Determination of Formation Rate Constant of Carrier-Free 111In(III) with EDTA

II. 7 Determination of Formation Rate Constant of Carrier-Free $^{111}In(III)$ with EDTA

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In-111($T_{1/2}$ = 2.83 d) is a very important isotope in the field of nuclear medicine and various labeled complexes have been prepared.[1] In the present paper, the complex formation mechanism of carrier-free ^{111}In with ethylene-diaminetetraacetate(EDTA) will be examined by means of cation-exchange method.

Experimental

a) Production of ^{111}In and preparation of carrier-free ^{111}In in 0.1 N hydrochloric acid solution

In-111 was produced by the $^{109}Ag(\alpha,2n)$ ^{111}In using an AVF cyclotron of Tohoku University. After short lived radioisotopes had decayed out, the silver foil was dissolved with concentrated nitric acid. The ^{111}In was separated from silver matrix by means of the solvent extraction using a 0.5 M acetylacetone benzene solution. The carrier-free ^{111}In was then prepared by the back extraction from the organic phase with a 0.1 N hydrochloric acid solution.

b) Determination of formation rate constants

To an aqueous solution containing a desired concentration of EDTA, the carrier-free ^{111}In solution was added to initiate the reaction. An aliquot was taken out from the reaction mixture at suitable time intervals and passed through a Dowex 50W-X8 column (50~100 mesh, 8 mmϕ × 40 mm). Thus, the $^{111}In(III)$-EDTA complex can be found in the eluate, while the free $^{111}In(III)$ is adsorbed on the column. The rate of formation of In(III)-EDTA was determined by measuring the radioactivity of the eluate.

Results and Discussion

The formation mechanism of In(III)-EDTA complex will in general be expressed as follows:

$$In^{3+} + H_nY^{(4-n)-} \underset{}{\overset{k_n}{\rightleftharpoons}} \begin{cases} InY^- + nH^+ \\ \downarrow\uparrow \\ InHY + (n-1)H^+ \quad (n=0\sim4) \end{cases} \tag{1}$$

in which contribution of $InOH^{2+}$ is ignored. Since the concentration of EDTA is in large excess over the carrier-free ^{111}In, the following equation can be derived from Eq. (1).

$$\ln\{([InY^-]_e - [InY^-])/[InY^-]_e\} = \ln(1-f) = k_{obs}\cdot t \tag{2}$$

in which $[InY^-]_e$ means the concentration of In(III)-EDTA complex in equilibrium.

An example of the results is shown in Fig. 1. The apparent rate constant k_{obs} can be obtained as functions of EDTA and hydrogen ion concentrations. From Eq. (1) the rate constant k_{obs} is also expressed as

$$k_{obs} = [Y^{4-}]\{k_0 + \Sigma(k_n[H^+]^n/K_n)\}, \quad (3)$$

in which

$$K_n = [H^+]^n[Y^{4-}]/[H_nY^{(4-n)-}].$$

Since $[Y^{4-}]$ is determined on the basis of total EDTA concentration and dissociation constants K_n, dependence of the hydrogen ion concentration on the rate constant is observed by a plot of log $\{k_{obs}/[Y^{4-}]\}$ against pH. As is seen in Fig. 2, a straight line of the slope -2.83 was obtained. This means that the principal reaction of In^{3+} with EDTA is considered to be

$$In^{3+} + H_3Y^- \underset{}{\overset{k_3}{\rightleftharpoons}} \begin{cases} KnY^- + 3H^+ \\ \downarrow\uparrow \\ InHY + 2H^+ \end{cases} \quad (4)$$

The rate constant can be determined. Thus,

$$k_3 = (1.3\pm0.1) \times 10^5 \ mol^{-1}cm^3s^{-1} \ (25°C)$$

The present information is very important on the syntheses of carrier-free ^{111}In complexes. In addition, rate constant will be determined using carrier-free metal ion and chelating agent in low concentration, even in the system that formation rate is very rapid.

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Reference

1) Thakur, M. L., Int. J. Appl. Radiat. Isotopes, 28 (1977) 183.

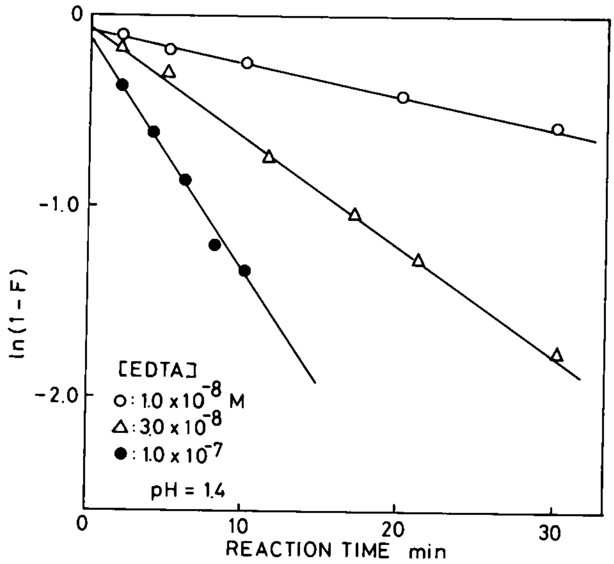

Fig. 1. ln(1-F) vs. reaction time.

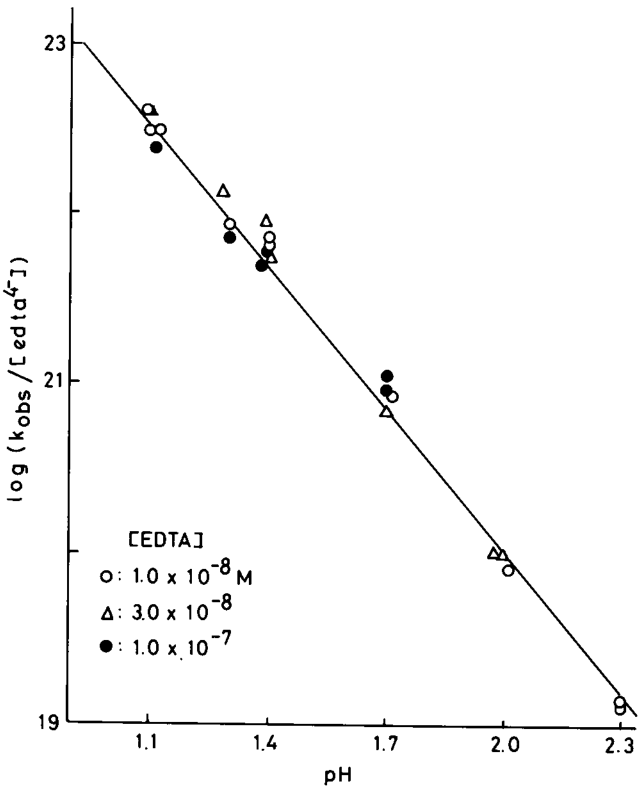

Fig. 2. Dependence of log(k_{obs}/[edta^{4-}]) on pH at 25°C.