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The Carbonate Complexation of the Am(III) Ion

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

Abstract

Am(III) carbonate complexation has been investigated in 0.1 M NaClO₄ (or 0.3 M NaClO₄) under Ar + 1% CO₂ atmosphere at pH = 6.0 – 9.2. Under these conditions the Am³⁺ ion precipitated is found to be Am₂(CO₃)₂(s). Solubility and spectroscopic experiments are carried out in parallel. The contribution of hydrolisis reactions to total reactions is found to be small at \( P_{CO₂} \approx 10^{-2} \) bar but considerable at \( P_{CO₂} \approx 10^{-3.5} \). The probability of formation of hydroxocarbonate species of Am(III) is discussed. The average constants determined by the two separate experiments are: \( \log K_p(\text{Am}_2\text{(CO}_3)_2) = -29.80 \pm 0.10 \), \( \log \beta_1 = 6.22 \pm 0.08 \) and \( \log \beta_2 = 9.76 \pm 0.17 \).

1. Introduction

The carbonate complexation of the Am³⁺ 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)CO₃(s) precipitate is postulated under 0.031% CO₂ partial pressure at 0.1 M or 0.3 M NaClO₄ [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 hydrogen carbonate 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 CO₂ partial pressure of a given system. For this reason, the present experiment is conducted under somewhat higher CO₂ partial pressure (1%) in 0.1 M NaClO₄ (or for some cases 0.3 M NaClO₄) 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 Ar gas plus 1% CO₂ atmosphere. The gas mixture with a precise CO₂ concentration is supplied by Linde Co. The ionic strength of the solution is adjusted by 0.1 M NaClO₄ at pH = 6 – 8 and 0.3 M NaClO₄ at pH = 8 – 9 so as to attain the desired carbonate ion concentrations in the pH range under the given CO₂ atmosphere. The Am²⁺ ion in 0.1 M HClO₄ 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 Na₂CO₃ solution. The solution with precipitate is left to stand under Ar + 1% CO₂ atmosphere for 14 days. During this time pH changes spontaneously to 6.4. The titration is made by addition of either 0.1 M HClO₄ or 0.05 M Na₂CO₃ for the pH region of 6 – 8, and 0.3 M HClO₄ or 0.1 M Na₂CO₃ 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 \( \alpha \)-energy region. A number of sample solutions collected at different pH were 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 \( \alpha \)-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 Guinier 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 \( \text{OH}^- \) and \( \text{CO}_3^{2-} \) 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\(_3\))\(_3\) · 8H\(_2\)O 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\(_3\))\(_3\) [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.

Table 1. Comparison of X-ray diffraction data of the Nd carbonate precipitate with the literature data of Nd\(_2\)(CO\(_3\))\(_3\) · 8H\(_2\)O [8]

<table>
<thead>
<tr>
<th>Nd carbonate</th>
<th>Nd(_2)(CO(_3))(_3) · 8H(_2)O (This work)</th>
<th>Nd carbonate</th>
<th>Nd(_2)(CO(_3))(_3) · 8H(_2)O (This work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>8.45</td>
<td>8.410</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>4.72</td>
<td>4.710</td>
<td>2.417</td>
</tr>
<tr>
<td></td>
<td>4.45</td>
<td>4.430</td>
<td>2.378</td>
</tr>
<tr>
<td></td>
<td>4.22</td>
<td>4.150</td>
<td>2.360</td>
</tr>
<tr>
<td></td>
<td>4.12</td>
<td>4.110</td>
<td>2.305</td>
</tr>
<tr>
<td></td>
<td>3.94</td>
<td>3.910</td>
<td>2.272</td>
</tr>
<tr>
<td></td>
<td>3.85</td>
<td>3.840</td>
<td>2.231</td>
</tr>
<tr>
<td></td>
<td>3.82</td>
<td>-</td>
<td>2.203</td>
</tr>
<tr>
<td></td>
<td>3.63</td>
<td>-</td>
<td>2.195</td>
</tr>
<tr>
<td></td>
<td>3.53</td>
<td>-</td>
<td>2.156</td>
</tr>
<tr>
<td></td>
<td>3.23</td>
<td>3.230</td>
<td>2.149</td>
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<td></td>
<td>3.17</td>
<td>-</td>
<td>2.126</td>
</tr>
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<td></td>
<td>3.15</td>
<td>3.130</td>
<td>2.087</td>
</tr>
<tr>
<td></td>
<td>3.06</td>
<td>-</td>
<td>2.086</td>
</tr>
<tr>
<td></td>
<td>3.02</td>
<td>3.020</td>
<td>2.062</td>
</tr>
<tr>
<td></td>
<td>2.99</td>
<td>-</td>
<td>2.042</td>
</tr>
<tr>
<td></td>
<td>2.97</td>
<td>2.979</td>
<td>2.024</td>
</tr>
<tr>
<td></td>
<td>2.91</td>
<td>2.909</td>
<td>2.009</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>2.811</td>
<td>1.957</td>
</tr>
<tr>
<td></td>
<td>2.68</td>
<td>2.681</td>
<td>1.926</td>
</tr>
<tr>
<td></td>
<td>2.57</td>
<td>2.565</td>
<td>1.870</td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>-</td>
<td>1.816</td>
</tr>
</tbody>
</table>

