Studies on Carrier-Free Yttrium-90 with Membrane Filters

by

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막여과지에 의한 무단체 이트룸-90에 관한 연구

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ABSTRACT

The state of carrier-free yttrium-90 has been studied by filtration method with membrane filters. The studies include the adsorption ratio of carrier-free yttrium-90 on membrane filters by the change of PH, concentration of yttrium-90, and the pore size of membrane filters. The adsorption followed to Freundlich adsorption isotherm. The adsorption mechanism was proposed by the adsorption of transient state as an ionic form of Y^{3+}, and the experimental results were explained satisfactorily by the proposal. The adsorbed state of yttrium was present in the forms of yttrium such as Y^{3+}, $Y(OH)^{3+}$, $Y(OH)^{2+}$, $Y(OH)^{+}$, and $Y(OH)_3$, and the existing ratios of the forms of yttrium were sharply changed by PH. It seems to be valid tha the carrier-free yttrium-90 exists mostly in Y^{3+} state.

I Introduction

After the discovery of radiocolloids by Pan-eth[1,2,3] in 1912, many researches[4-15] on radiocolloids have been carried out, but the nature of radiocolloids, i. e. the state of

microquantity of radioelements has not been understood completely yet.

A study of the state of radioelements is one of the mein problem of radiochemistry and serves as a clue to the solution of various important problems in this field[4,5,6,15] such as analytical procedures, decontamination of radioistopes, biological problems, and isotope applications.

In spite of the enormous significance of the study of the state of radioelements, the accomplishment of such investigations is hindered by the absence of direct methods of studying the state of radioelements of extremely small dimensions.

The state of yttrium in solution was investigated by Kurbatovs[16] and by Schweitzer and his coworkers[17,18,19]. Kurbatovs investigated the PH dependence of the amount of yttrium-86 retained on paper filters. Schweitzer and his coworkers have done more detailed studies on yttrium in solution with the methods of filtration, centrifugation, and solvent extraction with yttrium-90.

The present investigation was planned to study the state of carrierfree yttrium-90 in filtration process with membrane filters (Type HA Millipore Filters). This type of the filters [20-23] is effectively impermeable to particles of colloidal size, and by the constant area and uniform pore size of the filters, it would be expected to obtain more quantitative results and to understand deeply the state of microquantity in solution.

As an example of microquantity state, carrier-free yttrium-90 was used because yttrium-90 can be prepared easily from strontium-90 and also it is convenient to manipulate the isotope because of its short half life of 64 hours.

From the above studies, the author intended to understand the adsoption mechanism of yttrium, and the state of yttrium in solution.

2 Experimental

1. Materials

All the inactive chemicals employed were of analytical reagent grade. Doubly distilled water was used.

2. Measurement of Radioactivity

Radioactivities were measured with a decade scaler (RCL Mode120302) connected with Nuclear Chicago end-window G-M counter. To protect the β-rays from both scattered radiation and strontium-90 which may remain in sample, 56 mg/cm aluminum absorber was placed just under the G-M counter. Counting time was adjusted to minimize the standard deviation less than one percent.

3. Separation of Yttrium-90

Yttrium-90 was separated by Schweitzer's method[19]. Out of 5 mc/ml of strontium-90 purchased from Radiochemical Center, England, approximately 1 mc of the radioactive solution was taken, then 5 ml of concentrated hydrochloric acid and 25 ml of distilled water were added. The PH of the resulting solution was adjusted to 12 with concentrated sodium hydroxide and filtered slowly through a small fine glass frit. The frit was then washed with 1 N sodium hydroxide and washed again with more dilute sodium hydroxide solution of PH of 9.0. One-hundredth N hydrochloric acid was then slowly passed through the glass frit. In order to eliminate a possibility of the presence of any trace quantity of strontium-90 in the filtrate, the procedure mentioned above was repeated. The resulting filtrate was shown to contain only yttrium-90 as evidenced by a half-life determination and absorption measurements.

