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Received October 18, 2007
Revised December 18, 2007
Accepted December 18, 2007

Research Article

Evidence of different stoichiometries for the limiting carbonate complexes across the lanthanide(III) series: A capillary electrophoresis-mass spectrometry study

The electrophoretic mobilities ($\mu_{ep,Ln}$) of twelve lanthanides (not Ce, Pr and Yb) were measured by CE-ICP-MS in 0.15 and 0.5 mol L^{-1} Alk$_2$CO$_3$ aqueous solutions for Alk$^+$ = Li$^+$, Na$^+$, K$^+$ and Cs$^+$. In 0.5 mol L^{-1} solutions, two different $\mu_{ep,Ln}$ values were found for the light (La to Nd) and the heavy (Dy to Tm) lanthanides, which suggests two different stoichiometries for the carbonate limiting complexes. These results are consistent with a solubility study that attests the $Ln(CO_3)_3^{3-}$ and $Ln(CO_3)_4^{5-}$ stoichiometries for the heavy (small) and the light (big) lanthanides, respectively. The Alk$^+$ counterions influence the $\mu_{ep,Ln}^{Alk_2CO_3}$ values, but not the overall shape of the $\mu_{ep,Ln}^{Alk_2CO_3}$ plots as a function of the lanthanide atomic numbers: the counterions do not modify the stoichiometries of the inner sphere complexes. The influence of the Alk$^+$ counterions decreases in the Li$^+$ > Na$^+$ >> K$^+$ > Cs$^+$ series. The $K_{3,Ln}$ stepwise formation constants of the $Ln(CO_3)_3^{3-}$ complexes slightly increase with the atomic numbers of the lanthanides while $K_{4,Ln}$, the stepwise formation constants of $Ln(CO_3)_4^{5-}$ complexes, slightly decrease from La to Tb, and is no longer measurable for heavier lanthanides.

Keywords:
Capillary electrophoresis / Carbonate / Complex / Inductively coupled plasma-mass spectrometry / Lanthanides DOI 10.1002/elps.200700764

1 Introduction

Elements of the f-blocks at the same oxidation state are often considered as chemical analogues. However, the stoichiometry of the aqueous carbonate limiting complex (complex with maximum number of ligands) of lanthanides (Ln) and actinides (An) is still discussed, even after the well-accepted Nuclear Energy Agency review of Am published thermochemical data [1, 2]. Indeed, two stoichiometries have been reported for their limiting complexes: $M(CO_3)_3^{3-}$ [3–9] and $M(CO_3)_4^{5-}$ [3, 9–16]. The latter stoichiometry has been reported for light lanthanides only, since the lanthanides heavier than Tb had never been evidenced as $M(CO_3)_4^{5-}$complexes. Solubility appeared to be a reliable method to determine the stoichiometries of the limiting complexes in concentrated carbonate solutions [4, 5, 7, 8, 12, 13].

In a companion study [3], we have performed solubility measurements of NaLn(CO$_3$)$_2$, xH$_2$O(s) (Ln = La, Nd, Eu and Dy) in concentrated Na$_2$CO$_3$ aqueous solutions with constant [Na$^+$], obtained by NaClO$_4$ additions. Indeed, NaLn(CO$_3$)$_2$, xH$_2$O(s) is the thermodynamically stable solid-phase controlling solubility in concentrated sodium carbonate solutions [4, 12, 13, 17]. These solid compounds are in equilibria with the carbonate limiting complexes using high carbonate concentrations. A classical slope analysis predicts that plotting log$_{10}$(solubility) *vs.* log$_{10}$[CO_3^{2-}] would result in a straight line with slope (i-2) related to $Ln(CO_3)_i^{3-2i}$ stoichiometry. The La and Nd experimental data approached accurately limiting slopes of two at high aqueous carbonate concentrations. This slope evidences the formation of $Ln(CO_3)_4^{5-}$ complexes. For heavier (smaller) Eu and Dy the limiting complexes are $Ln(CO_3)_3^{3-}$ since the slope is one [3]. These results confirmed the observation of $Eu(CO_3)_3^{3-}$ made by Vercouter *et al.* [5] and $Ce(CO_3)_4^{5-}$ made by Ferri *et al.* [13] using solubility measurements in concentrated Na$_2$CO$_3$ solutions. From these studies it appears that the light lanthanides form $Ln(CO_3)_4^{5-}$ while the heavy lanthanides form $Ln(CO_3)_3^{3-}$ limiting complexes. High carbonate concentra-

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tions necessarily imply significant OH^- concentrations, ranging typically from 10^{-5} to 10^{-2} mol L^{-1}, which can favor the formation of ternary mixed hydroxycarbonate complexes. In the case of Am(III), they were shown to be minor species that can be neglected in the conditions of the experimental studies [1, 2]. By analogy to Am^{3+}, mixed hydroxycarbonate of Ln^{3+} can be neglected as well in carbonate solutions.

The stoichiometries and structures of carbonate complexes of trivalent lanthanide ions have also been investigated in the solid state. Among the number of synthesized lanthanide solids containing carbonate, only a few may be representative of the structure of complexes in carbonate-rich aqueous solutions. The guanidinium [18] and cobalt hexaammine [19–21] cations have shown good properties for precipitating Ln(III) limiting carbonate complexes. Tetracarbonate complexes were proposed for Nd(III) [18, 20], Sm(III) [19], Ho(III) [21] according to single-crystal X-ray diffraction. Absorbance spectra of Nd(III) in concentrated guanidinium carbonate aqueous solutions were in fair agreement with diffuse reflectance spectra of the $Nd(CO_3)_4$ -$(H_2O)^{5-}$stoichiometry in the solid compound [18]. Consequently, $Nd(CO_3)_4^{5-}$ was considered to be the most probable stoichiometry in solution, while it could be partially dissociated. The $Ho(CO_3)_4^{5-}$ anion was stabilized in a crystal matrix and the Raman spectrum of the crystalline powder was compared with the one of a 0.01 mol L^{-1} Ho(III)/2.5 mol L^{-1} Na_2CO_3 solution [21]. The Raman shifts were found to be slightly different, which was interpreted as indicating the coexistence of the tetracarbonate complex and lower carbonate complexes in the solution. Other reported structures from solid-state analyses have shown both monodentate and bidentate carbonates, and also bridging ligands [19, 20], and are more hardly comparable with aqueous complexes. Solid-state methods provide useful structural information, but a definite conclusion about the stoichiometry of the aqueous complexes is difficult to draw. Then, a direct investigation of the stoichiometries in aqueous carbonate solutions would be helpful, which is proposed in the present study by the use of a CE-ICP-MS detector.

