Determination of Lanthanum(III) and Europium(III) – Lactate Interaction Constants by Capillary Electrophoresis for Environmental Applications

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ABSTRACT

In the present work, we investigated the ability of electrophoresis to determine the stability constant of the complex formed between lactate ions (a simple model of natural organic matter), and lanthanum (III) and europium (III), two model metal cations of actinides. The effect of lactate on lanthanide's effective mobility is studied, and conditional metal ion-ligand interaction constants are determined on the basis of the variation in the effective mobilities (log β_n = 2.23 for lanthanum (III) and 2.39 for europium (III), at 25°C and I=0.015 M). The originality of this contribution lies in the fact that we have chosen to detect the metal ion instead of the ligand by an indirect UV-visible detection and using a chromophoric compound (creatinine).

Keywords: Lanthanides (III); Lactate; Separation, Interaction constants, Capillary electrophoresis

INTRODUCTION

Natural organic matter plays a key role in the fate, bioavailability and mobility of pollutants including metal species in the environment [1,2]. As this matter is often complex, and its physico-chemistry is at present only partly understood, new analytical methods are still needed to characterise its

interaction with pollutants. In the present work, we investigated the ability of electrophoresis to determine the stability constant of the complex formed between lactate ions (a simple model of natural organic matter), and lanthanum (III) and europium (III), suitable homologues for trivalent actinides whose fate from deep radioactive waste depository needs to be understood for sustainable development of nuclear energy.

In the family of separation techniques, electromigration techniques give elution data based on a charge to mass ratio. The principle of complex formation evaluation is then based on the comparison of effective mobilities in the additive-free separation electrolyte and in the running electrolyte containing different concentrations of ligand. This methodology gives access to both, conditional interaction constants and migration parameters, leading to, for example, diffusion coefficients. In this work, we design and apply an electrophoretic method for the evaluation of non-visible absorbing cations/ligand interaction constants. Contrary to the literature [3-5] we chose to detect the metal ion instead of the ligand which offers broader possibilities. For this purpose, an indirect UV-visible detection is used while adding to the separation electrolyte a chromophoric compound which does not interfere with the metal ion / organic ligand system, and presents an electrophoretic mobility similar to the one of the detected compound. In order to validate the method, experiments are performed using lactate as a model molecule for complexing lanthanum (III) and europium (III). This organic was chosen for its carboxylic and hydroxyl functional groups, which are functional groups encountered for instance in humic substances. The effect of lactate on lanthanide's effective mobility is studied and conditional metal ion-ligand interaction constants are determined on the basis of the variation in the effective mobilities.

EXPERIMENTAL
Materials

CE experiments were performed on a Hewlett Packard System (HP 3D CE, Waldbronn, Germany) equipped with an auto-sampler, an automatic injector and a photodiode array detector. A 32 cm (inlet to detector) Beckman Instruments (Gagny, France) fused-silica capillary of 40 cm × 50 μm i.d. was used for lanthanum experiments whereas a 42cm (inlet to detector) Beckman Instruments (Gagny, France) fused-silica capillary of 50 cm × 50 μm i.d. was used for europium experiments. Samples were hydrodynamically injected at 50 mbar for 5 s. Experiments were performed at 25°C ± 0.1, and a voltage of +15 kV was applied in order to keep the total current at 10 μA. The electropherograms were recorded using a computer program supplied by Hewlett Packard (Chemstation Software, Waldbronn, Germany). Samples for the separation study were monitored at 200 nm. pH of the buffer solutions was measured with a LPH330T pH-meter (Tacussel électronique, Villeurbanne, France) using a Radiometer electrode (Villeurbanne, France).

Eu and La nitrate hexahydrate salts used were purchased from Aldrich (Saint Quentin Fallavier, France). All reagents used were of analytical grade. Creatinine (Fluka, Saint Quentin Fallavier, France) and lactic acid (Aldrich, Saint Quentin Fallavier, France) were used without further purification.

Methods

Each pH 5 buffer's system consisted in 30 mM creatinine, lactic acid and HCl for a constant ionic strength of 15 mM. A 30 mM creatinine and 15 mM HCl buffer allowed the determination of the free cation electrophoretic moblity μ_f. This value is necessary for the stability constants calculation. Lanthanum and europium samples were prepared by dissolving appropriate amounts of their respective salts in a 50/50 (v/v) mixture of 30 mM creatinine, 15 mM HCl buffer and water (Milli-Q water purification system, Millipore, Molsheim, France). Samples of 10 mM lanthanum (III) and 1 mM europium (III) were then prepared.

Procedures

Before each set of experiments, the capillary was 5min purged with Milli-Q water, 5 min with 0.1 M NaOH, 10 min with Milli-Q water and 15 min with appropriate buffer electrolyte. The sample was then successively injected in triplicate. Between each run, the capillary was 2 min flushed with Milli-Q water and 5 min by the running buffer. Injections were repeated until constancy of electrophoretic mobilities was achieved. For each buffer, the electro-osmotic flow was determined with a sample of benzylic alcohol (neutral molecule in our experimental conditions) before and after the runs with the sample. Experimental values of the effective electrophoretic mobilities were calculated as the difference between the apparent mobility (μ_{app}, obtained by the determination of migration time) for each buffer (with various quantities of lactic acid) and the mobility of the neutral marker, μ_{eof}.