4. Method of a Removal of Carbonates in Sodium Hydroxide

· About 50 ml of anion exchange resin Amberite IR-400 (60 mesh) were put into a column of 20 cm diameter to a height of 35 cm and 1 M sodium hydroxide solution was poured. To change the resin from hydroxide to chloride form, 0.1 M sodium chloride solution was poured in the column. Eluate solution used was a dilute sodium hydroxide solution because carbonate was adsorbed in the resin. Thus, we were able to obtain pure carbonate-free sodium hydroxide solution.

5. Sample Preparation

The solution of yttrium-90 in 0.01 N hydrochloric acid prepared by the procedure mentioned above was diluted to a desired concentration with 0.01 N hydrochloric acid. Then the PH of solution was adjusted to a value of 6 with dilute carbonate free hydroxide solution. Several 5 ml portions of the resulting solution were placed in 10 ml beakers with 5 ml pipette. A PH of each divided solutions was adjusted further to a desired PH by 0.01 N hydrochloric acid solution containing the same activity of yttrium-90 as the bulk solution.

All the PH measurements were made with a PH meter attached with a combined glass electrode (Analytical Measurements, Summit, New Jersey). The solutions were allowed to stand for an hour to reach equilibrium. A 0. 100 ml to 0.500 ml portion of the bulk solution was taken with a micropipette depending on the activity of yttrium-90, was placed on a I inch aluminum planchet, and dried under an infrared lamp.

Its radioactivity was then determined. A membrane filter (HA Type, Millipore) was attached to micro-syringe filter holder (Cat. No. XX30025 00, Millipore). After measurments of a PH of the solutions of yttrium-90 again, each solution was inspired to 10 ml injector and the injector was connected to the filter. Then the solution
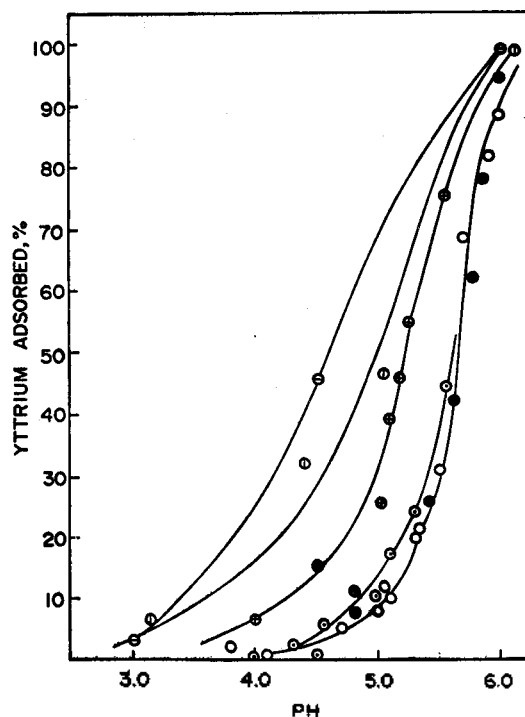
Fg1. 1 Percent yttrium adsorbed on 450 mμ membrane filters versus PH at yttrium concentatrions of 2.3×10^{-12} M($\oslash$); 9.4×10^{-12} M($\ominus$) 3.6×10^{-12} M($\oplus$); 2.1×10^{-11} M($\odot$); 3.8×10^{-11}M($\bigcirc$); 7.6×10^{-11}M($\bullet$)

was filtered through the membrane filter with pressure. Approximately 1 ml of first filterate was discarded, and the remaining filtrate was sampled. The 0.100 ml to 0.500 ml portion of the samples depending on their activity, was placed on a aluminum planchet, dried, and its radioactivity was measured. The concentration of yttrium-90 was calculated by measuring a counting efficency of strontium-90. From the activities of the samples of the bulk solution and filtrats, the percentage yttrium removed was calculated.

