

막여과지에 의한 무단체 Ag-111에 관한 연구

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Studies on Carrier-Free Silver-111 with Membrane Filters

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요 약. 무단체 Ag-111의 상태를 여과법에 의하여 연구하였다. 이 연구는 막여과지에 의하여 수용액에 있어서 Ag-111의 pH 및 농도변화에 대한 효과를 조사하였다.

이 연구결과 막여과지에 대한 Ag-111의 부착은 Freundlich 흡착 등온식에 따르고 Ag-111의 흡착 상태는 AgOH 형태로 존재하며 높은 pH에서 흡착성이 없는 $\text{Ag}(\text{OH})_2^-$ 는 Ag의 흡착을 방해하는 것으로 생각된다. 또한 무단체 Ag-111는 수용액중에서 Ag^+ 상태로 존재하고 있다.

Abstract. The state of carrier-free silver-111 has been studied by applying filtration method. The studies involved that the effects of pH and concentration of silver-111 in aqueous solution have been determined with membrane filters.

The present studies revealed that the retainment of silver-111 on membrane filters followed Freundlich adsorption isotherm, and the adsorbed state of silver-111 was present in the form of AgOH. Also it was supposed that the formation of the non-adsorbed hydroxide of $\text{Ag}(\text{OH})_2^-$ may prohibit the existence of AgOH at higher pH, and it seems to be valid that the carrier-free silver-111 in aqueous solution exists in Ag^+ state.

Introduction

The nature of radiocolloids¹, i.e. the state of microquantity of radioelements, was not yet completely elucidated. However, the studies on carrier-free yttrium-90 with membrane filters by the author^{2,3} revealed that the abnormality of the extremely dilute solution was not due to the characteristic of a carrier-free radioisotope but to adsorption phenomena in filtration pro-

cess.

In present studies it is attempted to examine whether the above viewpoint is valid or not with silver-111 which is a chemically simpler radioisotope than yttrium-90.

The radiocolloidal properties of silver was studied by Schweitzer⁴ and his co-workers. The studies involved the effects of coagulation time, pH, method of removal and the presence of non-aqueous solvents on the formation of radiocolloidal silver-111 with the method of

filtration and ultracentrifugation.

It is expected to obtain more quantitative results with membrane filters for the studies because of the constant area and uniform pore size of the filters, and also it is intended to show the identity of the adsorption mechanism of silver-111 with that of yttrium-90 on the filters.

Experimental

Material. All inactive chemicals used were of analytical reagent quality, and all water was doubly distilled. Carbonate-free sodium hydroxide solution was prepared as described in the previous paper.²

Measurement of Radioactivity. Measurements of the radioactivities of samples were made with a conventional Geiger counting apparatus. All radioactivities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

Preparation of Silver-111.^{4,5} One gram of palladium has been bombarded in a flux of 10^{12} neutron/cm²-sec of TRIGA Mark II reactor for a month. This contained approximately one millicurie of silver-111, a radioisotope of half-life 7.5 days emitting a 1.0 Mev. beta. The irradiated palladium was dissolved in aqua-regia, evaporated to dryness, and dissolved in 10 N hydrochloric acid. Then the solution was passed through anion exchange resin (Dowex 1 X-8). Palladium chloride complex thus formed was adsorbed on the resin, and silver complex was eluted. The elute was evaporated to dryness and 5 ml. of 4 N nitric acid were added to the product. The obtained silver-111 was purified by adding conc. sodium hydroxide solution and the solution was filtered through small glass frit with the aid of suction. The frit was then washed with a small amount of distilled water to remove the excess solution. The filtrate and

wash solution were discarded. Several ml. of 0.01 N nitric acid was slowly pulled through the frit, and diluted to 200 ml. with 0.01 N nitric acid. This solution was then used as a stock solution.

Preparation of Samples. The silver-111 solution in 0.01 N nitric acid was diluted to a desired concentration with 0.01 N nitric acid and then the pH of 50 ml. of the resulting solution was adjusted to a value of 10 with dilute carbonate-free sodium hydroxide solution. All pH measurements were made with a Coleman model 39 pH meter. Then the solution was divided 5 ml. portions in 10 ml. pyrex beakers. A pH of each divided solution was adjusted further to a desired pH with 0.1 N nitric acid containing the same concentration of silver-111 as the bulk solution to keep the same concentration in each sample solution. The solutions were then allowed to stand for an hour to reach equilibrium. A membrane filter (HA Type, Millipore) was attached to a micro-syringe filter holder (Cat. N. xx 3002500, Millipore). The solution was filtered through the membrane filter with pressing the syringe. By the measurement of the filtrate activity, the percent silver-111 removed could be calculated as described in the previous report².