Because the $Ln(CO_3)_i^{3-2i}$ targeted aqueous limiting complexes have different charges (-3 or -5 for $i = 3$ or 4), CE appears to be well suited to discriminate the two stoichiometries. However, most of the CE commercial instruments are equipped with UV detectors. These detectors are not adapted to the lanthanide detection since the classical absorption spectroscopy provides only a limited sensitivity for these elements, due to their small molar extinction coefficients (1 to 10 L mol^{-1} cm^{-1}) [22]. Thus, its application is restricted to relatively high concentrations, but lanthanides are not soluble enough in concentrated aqueous carbonate solutions. Furthermore, the absorption bands of these species partially overlap when coexisting in solution. Using an external ICP-MS detector should enable to bypass this issue since the detection limits for lanthanides are less than a few ppt for high-resolution ICP-MS [23]. Hyphenated with an ICP-MS, CE first separates species with different effective charge-to-hydrodynamic radius ratios. Consistently with the aim of the present study, CE can be used to preserve the lanthanide aqueous speciation up to the final ICP-MS detector [24]. In this study, the lanthanides are put in the same sample to make the comparison of the electrophoretic mobilities easier and more accurate since the ICP-MS detector enables simultaneous detection of each lanthanide in the mixture. Moreover, CE-ICP-MS may allow the determination of the stepwise formation constants of the limiting carbonate complexes of the lanthanides, which has never been done so far while the values of $\log_{10}K_1$ and $\log_{10}K_2$ for the stepwise formation of the mono- and dicarbonate complexes are well known [25–27]. Electrophoretic mobilities were measured at high Alk_2CO_3 concentrations and high ionic strength, far from the usual conditions of CE-ICP-MS samples, whose ionic strength typically ranges from 0.001 to 0.1 mol L^{-1}. After identifying the stoichiometries of the complexes, we report here a quantitative analysis of the speciation in Na_2CO_3 solutions. The effect of the alkali metal counter ions (Alk^+ = Li^+, Na^+, K^+ or Cs^+) on the electrophoretic mobilities of the lanthanides in concentrated Alk_2CO_3 solutions is investigated because some published experiments have suggested that specific ion interactions might change the stoichiometry of the limiting carbonate complex at high ionic strengths [5].

2 Materials and methods

2.1 Chemicals

Millipore deionized water (Alpha-Q, 18.2 MΩ cm) was used throughout the experiments. The carbonate solutions were prepared from weighted amounts of: Li_2CO_3 (Sigma, Sigmaultra $\geq$ 99%), Na_2CO_3 (VWR, Normapur $\geq$ 99.9%), K_2CO_3 (VWR, Normapur $\geq$ 99.9%) and Cs_2CO_3 (Aldrich $\geq$ 99.95%) used without further purification. All the solutions were filtered through 0.45-μm nylon filters (Nalge, Rochester, NY) prior to be used. The resulting aqueous solutions were titrated with 1 mol L^{-1} HCl (Merck, Titrisol) aqueous solution. Tetradecyltrimethylammonium bromide (TTAB Fluka, puriss. $\geq$ 99%) was added to the background electrolytes. A Spex, Certiprep, multi-lanthanide standard solution was used to introduce the lanthanides into the samples (100 mg kg^{-1}, 5% HNO_3) and the bismuth into the make-up liquid (1000 mg kg^{-1}, 10% HNO_3). The multi-lanthanide standard contains the fourteen natural lanthanides *i.e.* not Pm, which is radioactive. Its pH was neutralized by adding NaOH (VWR) aqueous solution to avoid the transformation of CO_3^{2-} into HCO_3^-or CO_2 during the introduction of the lanthanides into the samples made of Alk_2CO_3. N,N-Dimethylformamide (DMF, Sigma ≈99%) was added to the samples as a neutral UV active compound to measure the electroosmotic flow.

The fused-silica capillaries were preconditioned by rinsing with 1 mol L^{-1} NaOH (VWR, Titrinorm), 1 mol L^{-1} HCl (VWR, Titrinorm) and deionized water before use.

The UV spectrophotometric signal was collected by the capillary electrophoresis software (Karat 5.0). The transient MS signals were acquired by the axiom software (PlasmaLab). The signal of each electropherogram was fitted with a Gaussian function using the OriginPro software to determine the abscissa of the peak maximum.

2.2 Capillary electrophoresis

A Beckman Coulter P/ACE MDQ commercial CE system (Fullerton, USA) was used for all the separations, the UV data acquisitions, and the UV data analyses. It was provided with a tailor-made capillary cartridge support designed for the adaptation of an external detector. Indeed, two detectors were used: a UV conventional detector was used to measure the electroosmotic mobility of the neutral DMF UV active compound at 214 nm, and a mass spectrometer detector was used to measure the effective mobility of the lanthanides.

The separations were carried out using conventional fused-silica capillaries, 50 μm internal diameter and 64.1 cm total length (Beckman Coulter, Fullerton, USA). An optical window was created by removing a section of the polyimide cladding with a flame, followed by cleaning the area with ethanol. The detection window was placed at 10.1 cm from the inlet of the capillary.

2.3 CE-ICP-MS interface

Measurements were carried out using an Axiom (VG Elemental, Cheshire, UK) inductively coupled plasma sector field mass spectrometer (ICP-SFMS). A commercial parallel path micronebulizer (Mira Mist CE, Burgener) was used. A make-up liquid (HNO_3 2% + 1 ppb ^{209}Bi) provided the electrical connection and adapted the flow rate of the capillary to the flow rate of the nebulizer. The make-up liquid was introduced by a syringe pump (11 Pico Plus, Holliston, Massachusetts, USA). The nebulizer was connected to a borosilicate spray chamber (mini glass chamber + 0.5" ball joint adapter, Burgener). The ICP-MS operated in the low-resolution mode ($R = 362$). The fast scanning magnet of the mass spectrometer allowed sharp and narrow CE signals to be acquired. The least interfered isotope was analyzed for each lanthanide: ^{139}La, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{161}Dy, ^{166}Er, ^{165}Ho, ^{169}Tm, ^{171}Yb and ^{175}Lu.

