A TRLFS STUDY OF AQUEOUS CARBONATE COMPLEXES : COMPARISON OF Eu(III) AND Cm(III) AT 25°C, AND TEMPERATURE INFLUENCE ON CmCO₃⁺ STABILITY

Thomas Vercouter, Christophe Moulin, Pierre Vitorge

CEA DEN Saclay DPC/SECR/LSRM, 91191 cedex Gif-sur-Yvette, France.

INTRODUCTION

Actinide chemistry in natural environments is of great interest to predict radionuclide migration from possible radioactive waste repositories. In particular Am(III) aqueous speciation in groundwaters can be dominated by carbonate complexes [1]. The solubility of Am(III) solid compounds, and the stoichiometries and thermodynamic stabilities of its aqueous complexes have been critically reviewed by the NEA-TDB (Thermodynamic Data Base project of the OECD) [2]. The NEA-TDB have pointed out (i) that the species $AmCO_3^+$, $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ have been well established, but other carbonate complexes may be stable under environmental conditions, particularly hydroxo-carbonate mixed complexes ; (ii) a lack of available data at temperatures above 25°C ; (iii) discrepancies in the literature, so that it has not been possible to determine the ion interaction coefficients, ε, for ionic strength corrections with the specific ion interaction theory : the NEA-TDB has reported values among which many estimated coefficients.

Lundqvist *et al.* determined $\lg \beta_1 = 5.81 \pm 0.04$ and 5.91 ± 0.05, and $\lg \beta_2 = 9.72 \pm 0.10$ and 10.72 ± 0.08 for Am(III) and Eu(III) respectively for in 1M $NaClO_4$ [3] ; Kim *et al.* have proposed $\lg \beta_1$ of 6.65 ± 0.07 and 6.57 ± 0.08 for Cm(III) and Eu(III) respectively in 0.1M $NaClO_4$ [4]. The comparison of $\lg \beta_i$ values for Am, Cm, and Eu measured by the same author suggests that they are good chemical analogues. Thus we have chosen to study Eu(III) and Cm(III) by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Thanks to its high sensitivity [5], TRLFS enables the detection of metal ion species below solubility limits, so that there is no ambiguous interpretations due to the nature of the solid phases [6]. This technique has already been used to determine stabilities of $Cm(CO_3)_i^{3-2i}$ (i = 1-4) and $CmHCO_3^{2+}$ in NaCl media [7] ; the bicarbonate complex has also been proposed at higher $CO_2(g)$ pressure [8]. However the analogous $AmHCO_3^{2+}$ has not been observed even under up to 1-atm $CO_2(g)$ pressure [1]. Moreover both $M(CO_3)_3^{3-}$ [1,4,9] and $M(CO_3)_4^{5-}$ [7,10] have been proposed for the stoichiometries of lanthanides and actinides limiting carbonate complexes, which also affects the determination of other complexation constants in data treatments.

We will present our experimental data on Eu(III) and Cm(III) using TRLFS. Our experimental conditions have been chosen on the basis of Am(III) data. Quantitative results on Eu(III) carbonate complexation are obtained and speciation models considering $Eu(CO_3)_3^{3-}$ or $Eu(CO_3)_4^{5-}$ as the limiting complex are tested. This study has been extended to Cm(III) at temperatures from 10 to 50°C.

SENSITIVITY ANALYSES

A sensitivity analysis of Am(III) complexes in hydroxo-carbonate solutions has first been conducted using data from [1,4,9]. We use in particular solubility experiments with correct measurements of $[H^+]$ at high ionic strength, taking into account the junction potential of the

