concentrations of Am^{3+} and $AmCO_3^+$ are evaluated. The deconvolution is made by the relationship

$$[\mathrm{Am}]_t\,\varepsilon_t = [\mathrm{Am}^{3+}]\,\varepsilon_0 + [\mathrm{AmCO}_3^+]\,\varepsilon_1 + [\mathrm{AmOH}^{2+}]\,\varepsilon_H\,. \qquad (3)$$

For the correction of the small amount of $AmOH^{2+}$, its absorbance is assumed to be the same as that of $AmCO_3^+$. From this experiment the following two constants are obtained:

$$\log K_{sp} = -29.70 \pm 0.10$$
$$\log \beta_1 = 6.48 \pm 0.03.$$

Using these constants and the solubility results given in Fig. 3, the second carbonate complexation constant is further evaluated:

$$\log \beta_2 = 9.94 \pm 0.24.$$

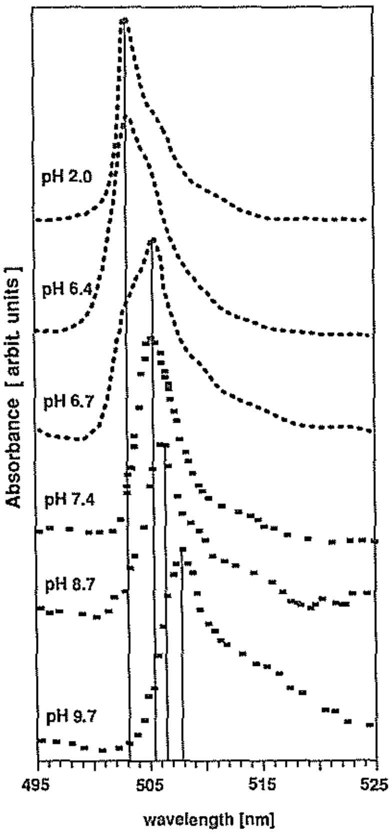

Fig. 4. A spectroscopic evolution of the Am(III) carbonate complexation as a function of the pH. The Am concentration ranges from 5.6×10^{-5} $mol\,l^{-1}$ to 3.0×10^{-7} $mol\,l^{-1}$ (from upper to lower spectra). Spectra at $pH < 7$ and at > 7 are measured by absorption spectroscopy and laser induced photoacoustic spectroscopy (LPAS), respectively.

Table 4. Comparison of Am(III) carbonation complexation constants

Method	lgβ_1	lgβ_2	lgβ_3	Other const.		lgK_{sp}	Medium	Ionic strength	Ref.
Sol	5.97 ± 0.15	9.58 ± 0.24				-29.89 ± 0.18	NaClO$_4$ 25°C	$0.1-0.3$	this work
Spec	6.48 ± 0.03	9.94 ± 0.24				-29.70 ± 0.10 $Am_2(CO_3)_3$			
Spec	6.69 ± 0.15						NaClO$_4$	0.1	[1]
Sol	5.08 ± 0.92	9.27 ± 2.2	12.12 ± 0.85			-21.03 ± 0.11 $AmOHCO_3$	NaClO$_4$ 25°C	$0.1-0.3$	[2]
				$AmOHCO_3$ $AmOH(CO_3)_2^{2-}$ $Am(OH)_2CO_3^-$	lgβ: 12.15 ± 0.15 lgβ: 16.16 ± 0.14 lgβ: 18.29 ± 0.17				
Extr		11.45 ± 0.08		$Am(HCO_3)^{2+}$ $Am(HCO_3)_2^+$ $AmOH(CO_3)_2^{2-}$	lgβ: 4.79 lgβ: 8.14 lgβ: 15.57		NaClO$_4$ 25°C	0.2	[3]
Extr	5.81 ± 0.04	9.72 ± 0.10					NaClO$_4$ 25°C	1.0	[4]

Sol: Solubility experiment; Spec: Spectroscopic; Extr.: Solvent extraction

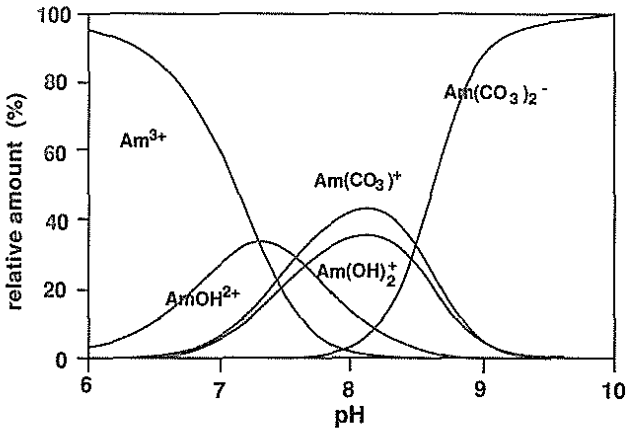

Fig. 5. A relative species distribution calculated for the atmospheric CO_2 partial pressure ($10^{-3.5}$) as a function of the pH. Calculation is based on the constants from the present solubility experiment and the hydrolysis constants determined previously [6].