Results and Discussion

The retainment percentages of silver-111 on 450 m μ membrane filters at several pH are shown in *Figure 1*. The curves in *Figure 1* show the results at various silver-111 concentration of 8.6×10^{-11} , 2.7×10^{-10} , 1.5×10^{-9} moles/l respectively. The dependence of the retainment percentages against pH are not sharp, compared with the case of yttrium-90 retainment. However, at a higher value of pH the retainments were increased gradually. Also

at lower concentrations of silver solution, the retainments show higher values as same as the case of yttrium-90.

Logarithm of the filtrate concentrations against logarithm of the retainment at given values of pH are shown in Figure 2, and the curves show straight lines at given values of pH. This relations represent that Freundlich adsorption isotherm is held in the retainments of silver-111 on membrane filters. This means

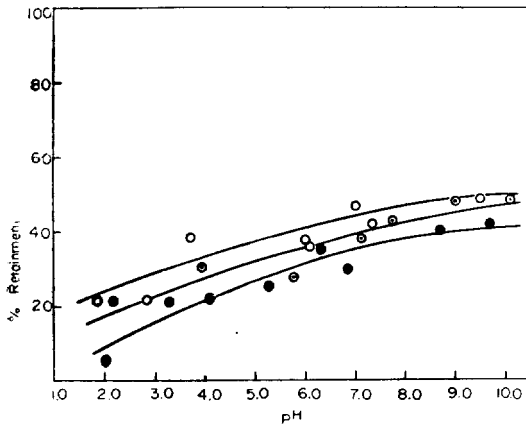


Fig. 1. Percent silver-111 retained on 450 m μ membrane filters versus pH at silver concentrations of 8.6×10^{-11} (○); 2.7×10^{-10} (◐); 1.5×10^{-9} moles/l (●)

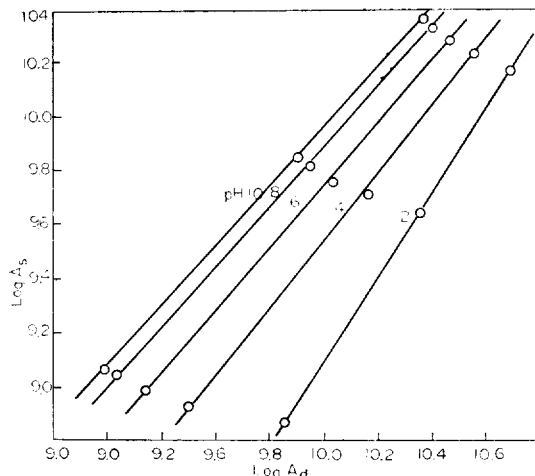


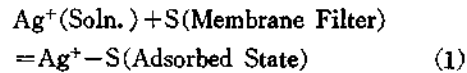
Fig. 2. Silver-111 concentrations of filtrates (A_s) v. s. silver-111 concentrations adsorbed (A_d) at various pH.

that the retainments are adsorption phenomena.

The variation of the slope n of Freundlich adsorption isotherm is shown in Figure 3. From the curve of Figure 3, it can be seen that n values depend sharply on pH values compared with the case of yttrium-90, and always show lower values than the case of yttrium-90. This shows that the dependence of membrane adsorption of silver-III on the concentration is less than that of yttrium-90 in the adsorption on membrane filters.

In order to explain the adsorption phenomena of silver-111, it is assumed that the state of silver-111 in aqueous solution were present in completely ionized form i. e., Ag^+ form, and Ag^+ is adsorbed primary on membrane filters in filtration process. Also it is thought that the adsorbed Ag^+ are in equilibrium with Ag^+ in solution.