2.4 Procedures

The background electrolytes were prepared by adding TTAB to Alk_2CO_3 0.5 mol L^{-1} solutions ($Alk^+ = Na^+$, K^+ and Cs^+) to reach a 2×10^{-3} mol L^{-1} TTAB concentration. The TTAB additive was used to inverse the electroosmotic flow since anions are expected. The pH of such solutions were typically 11.30 (which was not further adjusted). These background electrolytes were diluted in 2×10^{-3} mol L^{-1} TTAB solutions to prepare 0.15 mol L^{-1} Alk_2CO_3 solutions (which corresponds to the solubility of Li_2CO_3 in water). An extra solution containing Li_2CO_3 0.15 mol L^{-1}/TTAB 2x10^{-3} mol L^{-1} was prepared. The pH of the latter solutions were typically 11.22. The lanthanides were added to solutions similar to the background electrolytes but without TTAB. The samples were prepared from a 1 μL DMF solution, which corresponds to a 1.29 x 10^{-5} mol L^{-1} concentration, a 2 μL multi-lanthanide solution and a 1000 μL Alk_2CO_3 solution. No additive other than TTAB and DMF was used since the addition of other species could modify the aqueous speciation of the lanthanides. The affinity of lanthanides for water is higher than their affinity for DMF. They can form complexes with DMF only in non aqueous solvent [28]. Moreover, the DMF concentration is at least 4 orders of magnitude lower than the CO_3^{2-} concentration, and carbonate is a strong complexing agent of lanthanides. For these reasons, the presence of DMF does not modify the aqueous speciation of lanthanides. Preliminary tests confirmed that the mobility of each lanthanide was not sensitive to the presence of 1, 2 or 9 additional lanthanides. The measurements were then performed with solutions containing 14 lanthanides. The capillaries were washed with the corresponding background electrolyte before each experiment for 5 min at 20 psi. The make-up liquid was composed of HNO_3 2% and 1 ppb ^{209}Bi. ^{209}Bi was used to verify the sensitivity and the stability of the mass spectrometer signals. The samples were hydrodynamically injected at 1 psi during 4 s, which corresponds to sample volumes less than 7 nL. The voltage was fixed at the highest value (−6 kV) according to the linear portion of the Ohm plots for the most conductive background electrolyte (Cs_2CO_3). The capillaries were maintained at a constant temperature of 25°C. The capillary is housed in a liquid cooled cartridge. To prevent important electrolysis of the background electrolytes, it was renewed at least every 4 runs. The passage of current through the solution is accompanied with electrochemical reactions at the electrodes among which water decomposition. The production of protons and hydroxide ions in the vials could then change pH [29]. Due to the high salinity of the background electrolytes and the samples, the narrow orifice of the capillary may become clogged when submitted to the high flow rate of argon, which may open the electrical circuit. Thus, the separations were performed under 1.5 psi pressure. The small fluctuations in the electropherograms (Fig. 1) are attributed to the pressure regulation. Since the solutions are quite viscous, the piston hardly imposed a constant pressure.

Note that the interaction between HNO_3 from the make-up liquid and CO_3^{2-} from the background electrolytes and the samples can cause emissions of CO_2(g), which might cause instabilities or cuts off of the electric circuit. Different make-up liquids were tested showing that this problem was avoided by applying the 1.5 psi pressure during the separation. Using a 9 μL min^{-1} flow rate for the make-up solution reduced the amount of salt entering into the plasma, enhanc-

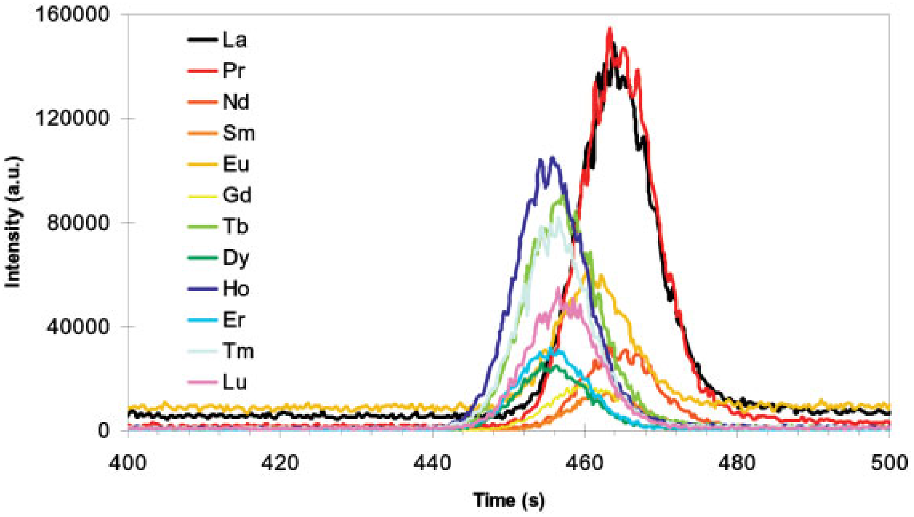

Figure 1. Electropherograms of a mixture of lanthanides in 0.5 mol L^{-1} Na$_2$CO$_3$.

ing the plasma performance. *HNO$_3$* flowed between the electrophoretic separations and assisted in removing salt deposits in the spray chamber.

The electrophoretic mobility was calculated from the migration time of each lanthanide, determined by ICP-MS ($t_{\mathrm{Ln}}^{\mathrm{ICP-MS}}$):

$$\mu_{\mathrm{ep,Ln}}^{\mathrm{I}} = \frac{L}{V}\left(\frac{L}{t_{\mathrm{Ln}}^{\mathrm{ICP-MS}}} - \frac{l}{t_{\mathrm{DMF}}^{\mathrm{UV}}}\right) \quad (1)$$

where L is the total length of the capillary, l is the length between the injection point and the UV window, V the voltage and $t_{\mathrm{DMF}}^{\mathrm{UV}}$ the migration time of the neutral UV active compound corresponding to the electroosmotic flow. All the detected lanthanide species were found to be anionic because their migration times were lower than the one of the neutral DMF UV active compound.

The results obtained with Ce are not presented because the oxidation of Ce(III) into Ce(IV) could not be prevented. Although the Nd, Sm, Gd and Yb isotopes used for detection without interference have a small natural abundance (less than 18%), accurate detection was achieved except for ^{171}Yb which was then discarded from our analyses.

2.5 Speciation calculation

The aqueous speciations of La and Dy in 0.15 and 0.5 mol L^{-1} Na$_2$CO$_3$ solutions were calculated from the mass balance equations and from the stepwise formation constants of negatively charged carbonate complexes. The latter were determined from solubility measurements (see Supporting Information). For Dy, a reliable value could only be determined for $\log_{10}K_{\mathrm{s,3}} = \log_{10}K_{\mathrm{s}} + \log_{10}\beta_3$ where β_3 is the overall formation constant of $\mathrm{Dy(CO_3)_3^{3-}}$. $\log_{10}K_3$ has been determined from our extrapolated $\log_{10}K_{\mathrm{s,3}}^0 = -5.5 \pm 0.3$ value, from $\log_{10}K_{\mathrm{s}}^0 = -20.0 \pm 0.5$[1] proposed by Vercouter *et al.* [5] (The value -20.9 ± 0.5 given in ref. [5] was found to be incorrect according to the data used for its calculation.) and from $\log_{10}\beta_2^0 = 13.2 \pm 0.1$ proposed by Liu *et al.* [25]. Ionic strength corrections were performed using activity coefficients (γ) calculated with the specific interaction theory (SIT) formula [1] (Table 1).