3 Results and Discussion

The adsorption percentage of yttrium-90 on 450 mμ membrane fiiters was measured at various yttrium concentration and at several PH. The results obtained at 15°C are shown in the
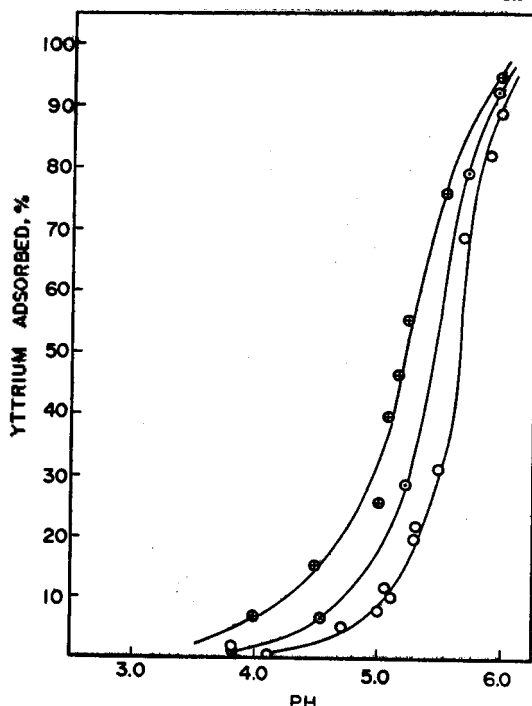
Fig. 2 Percent yttrium adsorbed on 450 mμ membrane filters at yttrium concentrations of 3.6×10⁻¹²M (⊕); 3.6×10⁻¹¹M(○); and 50mμ membrane filters at yttrium concentration of 3.8×10⁻¹¹M (◉)

curves of Figure I at yttrium concentration of 2.4×10^{-12}, 9.40×10^{-12}, 3.6×10^{-12}, 2.1×10^{-11}, 3.8×10^{-11}, and 7.6×10^{-11} moles/l respectively. The adsorption percentage of yttrium shows higher value at dilute solution than at concentrated solution over all ranges of PH. The difference of the adsorption percentage are narrower under a PH of 4 and over a PH of 6. The adsorption percentage on 50 mμ and 450 mμ at a given concentration is shown in Figure 2. The 50 mμ membrane filters adsorb slightly more yttrium-90 than 450 mμ filters nearly same concentration of yttrium-90 (3.6 – 3.8×10^{-11} moles/1), but the adsorption percentage on 450 mμ membrane filters in the concentration of 3.6×10^{-12} moles/1 shows higher values than the adsorption on 50 mμ filters at same PH. If yttrium-90 were retained simply on filters as radiocelloidal aggregates, the re-

sults of Figure 1 and Figure 2 can be hardly explained, because it would not be expected that there exist larger colloidal aggregates at low concentration than at high concentration. Hence, it would be valid that yttrium-90 is not retained simply but adsorbed on the filters. Slightly higher adsorption of yttrium on 50 mμ filters at same concentration can be explained by the fact that 50 mμ membrane filter contains larger surface area than 450 mμ filter. Schweitzer[24] pointed out that hardened papers retained slightly more radioelements than others of the same relative grade, but in all types the amount appeared to be function of the porosity, the more porous papers retaining less activity. Then it was insisted that adsorption is not the principal factor because the papers probably is covered with the largest areas.

But it was supposed that the retaining percentage of radioelements depends not only on the porosity of filters i.e., the surface area of filters, but also the pore size of filters. During filtration larger pore size filters would retain radioelements less than smaller pore size filters, because adsorption equilibrium was not attained during filtration. Hence, large portions of the radioelement passed through the filters without any interaction with the filter surface. The changes of adsorption percentage of 450 mμ membrane filtrats during successive filtering steps were examined. Ten ml of the yttrium solution was filtered with 450 mμ membrane filter at a PH of 5. From the First 0.5 ml portion of the filtrate, 100λ of a sample was taken and its radioactivity was measured.

In second, third, and fourth step, 5 ml, 2.5 ml and 1.5 ml of the filtrate was discarded respectively. Waiting for 5 minutes in each step, the same process as the first step were repeated. The adsorption percentage was 45% at first step and thereafter the adsorption percentage kept

