

## 막여과지에 대한 이트륨-90의 흡착 반응속도에 관한 연구

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## Adsorption Kinetics of Carrier-Free Yttrium-90 on Membrane Filters

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**Abstract** The adsorption kinetics on a membrane filter have been studied by an introduction of acid or alkali in yttrium-90 solution. The change of the adsorption in the filtration process was determined by the filtrate activities with using a microsyringe filter holder connected with a syringe. The over all reaction rate obeyed a reversible first order reaction, and the rate constants thus obtained, showed the values of  $k_1=0.12 \text{ sec}^{-1}$  and  $k_1'=0.039 \text{ sec}^{-1}$ .

As a result of the present studies, it would be reasonable that the rate determining step of the adsorption reaction was the hydrolysis reaction of the adsorbed yttrium ions.

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### Introduction

Radiocolloidal properties of yttrium in solution was intensively studied by Kurbatovs<sup>1</sup>, Schweitzer and their co-workers<sup>2,3,4</sup>. Recent studies on carrier-free yttrium-90 with 450 m $\mu$  membrane filters by the author<sup>5,6</sup> revealed that yttrium-90 was not retained but adsorbed on the membrane filters, and was present in completely ionized form in solution. In the present studies, it is

intended to study the adsorption kinetics on membrane filters by an introduction of acid or alkali in yttrium-90 solution and to understand the state of yttrium in solution and adsorption. For an adsorption the reaction completed in a few minutes in filtration process, it is impossible to study an adsorption kinetics with an ordinary filter holder of suction type, but with a microsyringe filter holder of pressure type, it is expected that the experiment can be done successfully.

### Experimental

Materials, preparation of yttrium-90, and measurements of radioactivities have been described in the previous paper<sup>6</sup>. The pH of 12 ml. portion of yttrium-90 solution thus prepared was adjusted to a desired value and 2 ml. portion of 0.01 N hydrochloric acid was added into yttrium-90 solution. The time of the mixing was recorded simultaneously. After mixing quickly by inspiring and expiring the solution with a syringe for several seconds, 10 ml. portion of the solution was taken, and the syringe was connected to a micro-syringe filter holder (Cat. No. xx3002500, Millipore) attached with a 450 m $\mu$  membrane filter, then filtered with pressing the syringe. First 1 ml. portion of the filtrate was discarded to eliminate the adsorption of yttrium-90 on the filter holder. Approximately 1 ml. portion of each filtrate was collected in 5 ml. pyrex beaker with recording time in the each filtering step. With 0.500 ml. micropipet 0.500 ml. portion of the each filtrate was taken and its activity was measured.

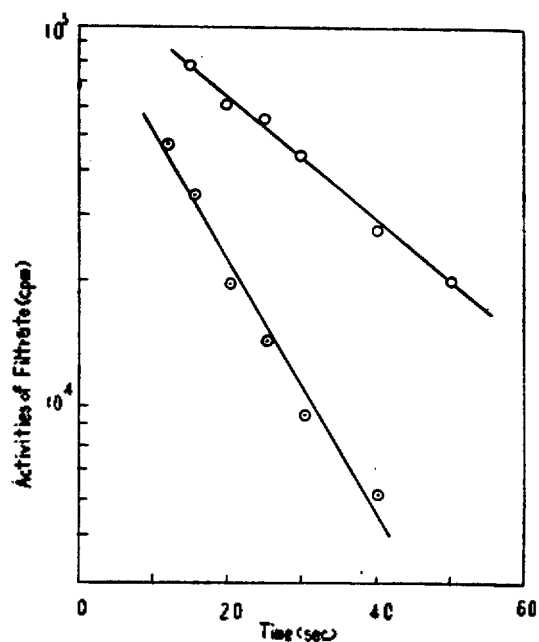
The activity of the adsorbed yttrium-90 ( $A_d$ ) could be calculated as

$$A_d = A_1 - A_2,$$

where  $A_1$  and  $A_2$  represent the activities of yttrium-90 solution before and after filtration.

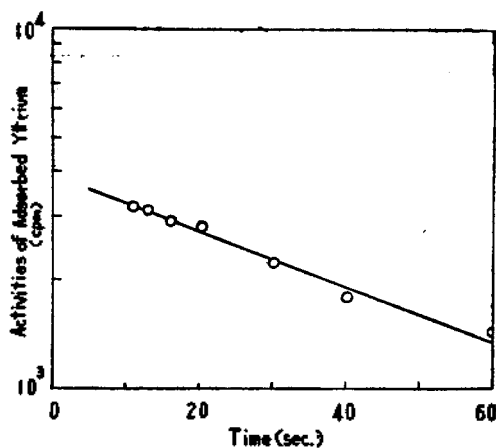
### Results and Discussion

The logarithms of filtrate activities (cpm/500 $\lambda$ ) of yttrium-90 on 450 m $\mu$  membrane filters with time are shown in *Figure 1* at yttrium concentration of  $9.8 \times 10^{-12}$  mole/l and  $1.6 \times 10^{-11}$  moles/l when 12 ml. portions of yttrium solution at a pH of 3.2 are mixed with 2 ml. portion of 0.01 N sodium hydroxide. As shown in *Figure 1*, logarithms of the filtrate activities show



*Figure 1.* Logarithm activities of yttrium in filtrate v. s. time at a pH of 3.2.