The set of constants determined in this way are in good agreement with the values from the solubility experiment, except the β_1 values which differ somewhat.

The solubility products of $Am_2(CO_3)_3(s)$ obtained from the two different experiments are in very good agreement with each other and somewhat less but still a good agreement is found for the β_2 values. The spectroscopic value of β_1 is larger than that from the solubility experiment but agrees fairly well with the β_1 value of Nitsche *et al.* [1]. The earlier values of β_1, β_2 and β_3 from this laboratory [2] were determined at 0.1 *M* NaClO$_4$ (or 0.3 *M*) under $10^{-3.5}$ CO_2 partial pressure. The solubility as a function of the pH was interpreted by considering two sets of possible reactions: the formation of carbonates and hydroxocarbonates. Taking into account, the recent experimental hydrolysis constants [6] and CO_2 partial pressure of $10^{-3.5}$, it is found that in the earlier experiment [2], the formation of hydroxocarbonate is quite plausible. For this reason, the carbonate complexation constants given in the earlier work [2] are considered to be not valid. The β_1 value of Lundqvist [4] is obtained from the ionic strength of 1.0 *M*. Once this value ($\log\beta_1 = 5.81$) is normalized to the zero ionic strength according to Nitsche *et al.* [1], $\log \beta_1$ $(I=0) = 7.95$ is calculated. By the same process the present spectroscopic value becomes $\log \beta_1$ $(I=0) = 7.76$. Since the normalization method used by Nitsche *et al.* involves many uncertain factors, the experimental verification of this method is still necessary. Because spectroscopic method (cf. Fig. 4) can verify directly the formation of $AmCO_3^+$, the β_1 value determined by this method is more accurate.

The β_2 values of the present experiment are difficult to compare with the literature data. The value of Bidoglio [3] is two orders of magnitude larger than the present values and that of Lundqvist [4] is determined at the ionic strength of 1.0 *M*. The normalization of β_2 to $I=0$ is not easy to realize. However, the agreement of the present β_2 values with the corresponding data of Lundqvist is fortuitous.

Carbonate and hydroxocarbonate complexation

In aqueous carbonate solution, the hydrolysis reactions and carbonate complexation of Am(III) are competing with each other because the first stability constants of both reactions are nearly the same ($\log\beta_1$ ($AmOH^{2+}$) $= 6.3 \pm 0.3$ $(I=0.1)$ [6]) and only the second and third stability constants differ considerably from one another. The competition of both sets of reactions are controlled by the pH and carbonate concentration of a given solution. Under these experimental conditions with $P_{CO_2} = 10^{-2}$ at pH = 6−9 as described above, the Am carbonate complexation is predominant with a small contribution of its hydrolysis reactions. When the CO_2 partial pressure is changed to the normal atmospheric condition ($P_{CO_2} = 10^{-3.5}$), the same solution will contain a much lower amount of carbonate ions. As a consequence the competition of hydrolysis reactions against the Am carbonate complexation will increase considerably.

Calculation is made, as given in Fig. 5, for hydrolysis reactions and carbonate complexation of Am(III) in 0.1 *M* $NaClO_4$ with $P_{CO_2} = 10^{-3.5}$. The hydrolysis constants are taken from previous work [6] and the carbonate complexation constants are from the present solubility experiment (Table 4). The relative amounts of species given in Fig. 5 demonstrate that both sets of reactions are equally important in the pH region under investigation: at pH < 8 hydrolysis reactions and at pH > 8 carbonate complexation are predominant. Around pH = 8, both reactions are equally dominant. A question is raised, whether or not in such a situation mixed ligand complexes, i.e. hydroxocarbonates, may be produced. Since there are no ligand selection rules known other than stability constants, the formation of hydroxocarbonates of Am(III) is conceivable in the solution under discussion. For this reason the previous work [2] at $P_{CO_2} = 10^{-3.5}$ was interpreted as the formation of hydroxocarbonates of Am(III) (cf. Table 4). The verification of the hydroxocarbonate complexation by spectroscopy is in progress.

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