a constant value of $31 \pm 1\%$. From the above results, the retainment of yttrium on filters would be an adsorption phenomena.
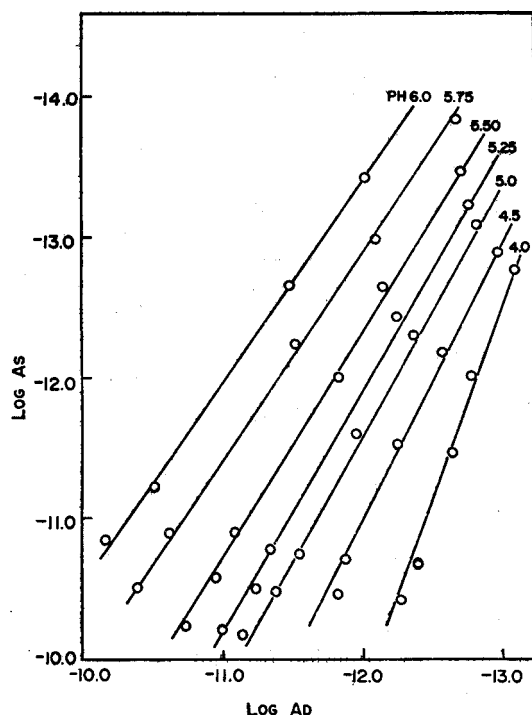

Fig. 3 Yttrium concentration of filtrate (As) versus yttrium concentrations adserbed (Ad) on 450 mμ membrane filters at various PH.

Adsorptions of yttrium on 450 mμ membrane filters against the filtrate concentrations at various PH were shown in Figure 3.

Logarithm of the filtrate concentration against logarithm of the adsorbed yttrium concentration shows straight line at a given hydrogen ion concentration. The relationships show that Freundlich adsorption isotherm can be applicable for the adsorption of yttrium-90 on the filters.

The variation of the slope n of Freundlich isotherm is presented in Figure 4. For lower PH the slope is increased. The increase of n

value meens that the adsorption becomes to saturation by increasing hydrogen ion concentration, and the adsorption does not depend on the filtrate concentration of yttrium. Also
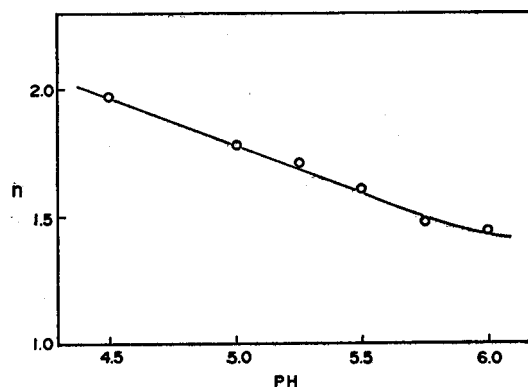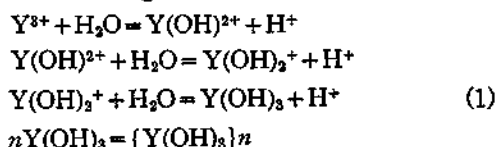

Fig. 4 Variation of nvalues of Freundlich isotherm versus PH at yttrium adsorption on 450 mμ membranefilters.

it can be seen from the curves of Figure 3 that the value of $\underline{k}$ of Freundlich isotherm is sharply dependent on the cocentration of hydrogen ion. This means that the adsorption is largely related with the state of yttrium in solution. However, the most difficult problem on the state of microquantity in solution is the identification of the chemical species of radioelements.

Compounds of radioelements in the hydrolysis region have received extremely little study as a result of the great experimental difficulties in carrying out such experiments. From the existing experimental method[25] it was found that there exist the following forms in solution: colloidal, molecular, ionic, and complex form. The coincidence of the values of the solubility products[26] of micro and macro quantities of the hydroxide indicates that the law of mass action is applicable at any concentration of the

substance, all the way down to the very samllest. when the law of mass action is applied to the solution of carrier-free yttrium-90, the hydrolysis of yttrium ion can be expressed in the following forms at an acidic condition.
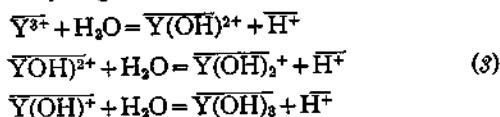
$$Y^{3+} + H_2O = Y(OH)^{2+} + H^+$$
$$Y(OH)^{2+} + H_2O = Y(OH)_2^+ + H^+$$
$$Y(OH)_2^+ + H_2O = Y(OH)_3 + H^+ \qquad (1)$$
$$nY(OH)_3 = \{Y(OH)_3\}n$$