That is,



Then the adsorbed Ag^+ would be stabilized

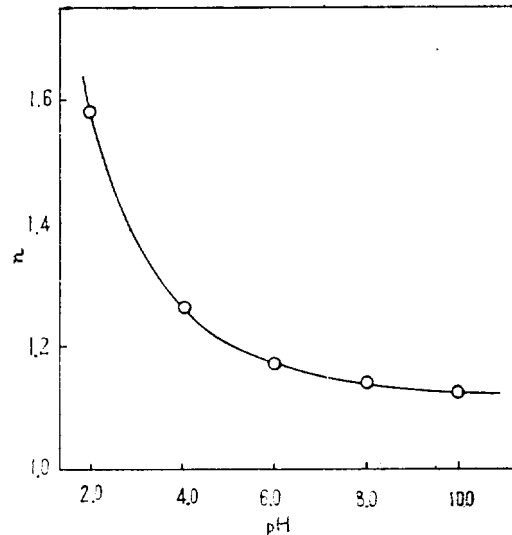
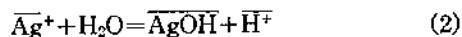


Fig. 3. Variation of n values of Freundlich adsorption isotherm versus pH for silver-111.

by the emission of hydrogen ion.



Where upper lines on chemical symbols represent the adsorbed states.

The first hydrolysis constant of silver ion in the adsorbed state can be obtained as

$$K_{h1} = \frac{[\overline{\text{AgOH}}][\overline{\text{H}^+}]}{[\overline{\text{Ag}^+}]} \quad (3)$$

Total concentration of silver in the adsorbed state (Ad) should be the sum of the concentration in the ionic and hydroxide state.

$$Ad = [\overline{\text{Ag}^+}] + [\overline{\text{AgOH}}] \quad (4)$$

From equation (3), equation (4) becomes

$$Ad = [\overline{\text{Ag}^+}] \left\{ 1 + \frac{K_{h1}}{[\overline{\text{H}^+}]} \right\} \quad (5)$$

According to Freundlich adsorption isotherm, the adsorbed state of silver ion is related with the filtrate silver ion in the form

$$[\overline{\text{Ag}^+}] = k[\text{Ag}^+]^{\frac{1}{n}} = k(As)^{\frac{1}{n}} \quad (6)$$

Where n and k represent the constants of Freundlich adsorption isotherm, and (As) represents the concentration of silver in the filtrate. When equation (6) is substituted in equation (5), it is obtained that

$$Ad = k As^{\frac{1}{n}} \left\{ 1 + \frac{K_{h1}}{[\overline{\text{H}^+}]} \right\} \quad (7)$$

Because the hydrogen ion concentration in the adsorbed state is proportional to the hydrogen ion concentration in solution, then

$$\begin{aligned} Ad &= k As^{\frac{1}{n}} \left\{ 1 + \frac{K_{h1}\alpha}{[\text{H}^+]} \right\} \\ &= k As^{\frac{1}{n}} \left\{ 1 + \frac{K'_{h1}}{[\text{H}^+]} \right\} \end{aligned}$$

Where $K_{h1}\alpha = K'_{h1}$.

Let us take the logarithm of equation (8)

and plot $(\frac{1}{n} \log As - \log Ad)$ against pH. Then in the condition of $(\overline{\text{Ag}^+}) \ll (\overline{\text{AgOH}})$, the curve should be straight and the slope has to be the value of -1 .

Experimentally obtained curve of $(\frac{1}{n} \log As - \log Ad)$ against pH is shown in Figure 4. The slope of curve shows a value of -1 at pH of 2.0~4.0, then increase gradually by the increment of pH, and approach to zero value at still higher pH. The result shows that the adsorbed state of AgOH would be transformed to silver di-hydroxide ion by the decrease of hydrogen ion, and it would desorb to the solution as Ag^+ state.

That is,

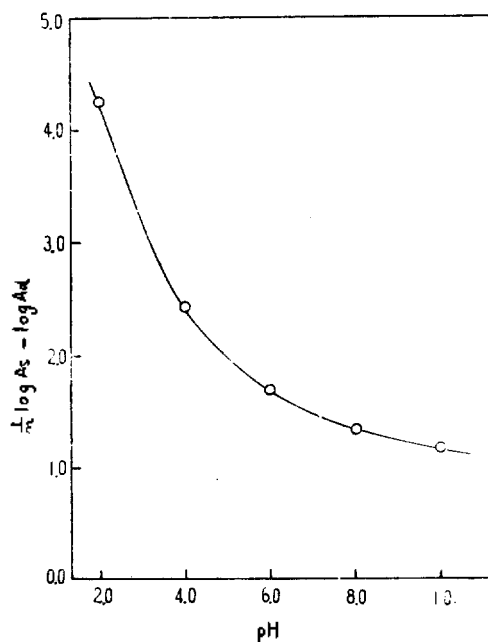
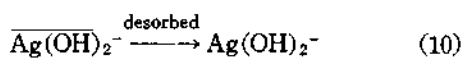
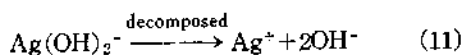