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:

- at 80°C Nd\(_2\)(CO\(_3\))\(_3\) · 5H\(_2\)O → Nd\(_2\)(CO\(_3\))\(_3\) · 2H\(_2\)O
- at 115°C Nd\(_2\)(CO\(_3\))\(_3\) · 2H\(_2\)O → Nd\(_2\)(CO\(_3\))\(_3\)
- at 400°C Nd\(_2\)(CO\(_3\))\(_3\) → Nd\(_2\)O\(_2\)CO\(_3\)
- at 620°C Nd\(_2\)O\(_2\)CO\(_3\) → Nd\(_2\)O\(_3\).

The differential thermal analysis displays a structural change taking place also at 840°C. According to the literature [13], the structure of Nd\(_2\)O\(_3\) changes at this temperature from cubic to hexagonal form. The final hexagonal product Nd\(_2\)O\(_3\) 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\(_3\))\(_3\) · 5H\(_2\)O, although the X-ray diffraction data were comparable with the literature values of Nd\(_2\)(CO\(_3\))\(_3\) · 8H\(_2\)O [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-
The carbonate complexation of the Am(III) ion

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:

\[
\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}
\]

and by the relationship:

\[
\log[\text{CO}_3^{2-}] = \log K_H K^* K_1 K_2 + \log P_{\text{CO}_2} + 2\text{pH}
\]

Fig. 2. FTIR spectrum of Nd$_2$(CO$_3$)$_3 \cdot 8\text{H}_2\text{O}$ in KBr pellet.

Table 2. Comparison of characteristic IR absorption bands of Nd carbonate precipitate with the literature values [15] of Nd$_2$(CO$_3$)$_3 \cdot 8\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>This work</th>
<th>Literature [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1489 (s)</td>
<td>1470 (s)</td>
<td></td>
</tr>
<tr>
<td>1377 (s)</td>
<td>1370 (s)</td>
<td></td>
</tr>
<tr>
<td>1342 (m,sh)</td>
<td>1340 (m,sh)</td>
<td></td>
</tr>
<tr>
<td>1082 (w)</td>
<td>1880 (m)</td>
<td></td>
</tr>
<tr>
<td>850 (s)</td>
<td>847 (s)</td>
<td></td>
</tr>
<tr>
<td>751 (m)</td>
<td>748 (m)</td>
<td></td>
</tr>
<tr>
<td>681 (w)</td>
<td>675 (m)</td>
<td></td>
</tr>
</tbody>
</table>

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

Table 3. Henry’s constant ($K_H$) of CO$_2$ and the first and second dissociation constants of H$_2$CO$_3$ at different ionic strengths

<table>
<thead>
<tr>
<th>Constant</th>
<th>Ionic strength (M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_H$</td>
<td>0</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.73</td>
</tr>
<tr>
<td>$pK_1$</td>
<td>3</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>6.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.96</td>
<td></td>
</tr>
<tr>
<td>$pK_2$</td>
<td>10.25</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.21</td>
<td></td>
</tr>
</tbody>
</table>

*: Here given $K_i$ is a combined constant of $K^*$ 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], $\log K^* K_1 = -1.13$ [18], $\log K_2 = -1.07$ [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

\[
[\text{Am}] = [\text{Am}^2+]^3 \sum_i \beta_i [\text{CO}_3^{2-}]^i
\]

which is a function of the CO$_3^{2-}$ concentration (and pH cf. Eq. (1)). The solubility product is given by

\[
K_{sp} = [\text{Am}^2+]^3 [\text{CO}_3^{2-}]^3
\]

and the stability constant of a ligand number ($i$) by

\[
\beta_i = [\text{Am}(\text{CO}_3)^{i-2}]^i
\]