The mean charge of the inner sphere complexes was calculated from the theoretical aqueous speciation ($\%\mathrm{Ln(CO_3)_i^{3-2i}}$) and from the charge of each inner sphere complexes (z_{i}):

$$z = \sum_{\mathrm{i}}^{\mathrm{i}=2\to4} z_{\mathrm{i}}\%\mathrm{Ln(CO_3)_i^{3-2i}} \quad (2)$$

3 Results and discussion

3.1 Electrophoretic mobilities of the lanthanides in Na$_2$CO$_3$ background electrolytes

The effective mobilities of 12 natural lanthanides were measured in 0.5 mol L^{-1} Na$_2$CO$_3$ background electrolyte. A single peak is obtained for each lanthanide (Fig. 1). It indicates fast ligand exchange kinetics on the time scale of the separation, as usually observed for inorganic complexing reactions in aqueous solutions, and for equilibria between the various $\mathrm{Ln(CO_3)_i^{3-2i}}$ complexes (i = 2 to 4), when coexisting in solution. Consequently, the electrophoretic mobilities only depend on the weighted average of the mobilities of the various aqueous species, namely the various negatively charged carbonate complexes:

$$\begin{aligned}\mu_{\mathrm{ep,Ln}}^{\mathrm{I}} &= \sum_{\mathrm{i}} \Phi_{\mathrm{i}}\mu_{\mathrm{ep,Ln,i}}^{\mathrm{I}} \\ &= \Phi_2\mu_{\mathrm{ep,Ln,2}}^{\mathrm{I}} + \Phi_3\mu_{\mathrm{ep,Ln,3}}^{\mathrm{I}} + \Phi_4\mu_{\mathrm{ep,Ln,4}}^{\mathrm{I}} \\ &= \frac{\mu_{\mathrm{ep,Ln,2}}^{\mathrm{I}} + K_3^{\mathrm{I}}[\mathrm{CO_3^{2-}}]\mu_{\mathrm{ep,Ln,3}}^{\mathrm{I}} + K_3^{\mathrm{I}}K_4^{\mathrm{I}}[\mathrm{CO_3^{2-}}]^2\mu_{\mathrm{ep,Ln,4}}^{\mathrm{I}}}{1 + K_3^{\mathrm{I}}[\mathrm{CO_3^{2-}}] + K_3^{\mathrm{I}}K_4^{\mathrm{I}}[\mathrm{CO_3^{2-}}]^2}\end{aligned} \quad (3)$$

Table 1. Overall formation constants for negatively charged carbonate complexes at 25°C and zero ionic strength

	La	Dy	La	Dy	La	Dy
$[Na_2CO_3]$ (mol L^{-1})	0	0	0.15	0.15	0.5	0.5
I (mol L^{-1})	0	0	0.45[a)]	0.45[a)]	1.5[a)]	1.5[a)]
Carbonates						
$log_{10}K_{3,M}$[b)]	0.7 ± 0.4[c)]	1.3 ± 0.6[c)]	1.4 ± 0.6	2.0 ± 0.7	1.6 ± 0.6	2.2 ± 0.7
$log_{10}K_{4,M}$[d)]	−2.7 ± 0.9[c)]		−0.6 ± 1.4		0.1 ± 1.4	
Aqueous speciation						
$\%Ln(CO_3)_2^-$			21	6	3	1
$\%Ln(CO_3)_3^{3-}$			76	94	62	99
$\%Ln(CO_3)_4^{5-}$			3		35	
Mean charge of the inner sphere complex						
z			−2.6	−2.9	−3.7	−3.0

The formation constants are extrapolated to the two ionic strengths used for the CE experiments.

a) $\in_{Na^+,CO_3^{2-}} = -0.08 \pm 0.03$

b) $\in_{Na^+,Ln(CO_3)_3^{3-}} = -0.15 \pm 0.05$ and $\in_{Na^+,Ln(CO_3)_2^-} = -0.05 \pm 0.05$

c) From the solubility measurements

d) $\in_{Na^+,Ln(CO_3)_4^{5-}} = -0.35 \pm 0.22$

where $\mu^I_{ep,Ln}$ is the lanthanide electrophoretic mobility at ionic strength I, Φ_i, $\mu^I_{ep,Ln,i}$ and K^I_i are the molar fraction, the electrophoretic mobility and the stepwise formation constants of $Ln(CO_3)_i^{3-2i}$ complexes (i = 2 to 4) at ionic strength I.

The effective mobilities decrease across the lanthanide series. The electropherograms show that the lanthanides are separated with migration times ranging from 455 s for La, Pr and Nd to 466 s for Dy, Ho, Er, Tm and Lu.

In a nonideal solution, the electrophoretic mobility of a species i at ionic strength I ($\mu^I_{ep,i}$), is given by:

$$\mu^I_{ep,i} = \mu^0_{ep,i} f \qquad (4)$$

where f is a correction factor counting for the deviation from ideality. The effective mobility of a species i depends on the pH, the temperature (T), the ionic strength (I), the dielectric constant (ε) and the viscosity (η) of the medium as well as it depends on the charge-to-hydrodynamic radius ratio (z_i/r_i) of the analysed species. Since the lanthanides are analysed simultaneously, the relative mobilities of the various lanthanides are only dependent on the z_i/r_i ratios since all the other parameters (ε, η, pH, I, T) are identical.

A sigmoid curve was obtained for the electrophoretic mobilities as a function of the atomic numbers of the lanthanides (Z_{Ln}) (Fig. 2). This variation reflects changes of the lanthanide major aqueous complexes consistently with our recent solubility measurements (see Supporting Information). The sigmoid curve shows a plateau for the heavy lanthanides (Dy, Ho, Er, Tm and Lu) at about 2.86×10^{-4} cm^2 V^{-1} s^{-1} suggesting that the heavy lanthanides form the same limiting complex assuming that the charge-to-hydrodynamic mean ratios of the aqueous complexes are similar for all the lanthanides. Another plateau is observed for the light lanthanides (La, Pr and Nd) at about 2.57×10^{-4} cm^2 V^{-1} s^{-1}. This is also consistent with solubility measurements that evidenced a supplementary complex – $Ln(CO_3)_4^{5-}$ – for light lanthanides compared to the heavy ones (Table 1). The mobilities of the intermediate lanthanides (Sm, Eu, Gd, Tb) were found to be in between the two plateaus. This variation indicates that their speciations smoothly vary between that of the the light and the heavy lanthanides.