RESULTS AND DISCUSSION

The most common method for estimating interaction constants by CE involves measuring the change in electrophoretic mobility of a solute through buffer solutions containing dissolved ligand. There are a few requirements for using CE to determine interaction constants. The solute must undergo a change in electrophoretic mobility upon complexation, and mobility change must be exclusively due to the association of the solute and ligand. In addition, the equilibrium time scale must be faster than the CE separation time scale, and sufficient concentrations of both free ligand and ligand/solute complex should be present.

The reversible 1:1 molecular association between a metal ion, M, and a ligand, L, in the reaction M + L $\leftrightarrow$ ML, can be described by the general

form of a binding isotherm which has been used to estimate binding constants using plotting methods reviewed in Table 1 [6-8].

Tab. 1. Plotting forms for interaction constants (K) determination where μ_i is the effective electrophoretic mobility of metal ion in presence of lactic acid), μ_f and μ_c are electrophoretic mobilities of free metal ion and complexed form, respectively. An example of plotting form (europium sample) is given

Plotting name	Plotting form	K determination
Isotherm	$\mu_i = \dfrac{\mu_f + \mu_c K[L]}{1 + K[L]}$	Non-linear fitting
Mobility ratio difference	$\dfrac{(\mu_f - \mu_i)}{(\mu_i - \mu_c)} = f([L])$	Slope
Double reciprocal	$\dfrac{1}{(\mu_i - \mu_f)} = f\left(\dfrac{1}{[L]}\right)$	$\dfrac{\text{Intercept}}{\text{Slope}}$
Y-reciprocal	$\dfrac{[L]}{(\mu_i - \mu_f)} = f([L])$	$\dfrac{\text{Slope}}{\text{Intercept}}$
X-reciprocal	$\dfrac{(\mu_i - \mu_f)}{[L]} = f(\mu_i - \mu_f)$	-Slope

Y-reciprocal
for europium sample

$y = -2281x - 11.133$
$R^2 = 0.98$

[L] in mol/L
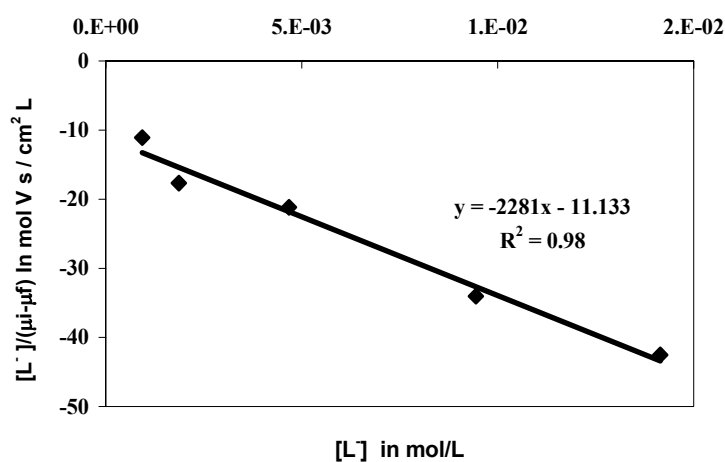
To approximate environmental conditions and to avoid additional interactions, a minimal electrolyte composition was used. In this work, electrolytes consist of increasing lactic acid concentrations in a creatinine buffer whereas the lanthanide ion is directly injected in the capillary. Creatinine buffer is shown to be inert toward lanthanide complexation and acts as a chromophore, permitting indirect detection of the metal ions. The appropriate concentration of lactic acid is then introduced and HCl is added so that ionic strength (15 mM) is kept constant. In addition, pH is maintained below 6 to preclude lanthanide hydroxide or carbonate precipitation.
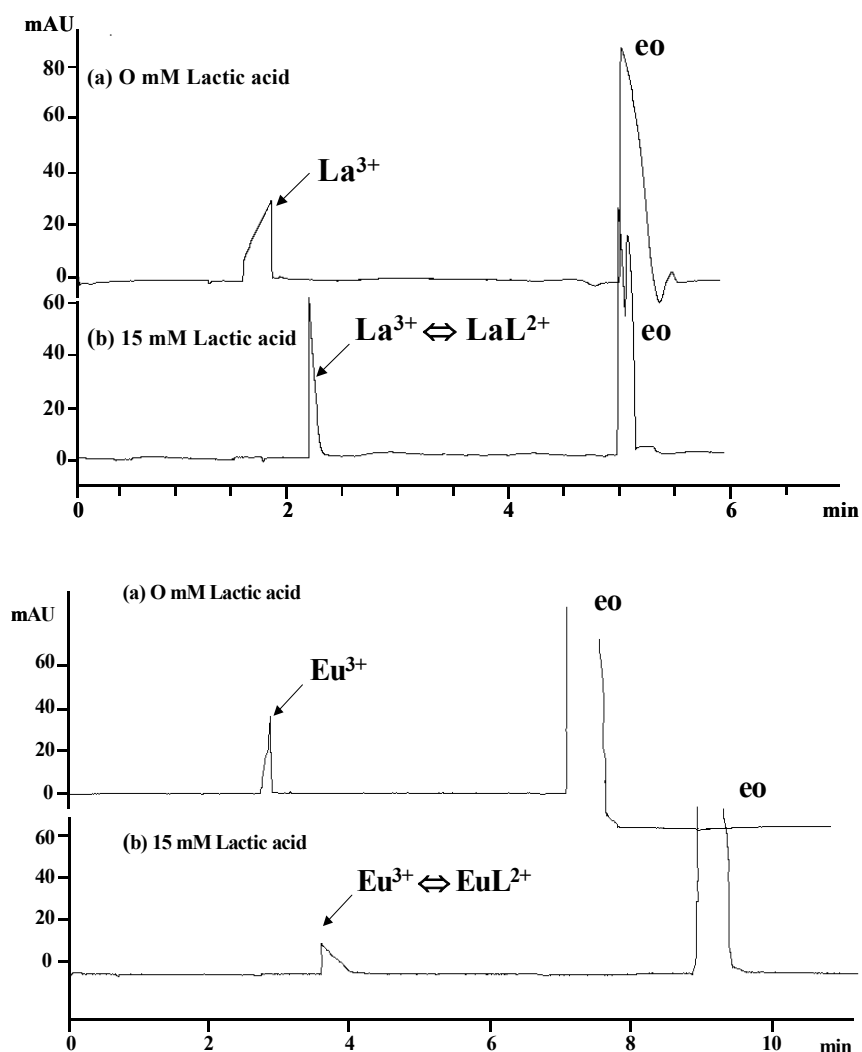