(○) yttrium concentration of  $9.8 \times 10^{-12}$  mole/l.  
(○) yttrium concentration of  $1.6 \times 10^{-11}$  mole/l.



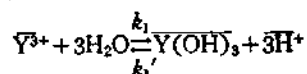
*Figure 2.* Logarithm activities of adsorbed yttrium v. s. time at a pH of 7.85 and yttrium concentration of  $4.2 \times 10^{-11}$  moles/l.

straight lines against time, but the slopes show different values with respect to the concentration of yttrium.

Figure 2 represents the logarithm of the adsorption activities (cpm/500 $\lambda$ ) of yttrium-90 with time at the concentration of  $4.2 \times 10^{-12}$  moles/l, when 10 ml. portion of the solution at a pH of 8.0 is mixed with 10 ml. portion of 0.01N hydrochloric acid. The slope shows also straight line, but it is much lower than the slopes of Figure 1. In each case of the adsorptions, the adsorption equilibriums are attained in a few minutes. Let us consider the adsorption reaction of yttrium on a membrane filter in filtration process by an introduction of acid or alkali. From the previous studies, the adsorbed state of yttrium exists mostly in  $Y(OH)_3$ , and the adsorption reaction can usually be broken into the following steps:

A) In the case of an introduction of alkali in the solution

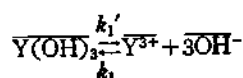
- (1) Diffusion of yttrium to a membrane filter  
 $Y^{3+}(\text{solution}) \rightarrow Y^{3+}(\text{membrane filter})$
- (2) Adsorption of yttrium at the surface  
 $Y^{3+}(\text{membrane filter}) \rightarrow \overline{Y^{3+}}(\text{adsorbed})$
- (3) Hydrolysis reaction on the surface



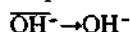
- (4) Desorption of adsorbed hydrogen ion  
 $\overline{H^+} \rightarrow H^+$
- (5) Combination of the hydrogen ion with the hydroxide ion in bulk solution  
 $H^+ + OH^-(\text{bulk}) \rightarrow H_2O$

B) In case of an introduction of alkali in the solution

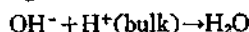
- (1) Diffusion of yttrium ion to a membrane filter in the solution  
 $Y^{3+}(\text{solution}) \rightarrow Y^{3+}(\text{membrane filter})$
- (2) Adsorption of  $Y(OH)_3$   
 $Y^3(\text{membrane filter}) + 3OH^- \rightarrow \overline{Y(OH)_3}$   
(adsorbed)
- (3) Dissociation of the adsorbed  $\overline{Y(OH)_3}$



- (4) Desorption of the hydroxide ion



- (5) Combination of the hydroxide ion with the hydrogen ion in bulk solution



These are consecutive steps and if any one is much slower than all the others, it will become rate-determining. Step (1) is usually rapid. Only with extremely rapid adsorption reaction might it determine the overall rate. Step(5) is the reaction of neutralization and it was known that the reaction is very rapid. Step (2) and (4) are generally more rapid than step(3). Therefore, it seems to be valid that step(3) would be rate-determining.

By an introduction of acid or alkali in the solution, the bulk solution could be neutralized rapidly with the reaction of  $H^+ + OH^- \rightarrow H_2O$ . In respective of rapid change of pH of the bulk solution, however, the pH of hydrated yttrium ion would not be neutralized like the bulk solution by the electrical attraction of yttrium ion. Consequently the pH around yttrium ion might not be changed rapidly. Then the adsorbed yttrium may be hydrolyzed slowly to  $Y(OH)_3$  or  $Y(OH)_3$  may be ionized to  $Y^{3+}$ . Assuming the hydrolysis obeys a first order reaction, the result is

$$[\overline{Y^{3+}}] = [\overline{Y^{3+}}]^0 e^{-k_1 t} \quad (1)$$

Where  $[\overline{Y^{3+}}]^0$  and  $[\overline{Y^{3+}}]$  represent the adsorbed yttrium ion concentration at time=0 and t. The adsorbed yttrium ion obeys Freundlich adsorption isotherm, then

$$[\overline{Y^{3+}}] = k[Y^{3+}]^{\frac{1}{2}} \quad (2)$$

Substituting equation(2) into(1), it is obtained that

$$\left\{ \frac{[Y^{3+}]}{[Y^{3+}]^0} \right\}^{\frac{1}{2}} = e^{-k_1 t} \quad (3)$$