We first tested the hypothesis of a unique species per plateau, and the progressive dissociation of the $Ln(CO_3)_4^{5-}$ complex with Z_{Ln}. The first plateau (from La to Nd) is assumed to correspond to the mobility of a unique major aqueous complex, namely $Ln(CO_3)_4^{5-}$ while the second one (from Dy to Lu) is assumed to correspond to the mobility of $Ln(CO_3)_3^{3-}$. Since a sigmoid curve may reflect a linear variation of the corresponding $\log_{10}K$ with Z_{Ln} [30], we assumed the relationship $\log_{10}K_{4,Ln}^{0.5M\ Na_2CO_3} = mZ_{Ln} + p$. Using this rough approximation, a quite good fit was obtained with the following parameters: m = 3.06 and p = −0.41, from which $\log_{10}K_{4,La}^{0.5M\ Na_2CO_3} = 2.6 \pm 1.5$ and $\log_{10}K_{4,Lu}^{0.5M\ Na_2CO_3} = -2.7 \pm 1.5$ are calculated. $\log_{10}K_{4,La}^{0.5M\ Na_2CO_3} = 2.6 \pm 1.5$ is very different from $\log_{10}K_{4,La}^{0.5M\ Na_2CO_3} = 0.1 \pm 1.4$ determined from our solubility measurements (Table 1). Conversely, we could not reproduce the experimental mobilities between the plateaus (Ln = Sm to Tb) when fixing $\log_{10}K_{4,La}^{0.5M\ Na_2CO_3}$ and $\log_{10}K_{4,Dy}^{0.5M\ Na_2CO_3}$ to the experimental solubility values. For these reasons, this interpretation is rejected, it should rather be considered as a proof that each plateau does not correspond to the mobility of a unique aqueous complex.

The speciation of La, as deduced from solubility measurements, indicates partial dissociation of its limiting complex: namely 3% of the total lanthanide concentration were present as $La(CO_3)_2^-$, 62% as $La(CO_3)_3^{3-}$ and 35% as $La(CO_3)_4^{5-}$ (Table 1). The calculated speciation of Dy indi-

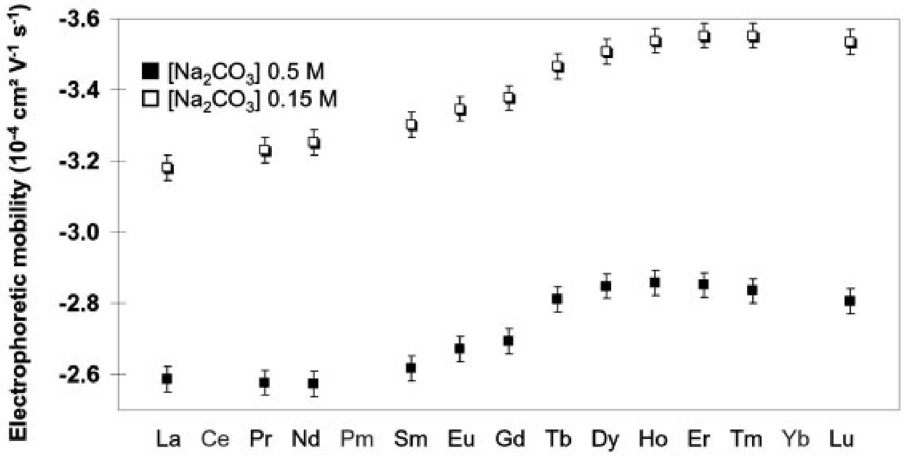

Figure 2. Electrophoretic mobilities of 12 lanthanides in 0.5 or 0.15 mol L^{-1} Na_2CO_3 solutions.

cates that $Dy(CO_3)_3^{3-}$ was predominating while $Dy(CO_3)_2^{-}$ complex represents only 1% of the total lanthanide concentration, which is within the uncertainty (Table 1).

In the elected interpretation, we assumed that all the complexes of same charge have the same mobility whatever the lanthanide; and we used our solubility measurements to interpret the CE data. Since the mobilities of La to Nd are similar, the speciation of these elements would also be similar: the ratios of the two major complexes $[Ln(CO_3)_4^{5-}]$/$[Ln(CO_3)_3^{3-}]$ would have identical values (Table 2). This ratio is actually proportional to the stepwise formation constant $K_4^{0.5M\ Na_2CO_3}$. $Ln(CO_3)_2^{-}$ was neglected since its contribution was within the uncertainty. Dy to Lu predominate as a unique carbonate complex: $Ln(CO_3)_3^{3-}$ and Eq. (3) simplifies:

$$\mu^{I}_{ep,Ln} = \frac{\mu^{I}_{ep,3} + K^{I}_{4}\left[CO_3^{2-}\right]\mu^{I}_{ep,4}}{1 + K^{I}_{4}\left[CO_3^{2-}\right]} \qquad (5)$$

Using the calculated aqueous speciations for La and Dy (Table 1), the electrophoretic mobilities of $Ln(CO_3)_3^{3-}$ ($\mu_{ep,3}$) and $Ln(CO_3)_4^{5-}$ ($\mu_{ep,4}$) in this background electrolyte were determined from the mobilities on the plateaus, typically from La and Dy:

$$\mu_{ep,La}^{0.5M\ \ Na_2CO_3} = 0.36\mu_{ep,3}^{0.5M\ \ Na_2CO_3} + 0.64\mu_{ep,4}^{0.5M\ \ Na_2CO_3} \qquad (6)$$

$$\mu_{ep,Dy}^{0.5M\ \ Na_2CO_3} = \mu_{ep,3}^{0.5M\ \ Na_2CO_3} \qquad (7)$$

We deduced the proportions of $Ln(CO_3)_4^{5-}$ and $Ln(CO_3)_3^{3-}$ by modeling the experimental electrophoretic mobilities as the weighted mean of the mobilities of the plateaus. We finally calculated

$$K_{4,Ln}^{0.5M\ \ Na_2CO_3} = \frac{\left[Ln(CO_3)_4^{5-}\right]}{\left[Ln(CO_3)_3^{3-}\right]\left[CO_3^{2-}\right]} \qquad (8)$$

for La to Tb (Fig. 3). The CE-ICP-MS measurements show that Dy is the first lanthanide for which $\log_{10} K_4^{0.5M\ \ Na_2CO_3}$ cannot be measured, *i.e.* Dy does not form $Ln(CO_3)_4^{5-}$ at a detectable level in 0.5 mol L^{-1} Na_2CO_3 background electrolyte. The calculated values ($-1.1 \pm 0.6 < \log_{10} K_4^{0.5M\ \ Na_2CO_3} < 0.1 \pm 0.6$) are consistent with the $\log_{10} K_4$ data published for Ce [13], Nd [4], Eu and Gd [12] extrapolated (using $\log_{10} K_{4,Gd}$ determined from the raw results of Faucherre *et al.* [12] by Vercouter *et al.* [5]) to 0.5 mol L^{1} Na_2CO_3 background electrolyte with the SIT formula. For the heaviest (smallest) lanthanides. Steric hindrance may prevent the formation of $Ln(CO_3)_4^{5-}$ due to the electrostatic repulsion of the numerous anionic ligands of the first coordination sphere. However, only a few data are available and the uncertainties are quite important due to the ionic strength corrections.

