Application of a Capillary Electrophoresis to the Speciation of Eu(III) Complexes in an Aqueous Solution

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1. Introduction

Actinide ions form stable aqueous complexes with anions such as hydroxide, carbonate and humic substance, which are ubiquitous in natural water. Since a dissolution and sorption of actinide ions largely depend on their species distribution in a groundwater condition, a microscopic understanding of their chemical behavior is required for a precise analysis of their safety in a radioactive waste disposal. Lanthanide ions, especially the Eu(III) ion, are used as chemical analogues of Am(III) or Cm(III) ions for a study of the chemical behaviors in a groundwater. Although the speciation of actinide ions has been studied by various means, still the exact feature in a natural aqueous solution is not clearly understood.

Capillary electrophoresis (CE) has been developed to be applied not only to a separation and analysis but also to the determination of the physical parameters of chemical compounds, such as the mobility of colloidal particles and the stability constants of complexes. CE has advantages of a high separation efficiency, a high analysis speed, and a small sample requirement. CE separates chemical species in an electric field based on their charge and size properties which is observed as a migration time. The measurement of the stability constants of quick reversible equilibrium and kinetically inert systems can be approached by a direct formation, a ligand exchange, a metal exchange and a double exchange technique. In this report, the experience of setting-up a primeval CE system, and the measurement of ligand [acetate, picolinate, pyridine-2,6-dicarboxylate (PDA) and ethylenediaminetetra-acetate (EDTA)] effect on the electrophoretic migration of Eu(III) ions in a capillary column are described.

2. Experimental

2.1. Instrumentation. The CE instrumental setup consists of a high voltage power supplier (DRP-2501A, Dae Do Electronics), a fractional collector (FRAC-100, Pharmacia Biotech) and a titrator (776 Dosimat, Methrom). The separation was carried out in a fused-silica capillary (i.d. of 75 or 100 μm and o.d. of 375 μm, Beckman) with a total length of 60 cm. The temperature of capillary was controlled by an air flow. The set-up CE system was shown at Fig. 1.

2.2. Separation. The capillary was conditioned by a sequential hydrodynamic flowing of 0.1 M HCl, water, 0.1 M NaOH, water and background electrolyte for 10 min of each reagent at 20 cm height difference. The sample was injected for 10 seconds, which loaded 25 and 80 nL sample solution for capillaries with i.d. of 75 and 100 μm, respectively. Positive electric voltage was applied to a capillary inlet against the grounding of a capillary outlet for a separation. The instance of the applying electric voltage was taken as a zero time of the migration. The separated ions flowing out the capillary outlet was rinsed by a flow of make-up solution (0.1 M HNO_3) and fractionally collected at vials with fixed time intervals. The dropping rate was 12 seconds a drop at a 0.25 ml/min make-up solution flow. Collected Eu in a vial was determined by using an ICP-AES (ULTIMA2C, Jobin Yvon).

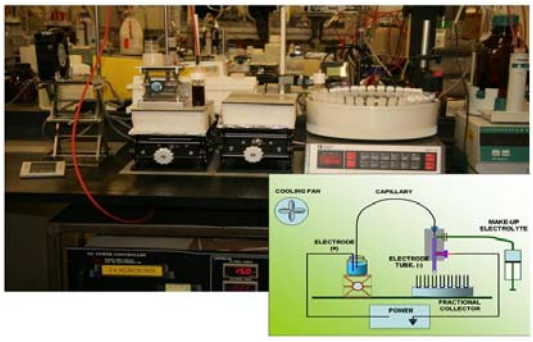

Fig. 1. Capillary electrophoresis system set up.

3. Results and discussion

The effect of ligand on the migration time of metal ions can be classified into two extreme cases according to the relative time of a migration to that of a reaction; quick reversible equilibrium and kinetically inert systems. In the case of a quick reversible equilibrium system, since the reaction time is much shorter than the migration time and the separated species quickly reach a new equilibrium state, the migration of a metal ion is measured in a background electrolyte solution containing ligand. The migration time reflects the averaged charge and size of a metal ion species, which are a function of the averaged coordination number. In the case of kinetically inert systems, since a change of the species during the separation time is negligible, the amount of separated species reflects the species distribution controlled by the stability constants. Metal ion species in equilibrium state with a ligand are separated in a background electrolyte containing no ligand.

The migration time of the Eu(III) ion (2.5 mM) was measured (i.d. of 100 μm, potential of 15 kV) in the background electrolyte of acetate, picolinate or mixed acetate-picolinate solutions (pH=4.7 ([Na^+]=32 mM), and the results are shown in Fig. 2.

