

RADIOCHEMICAL STUDY  
OF THE SORPTION OF TRACE ELEMENTS. VIII.\*  
ADSORPTION OF YTTRIUM ON GLASS  
AND THE EFFECT OF LOW CONCENTRATIONS OF IRON

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This study deals with the adsorption and desorption of traces of yttrium ( $c < 10^{-9} - 10^{-5} \text{ M}$ ), labelled with  $^{88}\text{Y}$ , on glass in relation to pH and composition of the solution, concentration of yttrium and time. On the basis of the data obtained a probable mechanism of the adsorption is proposed. In the pH range from 3.5 to 10 yttrium ( $c < 10^{-9} \text{ M}$ ) is adsorbed on glass by an ion exchange of yttric ions, and physically in the form of pseudocolloids. The role of the physical adsorption increases with pH and strongly predominates above pH 10. Particles of colloidal yttrium hydroxide are adsorbed on glass electrostatically or physically from solutions of higher concentrations of yttrium at  $\text{pH} > 8$ . The adsorption of yttrium on glass is strongly suppressed by the presence of  $\text{Fe}^{\text{III}}$  ( $c 3 \cdot 10^{-5} \text{ M}$ ), which is due mainly to co-precipitation of yttrium with colloidal ferric hydroxide.

The adsorption of yttrium on glass has been the subject of several papers<sup>1-5</sup>. Schindler<sup>1</sup> studied the adsorption of yttrium on different sorts of glass using mixtures of radionuclides  $^{90}\text{Y}$  and  $^{90}\text{Sr}$ . This author observed a preferential adsorption of yttrium, in agreement with Kirby<sup>2</sup>, who investigated the deposition of this radionuclide pair on glass and other materials by the method of residual adsorption in non-equilibrium states. Eichholz and coworkers<sup>3</sup> dealt with the adsorption loss of yttrium on the surfaces of glass and polypropylene in a neutral or slightly acid region of pH for analytical purposes. Other authors<sup>4,5</sup> searched for the optimum conditions for the separation of traces of yttrium by its adsorption on glass dust. All these studies are incomplete and the interpretations of the results, if given, are at variance with one another.

The objective of the present paper was to cast some more light on the mechanism of the sorption of yttrium on glass. Since we had observed interaction of traces of yttrium and iron in studying the adsorption of yttrium on polyethylene<sup>6</sup> it was of interest to investigate how the two trace elements would affect each other's adsorption on glass, whose properties as adsorbent are different from those of polyethy-

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lene. In this way we tried to get a better insight into the interactions of the trace elements<sup>7</sup>.

## EXPERIMENTAL

### Chemicals and Apparatus

All the stock solutions were prepared from three-times distilled water. The solutions employed for the adsorption measurements were prepared from 0.01M-HCl, the pH values being adjusted with NaOH. In this way the ionic strength was kept constant (0.01) in a pH range from 2 to 11. These solutions had been found<sup>8</sup> to contain iron in a concentration of  $c. 3 \cdot 10^{-7}M$ . Solutions of 1M-NaCl and  $10^{-3}M$  disodium ethylenediaminetetraacetate were prepared by dissolving accurately weighed amounts of A. G. chemicals. Radionuclide <sup>88</sup>Y was employed as indicator of yttrium. More details about the preparation of the solutions, their mixing *etc.* were described previously<sup>6</sup>.

The adsorption was studied on the inner surface of sealed glass ampoules (geometrical area  $66 \pm 1 \text{ cm}^2$ ) and evaluated from the difference in radioactivity of the solutions before and after the experiments, which were invariably allowed to proceed 15 hours (except when the kinetics were measured). Desorption from the surface of the glass ampoules was investigated by a direct method. Both methods were described previously<sup>8</sup>. Ampoules of two sorts of glass were employed, *viz.* Sial (74.6% SiO<sub>2</sub>, 6.8% B<sub>2</sub>O<sub>3</sub>, 6.0% Al<sub>2</sub>O<sub>3</sub>, 6.6% Na<sub>2</sub>O, 1.5% CaO, 4.4% BaO) and Neutral (70.2% SiO<sub>2</sub>, 7.0% B<sub>2</sub>O<sub>3</sub>, 7.5% Al<sub>2</sub>O<sub>3</sub>, 9.5% Na<sub>2</sub>O, 1.0% K<sub>2</sub>O, 1.8% CaO, 3.0% BaO). No difference has been found in the sorption of yttrium between the two.