We observed that the most anionic species are slower than the least anionic ones in 0.5 mol L^{-1} Na_2CO_3 background electrolyte according to the measured $\mu^{I}_{ep,Ln}$ (Fig. 2). The opposite tendency would be expected from the calculated charges of the inner sphere aqueous species (Eq. (2), Table 1). The hydrodynamic radius of $Ln(CO_3)_4^{5-}$ is likely to be larger than that of $Ln(CO_3)_3^{3-}$. Moreover, the effective charge of the analyzed species should be different from that of the inner sphere complexes (as assumed in Eq. 2), due to ion pairing between Na^+ and $Ln(CO_3)_4^{5-}$ for example, as already proposed for other carbonate complexes of actinides with charges −5 or −6 [31, 32]. More generally, this can be seen as retardation effects which would be stronger for compounds with higher charges. Indeed, in the presence of an electrolyte the effective charge of the solute is less than its actual charge due to the screening effect by the electrolyte counterions. The excess of oppositely charged ions in the solution can be seen as a diffuse ionic cloud at the Debye distance according to Debye-Hückel model for electrolyte solutions. The ionic cloud migrates in the opposite direction to that of the central ion. An extra viscous force is exerted on the central ion. The screening effect decreases as the ionic strength and the Debye distance decrease [29]. For example, the mobilities of 3 sulfonic acids with different charge numbers (−4, −5 and −6) showed a quite similar mobility in background electrolytes for ionic strengths ranging from 0.001 to 0.1 mol L^{-1} [33].

Table 2. Aqueous speciations of all the studied Ln(III) calculated from the experimental electrophoretic mobilities and the calculated aqueous speciation of La(III) and Dy(III) (Table 1)

[Alk_2CO_3]	Ln	La[a)]	Pr	Nd	Sm	Eu	Gd	Tb	Dy[a)]	Ho	Er	Tm	Lu
0.15 M	%$Ln(CO_3)_2^-$	22	20	19	16	14	12	8	6	4	4	4	5
	%$Ln(CO_3)_3^{3-}$	78	80	81	84	86	88	92	94	96	96	96	95
0.50 M	%$Ln(CO_3)_3^{3-}$	63	63	63	69	77	80	96	100	100	100	100	100
	%$Ln(CO_3)_4^{5-}$	37	37	37	31	23	20	4	0	0	0	0	0

a) These aqueous speciations have been calculated from the thermodynamic constants determined by solubility measurements.

In the 0.15 mol L^{-1} Na_2CO_3 background electrolyte, the electrophoretic mobilities are higher than in the 0.5 mol L^{-1} Na_2CO_3 background electrolyte. The increase of electrophoretic mobilities is also consistent with the decrease of the sodium concentration, which is 3 times less important, therefore the retardation effects are unfavored. The electrophoretic mobilities increase across the lanthanide series. While a plateau was observed in the 0.5 mol L^{-1} background electrolyte, a slight increase of the mobilities is observed for the lightest lanthanides (Fig. 2). This variation of the mobilities should also be related to a change in the speciation. According to the previous solubility measurements, the ionic strength and the carbonate concentration are not high enough to obtain $Ln(CO_3)_4^{5-}$ in detectable proportions for any of the lanthanides. No single complex was dominating in any of the solutions. The speciation is composed of $Ln(CO_3)_3^{3-}$ and $Ln(CO_3)_2^-$ in variable proportions. We calculated that in the 0.15 mol L^{-1} Na_2CO_3 solution about 21% of La were present as $La(CO_3)_2^-$, about 76% as $La(CO_3)_3^{3-}$ and about 3% as $La(CO_3)_4^{5-}$, which was neglected. For Dy, the limiting $Dy(CO_3)_3^{3-}$ complex is partially dissociated: 94% $Dy(CO_3)_3^{3-}$ and 6% $Dy(CO_3)_2^-$ (Table 1), Eq. (3) simplifies:

$$\mu_{ep,Ln}^{I} = \frac{\mu_{ep,2}^{I} + K_3^{I}\left[CO_3^{2-}\right]\mu_{ep,3}^{I}}{1 + K_3^{I}\left[CO_3^{2-}\right]} \tag{9}$$

Using the calculated aqueous speciations for La and Dy (Table 1), the electrophoretic mobilities of $Ln(CO_3)_2^-$ and $Ln(CO_3)_3^{3-}$ were determined from the mobilities of La and Dy:

$$\mu_{ep,La}^{0.15M\ \ Na_2CO_3} = 0.22\mu_{ep,2}^{0.15M\ \ Na_2CO_3} + 0.78\mu_{ep,3}^{0.15M\ \ Na_2CO_3} \tag{10}$$

$$\mu_{ep,Dy}^{0.15M\ \ Na_2CO_3} = 0.06\mu_{ep,2}^{0.15M\ \ Na_2CO_3} + 0.94\mu_{ep,3}^{0.15M\ \ Na_2CO_3} \tag{11}$$

We deduced the proportions of $Ln(CO_3)_2^-$ and $Ln(CO_3)_3^{3-}$ by modeling the experimental electrophoretic mobilities as the weighted mean of the mobilities of La and Dy. We finally calculated $K_{3,Ln}^{0.15M\ \ Na_2CO_3}$ for all the lanthanides (Table 2, Fig. 3). There is a fair agreement between our work ($1.4 \pm 0.3 < \log_{10}K_3^{0.15M\ \ Na_2CO_3} < 2.1 \pm 0.3$) and the $\log_{10}K_3$ values published for Ce [13] and Eu [5] extrapolated to 0.15 mol L^{-1} Na_2CO_3 background electrolyte with the SIT formula. Note that the evolution of $\log_{10}K_3$ across the lanthanide series looks like the variation of $\log_{10}K_1$ and $\log_{10}K_2$, which evolve of about 1 $\log_{10}$ unit [25, 26, 27]. The increase of $\log_{10}K_1$ and $\log_{10}K_2$ across the lanthanide series has been attributed to the increase of electrostatic interactions between the lanthanide cation and the anionic ligands with the decrease of the ionic radius.