In the concentration of tracer level, the existance of its aggregates may be neglected. Now let us consider about the adsorption mechanism of yttrium. It is assumed that the adsorption of yttrium were in an ionic form of Y^{3+}. Then transient state of the adsorbed ion becomes to equilibrium by the successive emission of hydrogen ion from the hydrated yttrium ion. Then the adsorbed Y^{3+} ion would attain to equilibrum with Y^{3+} ion in solution. The state of yttrium can be expressed in the type of reaction

$$Y^{3+} + S(\text{Membrane Filter}) = Y^{3+} - S(\text{Transient State of Absorbed } Y^{3+}) \qquad (2)$$
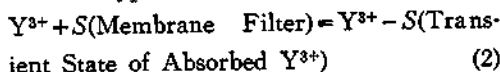
(Hereafter absorbed state is upperlined on chemical symbol such as $\overline{Y}$.)

The transient state of the adsorbed ion would emit hydrogen ion successively as follows.

$$\overline{Y^{3+}} + H_2O = \overline{Y(OH)^{2+}} + \overline{H^+}$$
$$\overline{Y(OH)^{2+}} + H_2O = \overline{Y(OH)_2^+} + \overline{H^+} \qquad (3)$$
$$\overline{Y(OH)^+} + H_2O = \overline{Y(OH)_3} + \overline{H^+}$$

It is assumed that the adsorption equilibium attained with the filtrate. Then according to Freundlich isotherm, it is obtained that

$$[\overline{Y^{3+}}] = k[Y^{3+}]^{\frac{1}{n}} \qquad (4)$$

The hydrolysis constant of yttrium in the adsorbed state can be written in the form

$$\overline{K}_{A1} = \frac{[\overline{Y(OH)^{2+}}][\overline{H^+}]}{[\overline{Y^{3+}}]}$$

$$\overline{K}_{A2} = \frac{[\overline{Y(OH)_2^+}][\overline{H^+}]}{[\overline{Y(OH)^{2+}}]} \qquad (5)$$

$$\overline{K}_{A3} = \frac{[\overline{Y(OH)_3}][\overline{H^+}]}{[\overline{Y(OH)^+}]}$$

Where the concentration of adsorbed chemical species on the filters are represented as adsorbed moles per unit area.

Total concentration of yttrium in the adsorbed state (Ad) is the sum of the concentration of the ionic and hydroxide state. Hence,

$$Ad = [\overline{Y^{3+}}] + [\overline{Y(OH)^{2+}}] + [\overline{Y(OH)_2^+}] + [\overline{Y(OH)_3}] \qquad (6)$$

From equation (5) it can be obtained that

$$[\overline{Y(OH)_3}] = \frac{[\overline{Y^{3+}}]\overline{K}_{A1}\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^3}$$

$$[\overline{Y(OH)_2^+}] = \frac{[\overline{Y^3}]\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^2} \qquad (7)$$

$$[\overline{Y(OH)^{2+}}] = \frac{[\overline{Y^{3+}}]\overline{K}_{A3}}{[\overline{H^+}]}$$

Substituting equation (7) into equation (6), it is obtained that

$$Ad = [\overline{Y^{3+}}]\left\{ \frac{\overline{K}_{A1}\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^3} + \frac{\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^2} + \frac{\overline{K}_{A3}}{[\overline{H^+}]} + 1 \right\} \qquad (8)$$

Taking $[Y^{3+}] = As$ (yttrium concentration of the filttrate), equation (8) can be written in the form.

$$Ad = kAs^{\frac{1}{n}}\left\{ \frac{\overline{K}_{A1}\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^3} + \frac{\overline{K}_{A2}\overline{K}_{A3}}{[\overline{H^+}]^2} + \frac{\overline{K}_{A3}}{[\overline{H^+}]} + 1 \right\} \qquad (9)$$

It was found that hydrogen ion was scarcely absorbed on the filters judging from the fact that no change of PH was observed during filtration. Therfore, hydrogen ion concentration absorbed on the filters would be much lower than the hydrogen ion concentration in solution.

