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Short Communication

Capillary tube isotachophoretic separation of lanthanide complexes using polyaminocarboxylic acid as terminating ion

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ABSTRACT

EDTA and TTHA solutions were used as terminating electrolytes and 10 mM HCl containing 45% (v/v) acetone as the leading electrolyte. Gd, Eu, Sm, Pr, Ce and La ions were separated as their anionic chelates when EDTA was used as the terminating ion. The migration order of the chelates was in accord with the order of their stability constants.

INTRODUCTION

Rare earth elements are industrially important and efficient methods for their determination are required. They are similar in nature and their separation is difficult. High-performance liquid chromatography [1] and capillary tube isotachopheresis (CITP) are excellent separation methods and some attempts have been made to apply them to metals ions [2,3]. Previously, we reported that the use of the complex-forming equilibria between α -hydroxyisobutyric acid in the leading electrolyte and lanthanide ions can be effective for their separation by CITP [4], but in this technique the concentration of α -hydroxyisobutyric acid must be strictly controlled.

We have also reported a new operating system involving reaction with the terminating ion [5,6]. In this method, sample species were converted into negatively charged species with the terminating ion and migrated according to complex-forming equilibria. Compared with the conventional method using complex-forming equilibria between the sample ions and the counter ion in the leading electrolyte, this method has the important advantage that the leading electrolyte does not contain any ligands and thus complicated preparation of the leading electrolyte is unnecessary. The concentration of the ligand as the terminating ion was controlled by the concentration of the leading ion according to the principle of CITP. Nakabayashi *et al.* [7,8] have also reported the separation of heavy metal-EDTA chelates with EDTA as the terminating ion in water-acetone mixed solvent.

In this paper, we describe the isotachophoretic behaviour of rare earth metal ions in the reaction with some polyaminocarboxylates as terminating ion. The order of migration of the chelates of rare earth metals was correlated with their stability constants. When EDTA was used as the terminating ion, seven rare earth metals could be separated.

EXPERIMENTAL

Apparatus

A Model IP-1B capillary tube isotachophoretic analyser equipped with a potential gradient detector (Shimadzu, Kyoto, Japan) was used. The PTFE tube for separation consisted of a main capillary column (150 mm \times 0.5 mm I.D.) and a precolumn (40 mm \times 1.0 mm I.D.). The capillary tube was filled with electrolyte by pressure of nitrogen. The step height given by the potential gradient detector was used for identification.

Reagents

All reagents were of analytical-reagent grade and solutions were prepared by dissolution in doubly distilled, deionized water. Solutions of rare earth metals were prepared by dissolving the oxides in dilute nitric acid.

Oxides of rare earth metals were obtained from Wako (Osaka, Japan). Ethylenediaminetetraacetic acid (EDTA), 1,2-cyclohexanediaminetetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DTPA) and triethylenetetraaminehexaacetic acid (TTHA) were obtained from Dojindo Labs. (Kumamoto, Japan).

RESULTS AND DISCUSSION

EDTA is a weak acid but it has a relatively large dissociation constant ($pK_1 = 2.0$). Hence even in a system with an acidic leading electrolyte it does not act sufficiently as a terminating ion because of its large mobility. However, Nakabayashi *et al.* [7,8] reported that the addition of acetone to the leading electrolyte lowers the mobility of EDTA and improves the separation of heavy metal ions. Therefore, the migration behaviour of rare earth metal chelates was studied using an electrolyte system with 10 mM HCl containing acetone as the leading electrolyte and EDTA solution as the terminating electrolyte. Fig. 1. shows the effect of the concentration of acetone in the leading electrolyte. With increasing concentration of acetone, the mobilities of both EDTA and the rare metal chelates were decreased, and the difference between the mobilities of the various rare earth metal chelates also became larger. However, with increasing concentration of acetone, the applied voltage required increased to an undesirable level. Therefore, the acetone concentration was maintained at 45% (v/v). In this system, seven metal chelates could be separated.

Addition of β -alanine as a buffering counter ion to the leading electrolyte made the difference in the mobilities of the rare earth metal chelates smaller because the apparent electric charges of the chelates based on their complex-forming equilibria

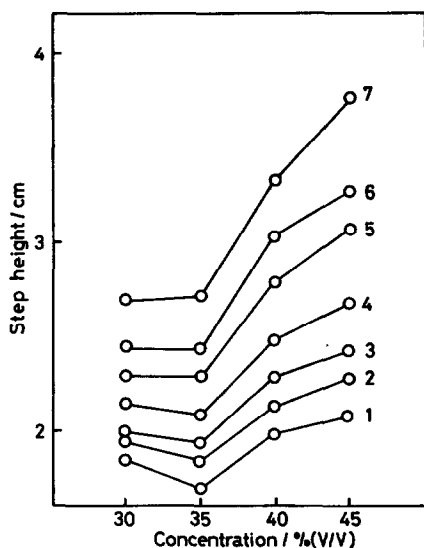
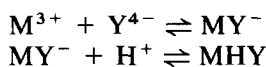


Fig. 1. Effect of concentration of acetone in the leading electrolyte. Leading and terminating electrolyte: 10 mM HCl and 5 mM EDTA, respectively. Current: constant at 75 μ A. 1 = Terbium; 2 = gadolinium; 3 = europium; 4 = samarium; 5 = praseodymium; 6 = cerium; 7 = lanthanum.

approached each other. In this system, a proton that migrates in the reverse direction to the chelates would associate with the chelates as follows:



where M^{3+} is the metal ion and Y^{4-} is EDTA. The chelates (MY^{-}) with smaller stability constants were easily associated with protons and the association equilibria made their effective mobilities smaller and improved the separating power. That is, the difference between the effective mobilities would be generated by the association equilibria with proton and chelates. Therefore, HCl was suitable as the leading electrolyte.

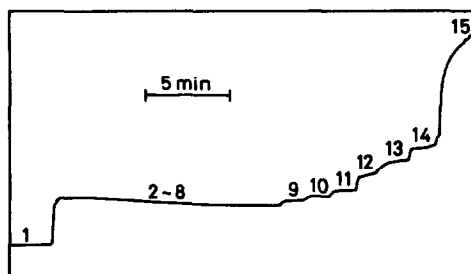


Fig. 2. Isotachopherogram of lanthanides. Leading electrolyte, 10 mM containing 45% (v/v) acetone; terminating electrolyte, 5 mM EDTA. Current: constant at 75 μ A. 1 = Chloride; 2-8 = lutetium, ytterbium, thulium, erbium, holmium, dysprosium and terbium; 9 = gadolinium; 10 = europium; 11 = samarium; 12 = praseodymium; 13 = cerium; 14 = lanthanum; 15 = EDTA.

Under conditions with the same leading electrolyte, EDTA, CyDTA, DTPA and TTHA were examined as terminating electrolytes. When EDTA or TTHA was used, seven rare earth metals, terbium, gadolinium, europium, samarium, praseodymium, cerium and lanthanum, were separated, but when CyDTA or DTPA was used, only six and three metals were separated, respectively. With all the polyaminocarboxylic acids, light rare earth metals, which have relatively smaller stability constants, were well separated. Fig. 2. shows the isotachopherogram of thirteen rare earth metals. The migration order was terbium > gadolinium > europium > samarium > praseodymium > cerium > lanthanum, and the metals from terbium to lutetium had the same effective mobilities. This migration order corresponded to the order of the stability constants of the chelates and the metal ions with larger stability constants had larger effective mobilities. Although the metals from terbium to lutetium have different stability constants, they could not be separated. It is concluded that the migration system presented is useful for the separation of comparative light rare earth metals.

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