CE-ICP-MS allows the determination of the relative variations of $\log_{10}K_{3,Ln}^{0.15M\ \ Na_2CO_3}$ and $\log_{10}K_{4,Ln}^{0.5M\ \ Na_2CO_3}$ across the lanthanide(III) series from the absolute values of these constants determined by solubility measurements for La and Dy (Fig. 3). The variation across the series is slightly larger than the uncertainties estimated from the experimental errors. Note that $\log_{10}K_{3,Ln}^{0.15M\ \ Na_2CO_3}$ and $\log_{10}K_{4,Ln}^{0.5M\ \ Na_2CO_3}$ are determined from, $\log_{10}K_{3,La}^{0.15M\ \ Na_2CO_3}$, $\log_{10}K_{3,Dy}^{0.15M\ \ Na_2CO_3}$ and $\log_{10}K_{4,La}^{0.5M\ \ Na_2CO_3}$ to which a 0.6, a 0.7 or a 1.4 uncertainty has been assigned. Propagating this uncertainty, which would correspond to systematic errors, would give a much larger error on the constants (not represented), but that would be the same for each lanthanide. Thus, we rather discussed relative variations of $\log_{10}K_{3,Ln}^{0.15M\ \ Na_2CO_3}$ and $\log_{10}K_{4,Ln}^{0.5M\ \ Na_2CO_3}$. The CE-ICP-MS results give a good picture of the variations across the lanthanide series, since it provides results for nearly all the lanthanides (Fig. 3). In 0.15 and 0.5 mol L^{-1} Na_2CO_3 background electrolytes, except for the heavy lanthanides in 0.5 mol L^{-1} Na_2CO_3 solutions, there is a mixture of aqueous complexes. Experimental evidences of the distribution of species are hardly obtained. The solubility measurements performed in the companion study [3] are rather used to calculate the aqueous speciation of La and Dy, which have been chosen to represent the light and the heavy lanthanides respectively. In the solubility measurements, the carbonate limiting complexes have been isolated in solution using favourable experimental conditions, *i.e.* high ionic strength, and the thermodynamic constants that have been determined are robust and compare with those previously determined by other authors using the same methodology [5, 13]. Note that a slightly different speciation than that obtained by CE-ICP-MS was obtained by solubility measurements for Nd and Eu. Solubility measurements have shown that Eu is likely not to form $Eu(CO_3)_4^{5-}$ while CE-ICP-MS measurements enable to detect this aqueous species in sufficient concentration to determine its stepwise

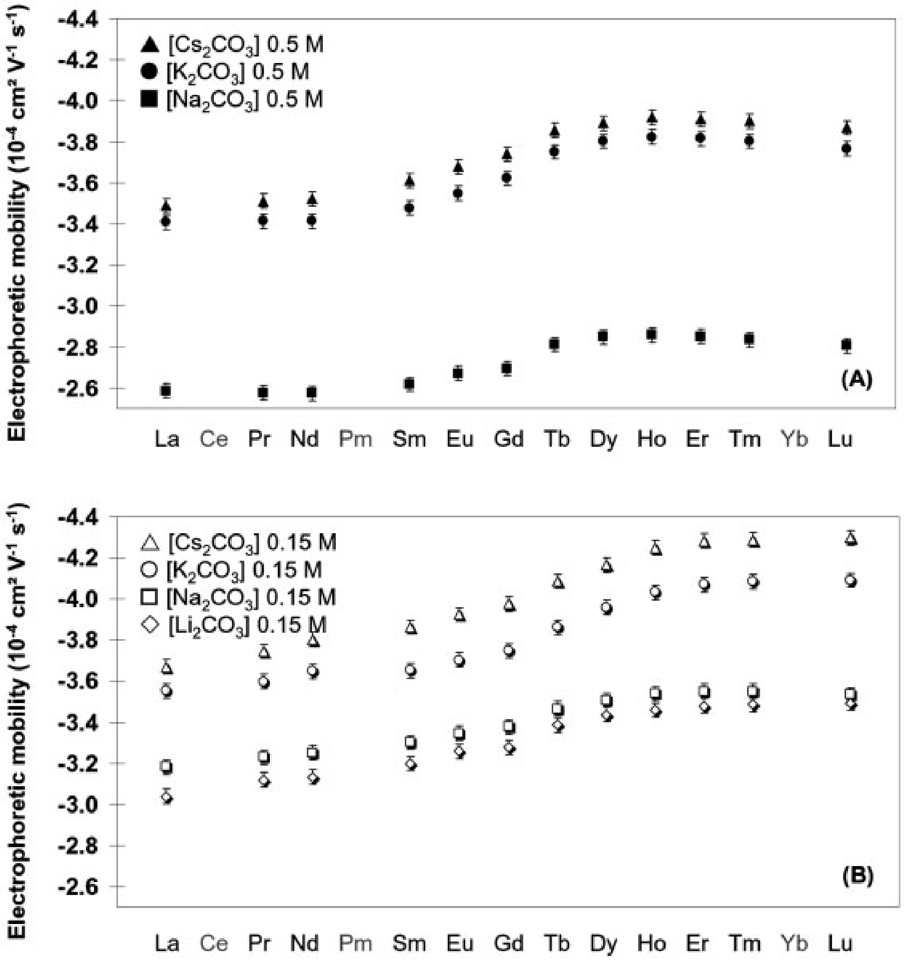

Figure 3. Variation of the stepwise formation constants of carbonate complexes estimated from our CE-ICP-MS study: $\log_{10}K_{3,\mathrm{Ln}}^{0.15\mathrm{M}\ \ \mathrm{Na_2CO_3}}$ and $\log_{10}K_{4,\mathrm{Ln}}^{0.5\mathrm{M}\ \mathrm{Na_2CO_3}}$ (solid squares). The complexing constants of La, Nd, Eu and Dy - corrected for ionic strength - from the companion solubility study [3] are superimposed (green squares), those that were used to calculate the theoretical aqueous speciation of La and Dy are given without uncertainty.

formation constant. Moreover, the aqueous speciation determined by solubility measurements for Nd indicates partial dissociation of its limiting complex in 0.15 and 0.5 mol L^{-1} Na_2CO_3 solutions: namely 19% of the total lanthanide concentration were present as $Nd(CO_3)_2^-$, 71% as $Nd(CO_3)_3^{3-}$ and 10% as $Nd(CO_3)_4^{5-}$ in 0.15 mol L^{-1} Na_2CO_3 background electrolyte, and 1% of the total lanthanide concentration were present as $Nd(CO_3)_2^-$, 37% as $Nd(CO_3)_3^{3-}$ and 63% as $Nd(CO_3)_4^{5-}$ in 0.5 mol L^{-1} Na_2CO_3 background electrolyte, which is slightly different from the speciation calculated by EC-ICP-MS. However, the stepwise formation constants determined by EC-ICP-MS are in good agreement with those determined by solubility measurements (Fig. 3).