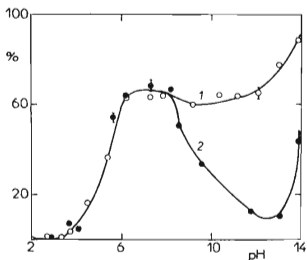


FIG. 1

Adsorption of Traces of Yttrium ( $c < 10^{-9}M$ ) on Glass in Relation to pH and Age ( $T$ ) of the Solution:

All solutions contained  $c. 3 \cdot 10^{-7}M$  Fe and  $\leq 0.01M$ -NaCl 1  $T$  1-3 h; 2  $T$  7 days.

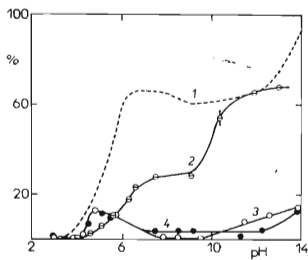


FIG. 2

Adsorption of Traces of Yttrium ( $c < 10^{-9}M$ ) on Glass in Relation to Composition and Age of the Solution

1  $\leq 0.01M$ -NaCl,  $\sim 3 \cdot 10^{-7}M$ -Fe, fresh solution; 2 1M-NaCl,  $\sim 3 \cdot 10^{-7}M$ -Fe, fresh solution; 3  $\leq 0.01M$ -NaCl,  $3 \cdot 10^{-5}M$ -Fe, fresh solution; 4  $\leq 0.01M$ -NaCl,  $3 \cdot 10^{-5}M$ -Fe, 7 days old solution.

## RESULTS

All the results are averages of 3 to 15 measurements. In some typical cases the spread of results is illustrated by the mean-square errors of arithmetic averages. Fig. 1 shows the adsorption from solutions of radioyttrium without an isotopic carrier (the "carrier-free" solutions). In view of the generally negligible abundance of yttrium its concentration in these solutions was supposed to be  $<10^{-9}$  M. A somewhat different course of sorption of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  in radioactive equilibrium was reported by Schindler<sup>1</sup>, who observed a steep increase in adsorption above pH 4, a sharp maximum at about pH 8.5, and a constant decrease with further increasing pH. However, the concentrations of the solutions are not given and the author investigated simultaneous sorption of the two elements. Fig. 1 further shows that at the given concentration of yttrium its adsorption is independent of the age of the solution up to pH 8.2, beyond which the adsorption from the aged solutions decreases rather steeply (curve 2) to a minimum at approx. pH 13, but is higher again in 1M-NaOH.

The dependence of the sorption of yttrium from its "carrier-free" solutions on the composition of the solution is illustrated in Fig. 2. As is seen, the indifferent electrolyte (1M-NaCl, curve 2) suppresses the adsorption up to pH  $\sim 11$ , but its effect is also pH-dependent. An increase in concentration of  $\text{Fe}^{\text{III}}$  in the solution by two orders of magnitude brings about a marked decrease in the adsorption of yttrium from both fresh and old solution (curves 3 and 4) through the range of pH.

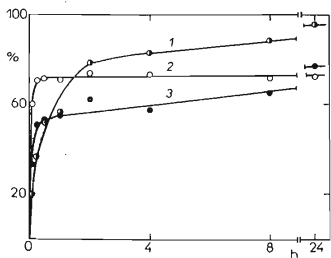


FIG. 3

Adsorption of Traces of Yttrium ( $c < 10^{-9}$  M) on Glass in Relation to Time

1 Fresh solution, pH 13; 2 fresh solution, pH 6.7; 3 7 days old solution pH 6.7.

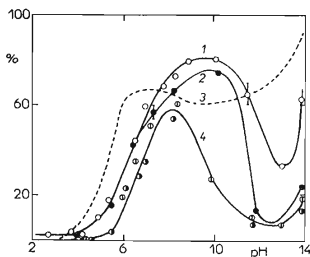


FIG. 4

Adsorption of Yttrium on Glass in Relation to pH, Age of the Solution ( $T$ ) and Concentration of Yttrium

1  $T$  1-3 h,  $2 \cdot 10^{-6}$  M-Y; 2  $T$  7 days,  $2 \cdot 10^{-6}$  M-Y; 3  $T$  1-3 h,  $<10^{-9}$  M-Y; 4 1-3 h ( $\odot$ ), 7 days ( $\bullet$ ),  $10^{-5}$  M-Y.