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
known hydrolysis constants [6] are also included so as to illustrate all Am species given in the experimental solution. The amount of the Am monohydroxyde is small but insignificant, whereas the Am dihydroxyde is given in negligible concentration. Whether or not the amount of the Am monohydroxyde 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 ≤ 6.7 are measured by normal absorption spectroscopy with a multis-scanning addition and the spectra at pH ≥ 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$_3$)$_3$ [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

$$[\text{Am}]_1 = [\text{Am}^{3+}]_6 + [\text{AmCO}_3^-]_e + [\text{AmO}H^{2+}]_8$$

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:

$$\log K_{eq} = -29.70 \pm 0.10$$

$$\log \beta_1 = 6.48 \pm 0.03.$$ 

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

$$\log \beta_2 = 9.94 \pm 0.24.$$
Table 4. Comparison of Am(III) carbonation complexation constants

<table>
<thead>
<tr>
<th>Method</th>
<th>$\log \beta_1$</th>
<th>$\log \beta_2$</th>
<th>$\log \beta_3$</th>
<th>Other const.</th>
<th>$\log K_{H}$</th>
<th>Medium</th>
<th>Ionic strength</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol</td>
<td>$5.97 \pm 0.15$</td>
<td>$9.58 \pm 0.24$</td>
<td></td>
<td></td>
<td>$-29.89 \pm 0.18$</td>
<td>NaClO$_4$</td>
<td>25°C</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>Spec</td>
<td>$6.48 \pm 0.03$</td>
<td>$9.94 \pm 0.24$</td>
<td></td>
<td>$\text{Am}_2(\text{CO}_3)_3^-$</td>
<td>$-29.70 \pm 0.10$</td>
<td>NaClO$_4$</td>
<td></td>
<td>[1]</td>
</tr>
<tr>
<td>Spec</td>
<td>$6.69 \pm 0.15$</td>
<td></td>
<td></td>
<td>$\text{AmOHCO}_3^+$</td>
<td>$-21.03 \pm 0.11$</td>
<td>NaClO$_4$</td>
<td>25°C</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>Sol</td>
<td>$5.08 \pm 0.92$</td>
<td>$9.27 \pm 2.2$</td>
<td>$12.12 \pm 0.85$</td>
<td>$\text{AmOHCO}_3^+$</td>
<td></td>
<td>NaClO$_4$</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Extr</td>
<td>$11.45 \pm 0.08$</td>
<td></td>
<td></td>
<td>$\text{AmHCO}_3^+$</td>
<td>$4.79$</td>
<td>NaClO$_4$</td>
<td>25°C</td>
<td>0.2</td>
</tr>
<tr>
<td>Extr</td>
<td>$5.81 \pm 0.04$</td>
<td>$9.72 \pm 0.10$</td>
<td></td>
<td>$\text{AmOHCO}_3^+$</td>
<td>$15.57$</td>
<td>NaClO$_4$</td>
<td>25°C</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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

The set of constants determined in this way are in good agreement with the values from the solubility experiment, except the $\beta_1$ 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 $\beta_2$ values. The spectroscopic value of $\beta_1$ is larger than that from the solubility experiment but agrees fairly well with the $\beta_1$ value of Nitsche et al. [1]. The earlier values of $\beta_1$, $\beta_2$ and $\beta_3$ 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 $\beta_1$ 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 $\beta_1$ value determined by this method is more accurate.

The $\beta_2$ 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 $\beta_2$ to $I=0$ is not easy to realize. However, the agreement of the present $\beta_2$ 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 $P_{\text{CO}_2} = 10^{-2}$ 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 ($P_{\text{CO}_2} = 10^{-3.5}$), 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 $P_{\text{CO}_2} = 10^{-3.5}$. 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 $P_{\text{CO}_2} = 10^{-3.5}$ was interpreted as the formation of hydroxocarbonates of Am(III) (cf. Table 4). The verification of the hydroxocarbonate complexation by spectroscopy is in progress.

References

8. JCPDS Powder Diffraction File, Table 29--918.
13. JCPDS Powder Diffraction File, Table 6--408.