

Potentiometric studies of REE-organic complexing

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The specific chemical properties of the Rare Earth Elements (*REEs*) make them to be often used as tracers of geochemical processes and actinides analogues. Nevertheless, these applications require a good understanding of these trace elements behaviour in natural solutions, which, in turn, implies the knowledge of the thermodynamic properties for all the species they can form in aqueous fluids. However, up to date, the literature offers only a few data usable at 25°C, for both organic and inorganic species. There is also very little knowledge on the effect of temperature on these values.

The aim of our work is to get reliable data on the hydrolysed-*REE* species, and on the complexes that *REE* can form with various organic ligands.

The first step of this study was to measure the solubility of La and Gd hydroxide over a wide range of temperature (40–150°C), pH (5–9.5) and in diluted non-complexing solutions ($\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$, $I = 0.025$). These experiments were carried out under pure N_2 flow to avoid the presence of carbonate species. In these conditions, the measured solubilities exhibit a linear dependence on pH with a slope close

to -3 (Fig. 1). This demonstrates the absence of carbonate contamination and the dominance of the trivalent REE^{3+} species over the pH range of natural solutions.

In a second step, we have studied the *REE* complexing with various simple organic ligands containing the major fonctionnal groups of the naturally occurring organic matter, such as humic and fulvic acids.

The choosen organic acids are acetic (AcOH), *o*-phthalic ($\text{Pht}(\text{OH})_2$) and salicylic ($\text{Sal}(\text{OH})_2$). Organic-*REE* (La, Gd, Yb) interactions were studied by potentiometric measurements performed in the range 25–80°C, in a double walled thermostated glass cell. The experiments consist in adding successive amounts of REECl_3 titrant to a buffered organic acid solution and to measure the stabilized potential after each step of the titration. Introduction of a pure nitrogen stream prevent CO_2 dissolution into the solution. The experiments cover a range of total organic ligand to total *REE* concentrations ratios from 1 to 120 for acetate and 1 to 160 for phthalate and salicylate ions. The measured potentials are fitted using a non linear least square regression including a speciation computer code. *REE*-ligand stability constants are derived from the computation including a minimal number of simple *REE*-ligand species which provides the best fit to the data (see Fig. 2).

For the three ligands studied, two *REE*-ligand complexes are needed to fit the measured pH changes. For both acetate and salicylate, 1:1 and 1:2 *REE*-ligand stoichiometries were considered (REEAcO^{2+} and $\text{REE}(\text{AcO})_2^+$ and $\text{SalO}_2\text{HREE}^{2+}$ and $(\text{SalO}_2\text{H})_2\text{REE}^+$ respectively). In the presence of phthalate, a monodentate and a bidentate species are necessary to regressed the obtained experimental data ($\text{Pht-O}_2\text{HREE}^{2+}$ and $\text{Pht-O}_2\text{REE}^+$)

Stability constants point out an increasing *REE*-organic association with increasing temperature (4.61 to 5.46 for $\log\beta_{12}$ Gd-acetate species between 25 and 80°C for example, see Fig. 3).

Futhermore, in opposition to inorganic complexes, no significant difference in stability constant along

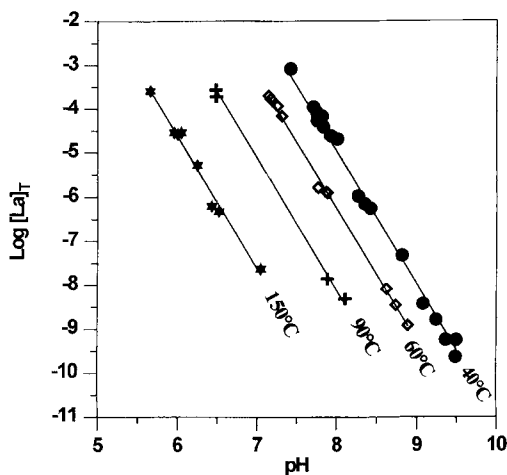


FIG. 1. Measured $\text{La}(\text{OH})_3$ solubility as a function of pH and temperature.

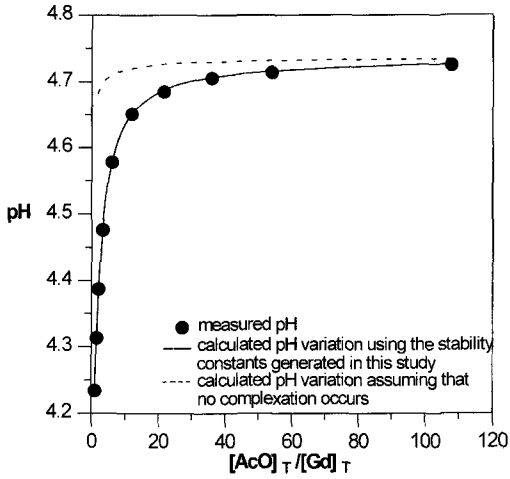


FIG. 2. Variation of the pH as a function of $[\text{AcO}]_T/[\text{Gd}]_T$ molal ratio at 25°C.

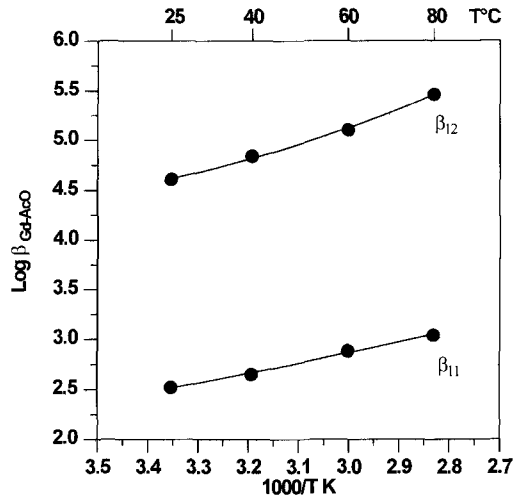


FIG. 3. $\text{Log } \beta_{\text{Gd-AcO}}$ values as a function of the reciprocal temperature.

the REEs serie was detected. This behaviour is in agreement with the flat REE pattern reported in natural rich organic water (Viers *et al.*, 1997).

References

- Viers J., Dupré B., Polvé M., Schott J., Dandurand J.L. and Braun J.J. (1997) *Chem. Geol.*, **140**, 181–206.