That is, $\qquad [H^+] \rangle\rangle [\overline{H^+}]$

Then $\qquad [H^+] = \alpha[\overline{H^+}] \qquad (10)$

Where $\qquad \alpha \rangle\rangle 1$

Let us put equation (10) into equation (9), then it is obtained that

$$Ad = kAs^{\frac{1}{n}}\left\{ \frac{\overline{K}_{A1}\overline{K}_{A2}\overline{K}_{A3}\alpha^3}{[H^+]^3} + \frac{\overline{K}_{A2}\overline{K}_{A3}\alpha^2}{[H^+]^2} + \frac{\overline{K}_{A3}\alpha}{[H^+]} + 1 \right\} \qquad (11)$$

Putting $\overline{K}_{A1}\alpha = K_{A1}'$, equation (11) becomes to

$$Ad = kAs^{\frac{1}{n}}\left\{ \frac{K_{A1}'K_{A2}'K_{A3}'}{[H^+]^3} + \frac{K_{A2}'K_{A3}'}{[H^+]^2} + \frac{K_{A3}'}{[H^+]^2} + 1 \right\}$$ (12)

In advance to examine the validity of equation (9), the possibilities of the another types of the transient states of yttrium such as $Y(OH)^{2+}$, $Y(OH)^{2+}$ and $Y(OH)^3$ must be considered. Applying the same procedures as the transient state of Y^{3+}, the result for the transient state of $Y(OH)^{2+}$ gives

$$Ad = kAs^{\frac{1}{n}}\left\{ \frac{K_{A2}'K_{A3}'}{[H^+]^2} + \frac{K_{A3}'}{[H^+]} + 1 + \frac{[H^+]}{K_{A1}'} \right\}$$ (13)

Similarly the result for $Y(OH)_2^+$ gives

$$Ad = kAs^{\frac{1}{n}}\left\{ \frac{K_{A3}'}{[H^+]} + 1 + \frac{[H^+]}{K_{A3}'} + \frac{[H^+]^2}{K_{A1}'K_{A2}'} \right\}$$ (14)

Finally the result for $Y(OH)_3$ is obtained as follows.

$$Ad = kAs^{\frac{1}{n}}\left\{ 1 + \frac{[H^+]}{K_{A3}'} + \frac{[H^+]^2}{K_{A2}'K_{A3}'} + \frac{[H^+]^3}{K_{A1}'K_{A2}'K_{A3}'} \right\}$$ (15)
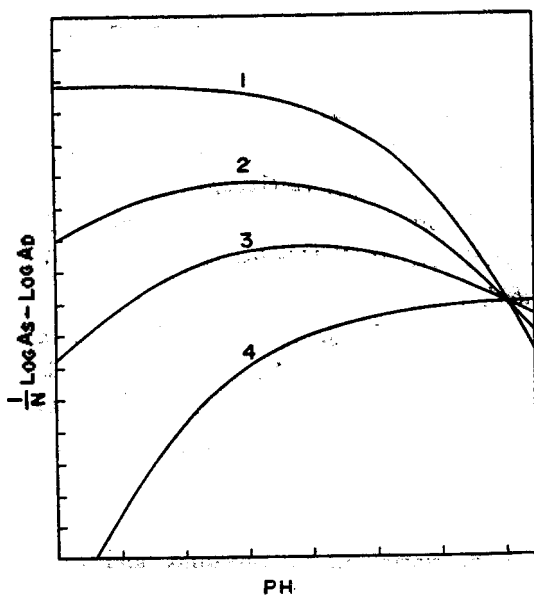

Fig. 5   Hypothetical curve of $\frac{1}{n}$ logA s-logA d) against PH for transient state of(1) Y^{3+} (2) $Y(OH)^{2+}$(3) $Y(OH)_2^+$ (4) $Y(OH)_3$