Fig. 1. Influence of lactic acid addition on La(III) and Eu(III) mobilities. (EO: electroosmotic flow).

Figure 1 shows the electropherograms of the samples containing La(III) or Eu(III) with increasing concentrations of lactic acid in the buffer. Due to a decrease in the charge-to-size-ratio when complexation occurs, the effective mobility of the complexed metal ion decreases compared to the one of the free metal ion, which corresponds to an increase of the migration time with lactic acid concentration. Since the metal ion has a greater mobility compared to the buffer co-ion (CREAH$^+$), a free metal ion peak fronts. After addition of lactic acid, the mobility decreases, leading to a more symmetrical peak. With sufficient lactic acid concentrations, CREAH$^+$ buffer mobility becomes greater than the metal ion effective mobility, resulting in tailing peaks. This phenomenon brings to the fore that creatinine has an adequate mobility to be used as chromophore.

Table 2 summarizes log β_{ML} and correlation coefficients obtained for La(III) and Eu(III) – lactate interactions. The complexation constant β_{ML} is given by:

$$\beta_{ML} = \frac{[ML]}{[M^{3+}] \times [L]} = K_{ML}$$

Tab. 2. Calculated stability constants at 25°C and at 15 mM ionic strength from CE experiments and comparison of the average values with those of the literature [7]

Lanthanum(III)	Log β_{ML} (literature [7]) 2.44 (0.2 M à 25°C)	
Method name	r^2, squared correlation coefficient	Log β_{ML}
Mobility ratio difference	0.981	2.07 ± 0.23
Double reciprocal	0.982	2.27 ± 0.12
Y-reciprocal	0.983	2.27 ± 0.15
X-reciprocal	0.975	2.29 ± 0.12
Exp. log β_{ML} (average)		2.23 (0.015 M at 25°C)
Europium(III)	Log β_{ML} (literature [7]) 2.55 (0.2 M à 25°C)	
Method name	r^2, squared correlation coefficient	Log β_{ML}
Mobility ratio difference	0.988	2.64 ± 0.12
Double reciprocal	0.999	2.22 ± 0.13
Y-reciprocal	0.980	2.49 ± 0.16
X-reciprocal	0.979	2.19 ± 0.17
Exp. log β_{ML} (average)		2.39 (0.015 M at 25°C)

Four different plotting methods [6] were used to evaluate the interaction constants. In this table, log β_{ML} values were given at the ionic strength of the experiments (15mM). The values obtained from the various linear plotting methods (Table 1) are all-consistent and correspond with a 1:1 metal ion-ligand complex. In addition, the interaction constants obtained from the experimental data are in good agreement with those from the literature.

CONCLUSION

In conclusion, the results presented in this paper show that CE technique with indirect detection of metal cations using a chromophore combined with the data analysis methods makes possible the determination of interaction constants between a metal cation non-absorbing in UV-visible and a complexing agent.

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