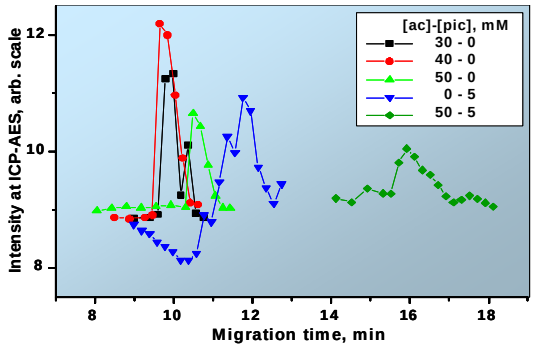

Fig. 2. Electropherograms of Eu(III) species in solutions of acetate and/or picolinate of pH 4.7. V=15 kV, i.d.=100 μm, L=60 cm.

The electropherograms of Eu(III) in acetate solutions show a feature of a single peak shape indicating the migration of Eu(III) ions as a single species with an averaged coordination number. The migration time increased from 9.8 to 10.5 min as the concentration of acetate increased from 30 to 50 mM, which coincides with the increase of a calculated mean coordination number from 1.7 to 2.2. In a picolinate solution without acetate, the migration time of Eu(III) ion appears at 11.7 min with a feature of a single peak shape. The calculated mean coordination number is 1.4 in a 5 mM picolinate solution. The slower migration of Eu(III), in spite of the smaller mean coordination number, in the picolinate solution than in the acetate solution is due to the larger size of the picolinate complex than acetate complex. In a mixed acetate-picolinate solution, the migration time increased to 16 min, which is explained by an additive effect of Eu-acetate and Eu-picolinate complexes. The calculated mean coordination number of 2.1 including both ligands is smaller than that in 50 mM acetate. However, mean coordination number of Eu-picolinate complex increased to 1.9 while that of Eu-acetate decreased to 2.2. This results in increasing contribution of Eu-picolinate complex to the migration time of Eu(III) ions. The mole fractions of acetate and picilinate complexes are 0.45 and 0.53, respectively. The ligand effect on the migration of metal ion in a quick reversible equilibrium system can be applied to a mixed ligand system.

As a kinetically inert system, the migration of the Eu(III) complexes of PDA (2.5, 5.0 and 8.0 mM) and EDTA (3.0 mM) were measured in a background electrolyte of acetate (50 mM of pH 4.7 with [Na^+]=32 mM). Since the complexes have a low positive charge and a large size, their separation required an increased electric field strength for a large electroosmotic flow. However, the increase in electric field strength induced an increase in the current and heat generation through the solution in a capillary which resulted in a gas bubble in the solution to stop the capillary. This was avoided by decreasing the diameter of the capillary to 75 μm to decrease a current, and the potential could be increased up to 25 kV. The results are shown in Fig. 3.

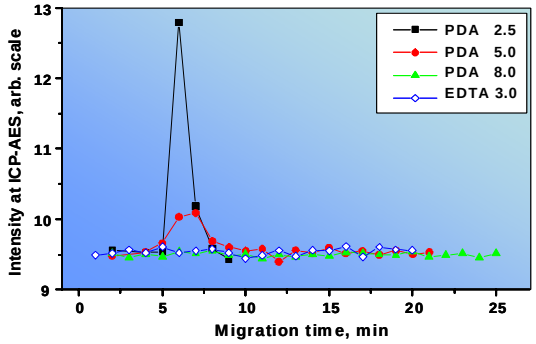

Fig. 3. Electropherograms of Eu(III) species of PDA or EDTA complex in the background electrolyte of acetate (50 mM, pH 4.7). V=25 kV, i.d.=75 μm, L=60 cm.

Eu was detected at about 6.5 min of a migration time for both the PDA concentrations of 2.5 and 5.0 mM, where the observed amount of Eu is smaller for 5.0 mM than for 2.5 mM. Eu was not detected within 25 min for the concentration of 8.0 mM. The observed trend of the migration time coincides with the calculated species distribution. The main species of Eu(III) equilibrated in the PDA solutions of 2.5, 5.0 and 8.0 mM are EuL^+, EuL_2^- and EuL_3^{3-}, respectively. The detected Eu is a EuL^+ species, which is a minor species at the PDA concentration of 5.0 mM. In the case of the EDTA ligand, most of the Eu(III) existed as a negatively charged EuL^- species at a concentration of 3.0 mM, which was not detected at the cathode capillary outlet like the PDA species of EuL_2^- and EuL_3^3.

4. Summary

A primeval CE system was set up and the effect of some ligands on the migration time of the Eu(III) ion was measured. Eu(III) ion in the presence of acetate or picolinate in a background electrolyte is observed like as a single species. Coexistence of acetate and picolinate slowed down the migration of a Eu(III) ion. It can be explained by an additive effect of both ligands and suggests that a quick reversible equilibrium can be effective in a mixed ligand system. Eu(III) species with PDA is so inert that their species can be separated in a background electrolyte containing no ligand. The formation of negatively charged species hindered the detection of the Eu(III) ion at the cathodic capillary outlet, and requires an increase of the electric voltage over 25 kV.

Acknowledgements

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