3.2 Electrophoretic mobilities of the lanthanides in Li^+, K^+ and Cs^+ background electrolytes

Electrophoretic mobilities of the lanthanides were measured in lithium, potassium and caesium carbonate solutions under the same experimental conditions as in the sodium media: 0.5 and 0.15 mol L^{-1} Alk_2CO_3 solutions (Fig. 4A and B respectively). Whatever the counter-ion, the electrophoretic mobilities are represented by sigmoid curves, indicating that the aqueous speciations are similar. For a given carbonate concentration, the various curves are parallel. The relative mobility of a lanthanide is only dependent on ε, η and z_i/r_i ratio since all the other parameters (pH, *I, T*) are similar. Electrophoretic mobilities in lithium and sodium are quite similar, but different from potassium and caesium media in which lanthanide migrate faster. The $\mu_{\mathrm{ep,Ln}}^{\mathrm{Alk_2CO_3}}$ values increase in the order lithium < sodium << potassium < caesium. The shifts between the parallel mobility curves are likely due to changes in physical parameters with the alkali metal ions. However, the variations of ε, η should not be sufficient to explain the significant difference of mobility between Li^+/Na^+ and K^+/Cs^+ media. The viscosity ratio in Na_2CO_3 and K_2CO_3 0.5 mol L^{-1} is about 0.9 [34] whereas the mobilities ratio attains 0.75. No data on viscosity and dielectric constant are available for the other media. Moreover, spectroscopic measurements on the Eu(III) samples have shown that a single fluorescence spectrum was observed, whatever the counter ion, suggesting that the inner sphere of the complexes are identical [3].

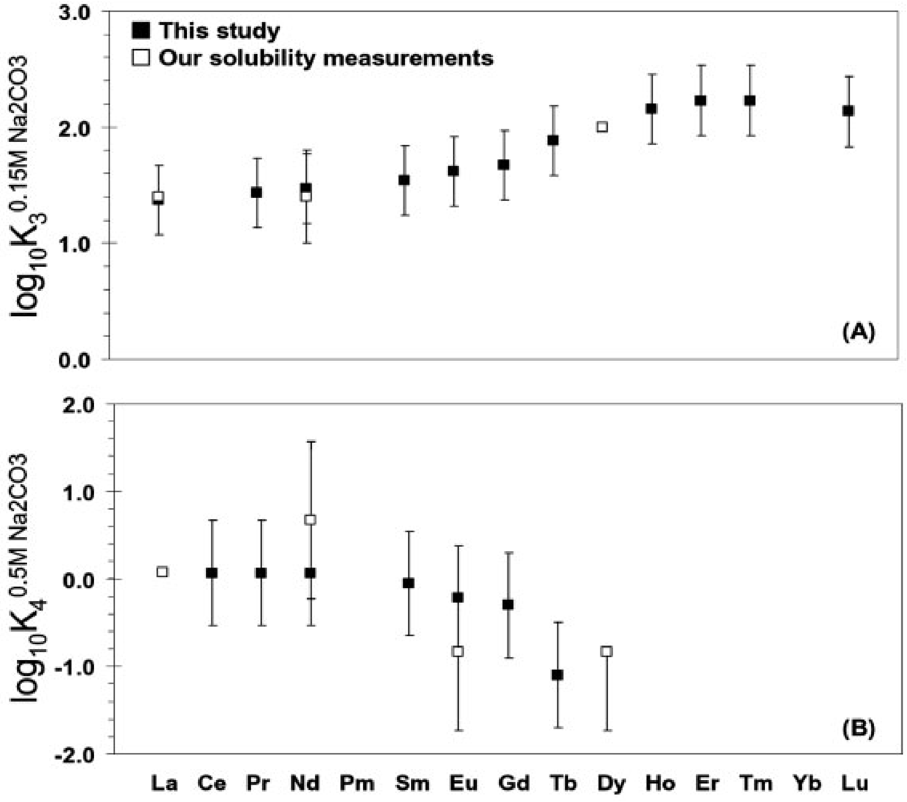

Figure 4. Electrophoretic mobilities of 12 lanthanides in 0.5 (A) and 0.15 (B) mol L^{-1} Alk_2CO_3.

Two studies reported the influence of the alkali metal counterions on the mobilities of anions [35, 36]. Li *et al.* studied the effect of univalent cations (Li^+, Na^+ and K^+) in borate buffers on the mobilities of benzoate, 2-naphthalenesulfonate and phthalate [35]. Li^+ caused a greater decrease in the mobilities than Na^+ than did K^+. This trend was attributed to the increase of ion association between the univalent cations with the anions. It is consistent with the trend noted by Neilen *et al.* for mobilities of aminobenzoate and *p*-toluenesulfonic acid in acetate buffer [36]. In their study, the mobilities decrease from K^+ to Na^+ to Li^+. Our observed trend is similar, moreover the behaviour of Cs^+ is equivalent to that of K^+. A different solvation of the lanthanide complexes by the different alkali metal counterions may explain the observed shift of the sigmoid curves, but since they are parallel, it is more likely that the solvation is not that different. The combination of various weak differences: the viscosity, the dielectric constant, the hydrodynamic radii of the complexes and the solvation may explain the difference of electrophoretic mobilities.

4 Concluding remarks

The carbonate limiting complexes were studied by means of CE-ICP-MS for 12 natural lanthanides. A change of carbonate limiting complex stoichiometries across the 4f-block element series was confirmed in concentrated Alk_2CO_3 solutions. A tetracarbonate can be stabilized for the lighter lanthanides, while a tricarbonate complex appears to be the limiting complex for the heavier lanthanides. The variations of $\log_{10}K_3^{0.15\mathrm{M}\ \mathrm{Na_2CO_3}}$ and $\log_{10}K_4^{0.5\mathrm{M}\ \mathrm{Na_2CO_3}}$ values across the lanthanide series were estimated from the measurements of the electrophoretic mobilities. The *Alk*$^+$ counterion does not modify the stoichiometry of the inner sphere complex since similar profiles are observed whatever the alkali metal. The alkali metals modify the electrophoretic mobilities of $\mathrm{Ln(CO_3)}_i^{3-2i}$ and the electrophoretic mobilities decrease from Cs^+ to K^+ to Na^+ to Li^+.

We are grateful to P. Hemet from CEA/DAM/DIF/DASE for his technical help and his fruitful experimental advice concerning ICP-SFMS.

The authors have declared no conflict of interest.

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