Taking logarithm of equations (12), (13), (14) and (15), the hypothetical curves of $(\frac{1}{n}\log As -\log A\ d)$ against PH are given in Fig (5). As shown in curve (1) of Fig 5, the slope of the slope of the curve varys from minus three to zero by decreasing of PH. It is seen that the curve (1) fits the experimental curve of $(\frac{1}{n}\log As - \log Ad)$ against PH shown
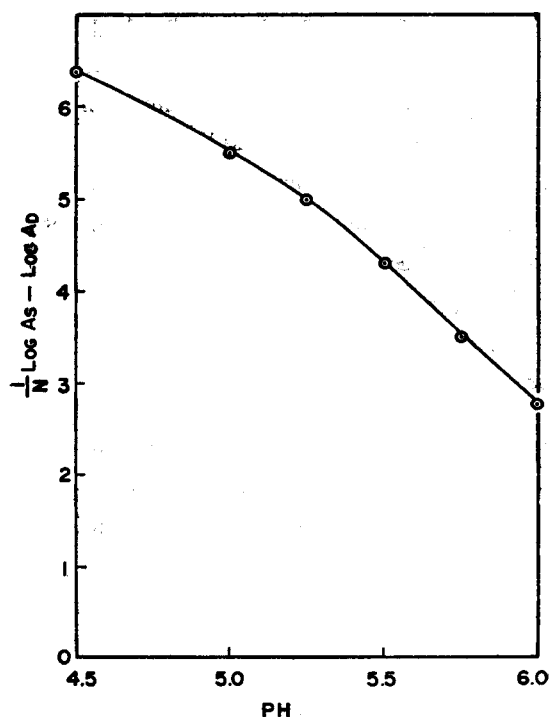

Fig. 6   Change of the value of $(\frac{1}{n}\log A\ s-\log A\ d)$ versus PH

in Fig. 6. Hence, the adsorption mechanism of the transient state of Y^{3+} would be valid, and yttrium in carrier-free state seems to exist in almost completely ionized form. The slope of the curve of Fig. 6 varys from -1.7 at a PH of 4.5 to -3.0 a ta PH of 6.0

This means the state of the adsorbed yttrium changes from ionic to hydroxide form by decreasing hydorogen ion concentration. From the slope of the curve, it is

known that various of the adsorbed state of yttrium exist i.e., $Y(OH)_3$ form of the adsorbed state exists mainly from a PH of 5.5 to 6.0, and $Y(OH)$ and $Y(OH)^{2+}$ form from a PH of 5.5 to 6.0, and $Y(OH)^{2+}$ and $Y(OH)^{2+}$ form from a PH of 4.5 to 5.0. At further higher concentration of hydrogen ion, it is expected that there exists the adsorbed state of Y^{3+}.

Let us compare $\overline{K}_{hi}$ of hydrolysis constant in the adsorbed state with K_{hi} of hydrolysis constant in solution. Fundamentally both hydrolysis constants would possess the same values when expressed in the same dimension of concentration, because it would be expected that the same equilibriums are attained irrespective of surface or volume dimension. When $\overline{K}_{hi}$ and $\overline{K}_{hi}$ are expressed as same dimension,

$$K_{hi} = \overline{K}_{hi}$$

Hence, $K_{hi}' = K_{hi}\alpha.$

Because $\alpha \gg 1,$

$$K_{hi}' \gg K_{hi}$$

There fore, it can be seen that the hydrolysis proaucts of yttrium in solution hardly exist even though there exist hydrolysis products in adsorbed state.

4 Conclusion

In conclusion it appears that carrier-free yttrium-90 is adsorbed on membrane filters during filtration process rather than simply retained on the filters from the fact that Freundlich adsorption isotherm can be applicable for the retainment of yttrium. On the adsroption mechanism of yttium-90, the theory of the transient state of the adsorbed yttrium ion was proposed. According to the theory, the adsorbed state of yttrium-90 exists in the forms of $Y(OH)_3$, $Y(OH)^{2+}$ $Y(OH)^{2+}$ and Y^{3+}, and the existing rtios of the each form are changed with hydrogen ion concentration. The state of carrier-free yttrium-90 in

solution seems to be almost completly in an ionic form of Y^{3+}. The theory of the transient state of the transient state of the adsorbed ion will be examined by further experiments.

Acknowledgements

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