electrode and the activity coefficient of H^+ by a calibration method with adequate buffer solutions [1,9]. Figure 1 shows the speciation of Am(III). Only validated complexes [2] are represented on this diagram and dotted lines are drawn when other possible stoichiometries could be considered. The chemical conditions of interest for our studies have been extracted from such calculated speciation diagrams.
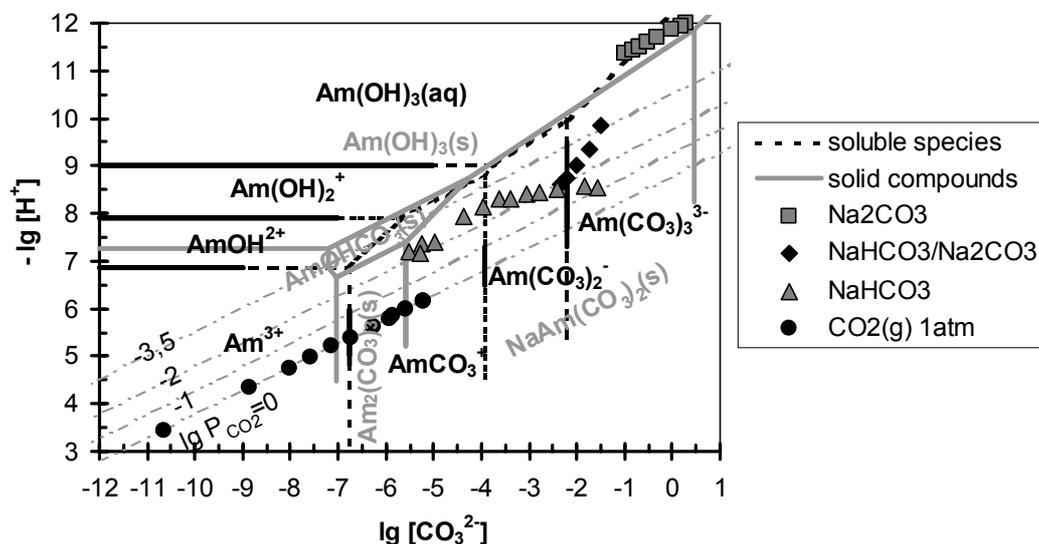

Figure 1 : Speciation of Am(III) as a function of $-$ lg $[H^+]$ and lg $[CO_3^{2-}]$ calculated with $[Am(III)] = 10^{-4}M$ and $[Na^+] = 0,1M$ according to validated stoichiometries of soluble complexes and solid compounds and using stability constants from [1] and [2]. The dots represent our conditions for the experimental study of Eu(III).

CARBONATE COMPLEXES OF Eu(III)

Each Eu(III) species is characterised by specific fluorescence lifetime and spectrum (Figure 2). Our sensitivity analysis suggests the presence of at least the species $EuCO_3^+$, $Eu(CO_3)_2^-$ and $Eu(CO_3)_3^{3-}$. Only mixtures of these can be obtained by varying the chemical conditions in the solutions, except the limiting carbonate complex that could be isolated at high ionic strength taking advantage of its elevated charge. Thermodynamic constants are determined by curve fitting based on fluorescence intensity ratios as shown on Figure 3. No bicarbonate or hydroxo-carbonate mixed complex seems to be significant under our experimental conditions.
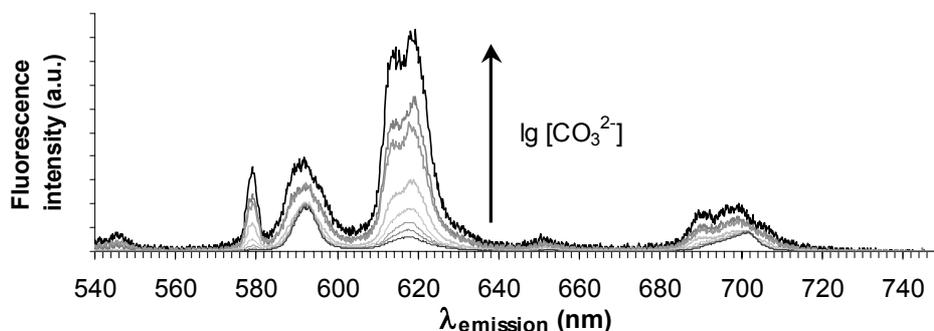

Figure 2 : Variation of fluorescence spectra with lg $[CO_3^{2-}]$, measured in Eu(III) solutions with $[Na^+] = 0.1M$ under 100% CO_2 atmosphere ; formation of $EuCO_3^+$.