Taking logarithm of equation (3), then

$$\ln[Y^{3+}] = \ln[Y^{3+}]^0 - nk_1 t \quad (4)$$

Representing yttrium ion in solution as  $A_s$ ,

$$[Y^{3+}] = A_s \text{ and } [Y^{3+}]^0 = A_s^0.$$

Then

$$\ln A_s = \ln A_s^0 - nk_1 t \quad (5)$$

Equation(5) shows that the rate constant of hydrolysis can be expressed actually as  $nk_1$  when the adsorbed yttrium concentration is replaced by the yttrium concentration in solution. Accordingly for a reversible first order

reaction of  $Y^{3+} + H_2O \xrightleftharpoons[k_1']{k_1} Y(OH)_3 + 3H^+$ , the reaction rate can be expressed as

$$\frac{dA_d}{dt} = nk_1(A_s^0 - A_d) - k_1' A_d \quad (6)$$

Integrating equation (6), the result is

$$nk_1 + k_1' = \frac{1}{t} \ln \frac{A_d^0}{A_d^0 - A_d} \quad (7)$$

where  $A_d^0$  is an equilibrium value of  $Y(OH)_3$ . From the relation of  $A_d^0 = A_s^0 - A_s^0$ , equation (7) becomes

$$(nk_1 + k_1')t = \ln(A_s^0 - A_s^0) - \ln(A_s - A_s^0). \quad (8)$$

$$\therefore \frac{k_s}{2.303t} = C - \log(A_s - A_s^0), \quad (9)$$

where  $k_s = nk_1 + k_1'$ .

The curves of Figure 3 are obtained from the values of  $A_s$  in Figure 1 by subtracting equilibrium values of  $A_s^0$ . The curves of Figure 3 show also straight line and over all rate constant  $k_s$  obtained from the slopes of the curve shows a value of  $0.20 \text{ sec}^{-1}$ .

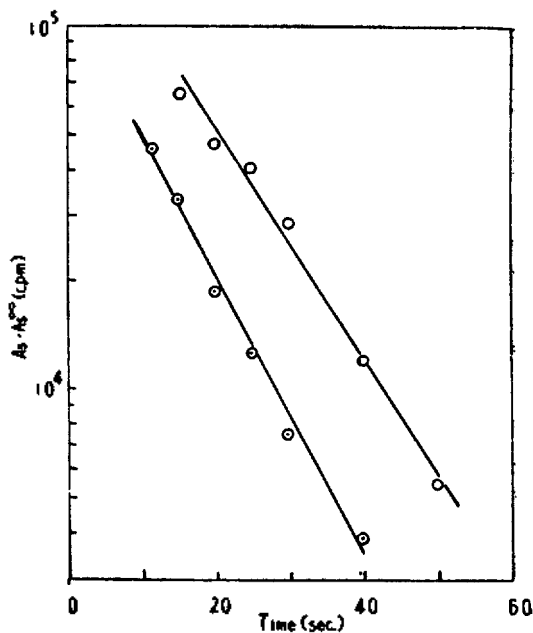


Figure 3.  $\log(A_s - A_s^0)$  v. s. time at a pH of 3.2.  
 (⊙) yttrium concentration  $9.8 \times 10^{-12}$  moles/l.  
 (○) yttrium concentration of  $1.6 \times 10^{-11}$  moles/l.

As shown in Figure 2 the reaction of the dehydrolysis is much slower than the reaction of hydrolysis. Hence, it can be neglected to take into consideration of reverse reaction, and dehydrolysis of adsorbed  $Y(OH)_3$  obeys a first order reaction, then

$$[Y(OH)_3] = [Y(OH)_3]^0 e^{-k_1' t} \quad (10)$$

$$\therefore \log A_d = C - \frac{k_1'}{2.303} t \quad (11)$$

The value of  $k_1'$  obtained from the slope of the curve shows  $0.039 \text{ sec}^{-1}$ .

Then from  $k_s = nk_1 + k_1'$ ,

$$k_1 = \frac{k_s - k_1'}{n} = \frac{0.20 - 0.039}{1.35} = 0.12 (\text{sec}^{-1}),$$

where  $n$  value is obtained from the previous paper.

### Summary

It appears that a micro-syringe filter holder of pressure type is very useful to study adsorption kination in a filtration process, when an adsorption equilibrium is attained rapidly in a few minutes. The rate determining step of the adsorption of yttrium on a membrane filter seems to be the hydrolysis reaction of yttrium ion, and the reaction obeys a first reversible reaction. The rate constant thus obtained, are  $k_1=0.12 \text{ sec}^{-1}$  and  $k_1'=0.039 \text{ sec}^{-1}$ .

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