Fig. 4. Change of the value of $(\frac{1}{n} \log As - \log Ad)$ versus pH.



and secondary hydrolysis constant is

$$\overline{K}_{h2} = \frac{[\overline{\text{Ag}(\text{OH})_2^-}][\overline{\text{H}^+}]}{[\overline{\text{AgOH}}]} \quad (12)$$

The concentration of $\overline{\text{Ag}(\text{OH})_2^-}$, assuming to exist 100 % adsorbed state, can be expressed from equation (3) and (12) in the form

$$\begin{aligned} \overline{[\text{Ag}(\text{OH})_2^-]} &= \frac{K_{h2}[\overline{\text{AgOH}}]}{[\overline{\text{H}^+}]} = \frac{K_{h1}K_{h2}[\overline{\text{Ag}^+}]}{[\overline{\text{H}^+}]} \\ &= \frac{K_{h1}'K_{h2}'[\overline{\text{Ag}^+}]}{[\overline{\text{H}^+}]^2} \end{aligned} \quad (13)$$

Therefore, total adsorbed state of silver can be represented by

$$\text{Ad} = [\overline{\text{Ag}^+}] + [\overline{\text{AgOH}}] - [\overline{\text{Ag}(\text{OH})_2^-}] \quad (14)$$

$$\therefore \text{Ad} = k\text{As}^{\frac{1}{2}} \left\{ 1 + \frac{K_{h1}'}{[\overline{\text{H}^+}]} - \frac{K_{h1}'K_{h2}'}{[\overline{\text{H}^+}]^2} \right\} \quad (15)$$

From the curve of *Figure 4*, the condition of $[\overline{\text{Ag}^+}] \ll [\overline{\text{AgOH}}]$ was attained. Therefore equation (15) can be written as

$$\text{Ad} \cong k\text{As}^{\frac{1}{2}} \frac{K_{h1}}{[\overline{\text{H}^+}]} \left\{ 1 - \frac{K_{h2}'}{[\overline{\text{H}^+}]} \right\} \quad (16)$$

Taking logarithm of equation (16), the result is

$$\begin{aligned} \log \text{Ad} - \frac{1}{n} \log \text{As} \\ = \log kK_{h1}' + \text{pH} + \log \left(1 - \frac{K_{h2}'}{[\overline{\text{H}^+}]} \right) \end{aligned} \quad (17)$$

$$\begin{aligned} \text{Assuming } K_{h2}'/[\overline{\text{H}^+}] \ll 1, \log \left(1 - \frac{K_{h2}'}{[\overline{\text{H}^+}]} \right) \\ \cong - \frac{K_{h2}'}{[\overline{\text{H}^+}]} \end{aligned}$$

Then

$$\frac{1}{n} \log \text{As} - \log \text{Ad} + C = -\text{pH} + K_{h2}'10^{\text{pH}} \quad (18)$$

Differentiating equation (19) with pH,

$$\begin{aligned} \frac{d \left(\frac{1}{n} \log \text{As} - \log \text{Ad} \right)}{d\text{pH}} \\ = -1 + K_{h2}'10^{\text{pH}} \log e \end{aligned} \quad (19)$$

According to equation (19), it could be reasonably explained that the slope in the curve of *Figure 4* increase at higher pH.

From the above discussion, it was concluded that the carrier-free silver-111 in aqueous solution is regarded to exist in Ag^+ state, as the same as the state of carrier-free yttrium-90 reported in the previous paper.^{2,3}

Also it seems to be valid that the adsorbed state of silver-111 on membrane filters in the filtration process, exists in AgOH throughout all range of pH, but at higher pH AgOH forms $\text{Ag}(\text{OH})_2^-$, and $\text{Ag}(\text{OH})_2^-$ is desorbed to decompose into Ag^+ and OH^- .

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