Indications on stoichiometries result from the fluorescence spectra and lifetimes measured at various $[CO_3^{2-}]$. Two interpretations are tested depending on the nature of the limiting complex $Eu(CO_3)_3^{3-}$ or $Eu(CO_3)_4^{5-}$, but no definitive conclusion is obtained (Figure 3). To conclude this point, solubility measurements of $NaEu(CO_3)_2(s)$ in concentrated carbonate solutions at high ionic strength are currently carried out.

TEMPERATURE DEPENDENCE OF Cm(III) FLUORESCENCE SPECTRA

At constant $[CO_3^{2-}]$, the spectra of thermostatically-controlled Cm(III) solutions between 10 and 50°C show differences in their shapes and intensities from that at 25°C : in addition to the effect of temperature on spectroscopy, values of the stability constants should change with temperature since complexation reactions are not athermanous. TRLFS is then used for a determination of enthalpy variations corresponding to the formation of $CmCO_3^+$.
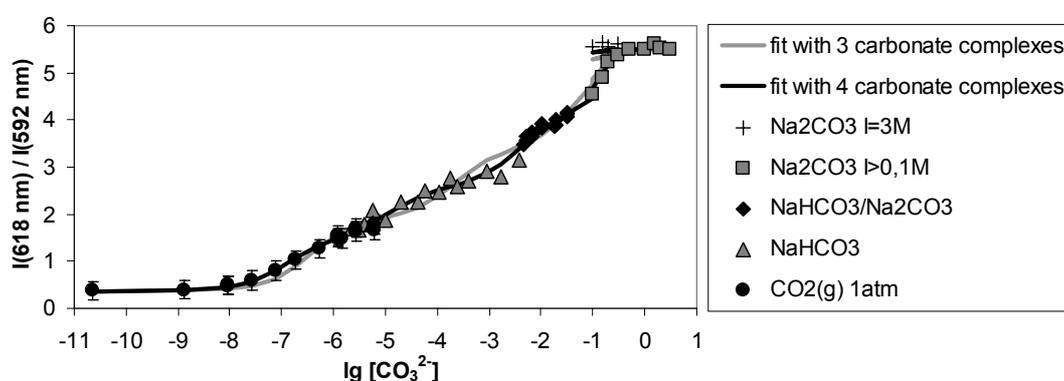

Figure 3 : Measured fluorescence intensity ratios plotted against $lg\ [CO_3^{2-}]$. Comparison of fitted curves depending on the limiting complex $Eu(CO_3)_3^{3-}$ or $Eu(CO_3)_4^{5-}$.

REFERENCES

[1] Robouch P. : Thèse Université Louis Pasteur, Strasbourg (France), 13/11/1987.
[2] Silva R. J., Bidoglio G., Rand M.H., Robouch P. B., Wanner H., Puigdomenech I. : *Chemical thermodynamics of americium*, Elsevier (1995).
[3] Lundqvist R. : *Acta Chem. Scand. A*, **36**, 741-750 (1982).
[4] Kim J.I., Klenze R., Wimmer H., Runde W., Hauser W. : *J. All. Comp.*, **213/214**, 333-340 (1994).
[5] Moulin C., Decambox P., Mauchien P., Moulin V., Theyssier M. : *Radiochim. Acta*, **52/53**, 119-125 (1991).
[6] Vitorge P. : *Radiochim. Acta*, **58/59**, 105-107 (1992).
[7] Fanghänel T., Könnecke T., Weger H., Paviet-Hartmann P., Neck V., Kim J.I. : *J. Sol. Chem.*, **28(4)**, 447-462 (1999).
[8] Fanghänel T., Weger H.T., Schubert G., Kim J.I. : *Radiochim. Acta*, **82**, 55-57 (1998).
[9] Giffaut E. : Thèse Université Paris-sud, Orsay (France). 22/09/1994.
[10] (a) Ferri D., Grenthe I., Salvatore, F. : *Inorg. Chem.*, **22**, 3162-3165 (1983). (b) Runde W., Neu M.P., Van Pelt C., Scott B.L. : *Inorg. Chem.*, **39**, 1050-1051 (2000) (c) Rao R.R., Chatt A. : *Radiochim. Acta*, **54(4)**, 181-188 (1991). (d) Dumonceau J. : Thèse Université de Reims (France), 1977.