To ascertain whether the results corresponding to 15 hours' adsorption are close to the final values we studied the kinetics of the adsorption from fresh solutions at pH 6.7 and 13 and from old solutions at pH 6.7. The results are given in Fig. 3. The adsorption was found most rapid in the fresh solution of pH 6.7 (curve 2), where it reached its final value in 30 minutes. This finding accords with the results reported by Eichholz and coworkers<sup>3</sup>, who found that at a neutral pH the adsorption of traces of yttrium on glass was very rapid (the equilibrium was attained in 10 to 20 min). The adsorption from the fresh solutions of pH 13 (curve 1) and from the old solutions of pH 6.7 (curve 3) took a different course. It reached a certain degree in a rather short time, after which it exhibited a further moderate increase, which continued even after 24 hours.

The adsorption of yttrium on glass in relation to concentration of yttrium in the solution is shown in Fig. 4. It is seen that with an increase in concentration the dependence of the adsorption on pH is changed. The rise of adsorption from both the fresh and the old solutions is shifted to higher values of pH and a more or less sharp sorption-maximum appears, whose position on the pH scale depends on the concentration of yttrium. With an increase in the concentration of yttrium the dependence of its adsorption on the age of the solution becomes less marked. What is common to all the concentrations, however, is the increase in adsorption above pH 13.

To obtain some idea on the firmness of the bonding between yttrium and glass we have studied the desorption of yttrium in relation to pH in the preceding adsorption and to composition of the desorption solution. The time between the starts of the adsorption and the desorption was approx. 24 hours in all cases. The results show that the dependence of the desorption on the composition of the desorption solution is very marked (Table I).

TABLE I

Desorption of Yttrium (%) after 15 h in Relation to pH in the Preceding Adsorption and to Composition of the Desorption Solution

Composition of the adsorption solution:  $< 10^{-9}$  M-Y,  $\approx 3 \cdot 10^{-7}$  M-Fe,  $\leq 0.01$  M-NaCl.

Adsorption at pH	Desorption solution			
	1M-HCl	1M-NaOH	0.001M-Na <sub>2</sub> EDTA	H <sub>2</sub> O
3.7	98.9	34.3	100	13.3
6.5	99.7	26.1	99.9	14.3
8.5	100	20.9	98.2	10.3
13.9	99.9	28.0	99.3	37.6

## DISCUSSION

The interpretation of the results is based on the findings on the state of the traces of yttrium in the solutions, obtained by studying their dialysis, centrifugation and electrophoresis<sup>9</sup>, employing the present-day ideas on the mechanism of sorption of the trace elements on glass<sup>10-12</sup>. In acid solutions, pH < 3.5, yttrium is present in the form of  $Y^{3+}$  cations. These get adsorbed to a slight extent only, because the concentration of protons in the solution is considerable and the ion-exchange activity of the  $\equiv SiOH$  groups of glass is low. The increase in the adsorption of yttrium ( $c < 10^{-9}M$ ) from pH c. 3.5 to pH 6.5 is due to ionic exchange of yttric ions, and probably even to physical or electrostatic adsorption of pseudocolloids of yttrium, whose content in the solution increases beginning from pH 3.5 and which are positively charged<sup>9</sup>. The ion exchange of yttric ions on the silanol groups of glass probably occurs even in the pH region 6-8. In this region, however, yttrium is present mainly in the form of negatively charged pseudocolloids, whose nuclei are particles of ferric hydroxide<sup>9</sup>, so that the ion-exchange mechanism of the sorption of yttrium is based on its desorption from these particles. This may account for the difference in the sorption kinetics between the fresh and the old solutions of pH 6.7, so long as the desorption of yttrium is the rate-controlling step for its adsorption on glass. For it can be expected that yttrium will desorb faster and more readily from freshly precipitated colloids of ferric hydroxide than from the old ones. Apart from the ion exchange of yttrium its physical sorption in the form of the pseudocolloids is also likely to take place. However, the latter mechanism alone could not account for the adsorption of yttrium, since we had found<sup>8</sup> that the adsorption of colloidal ferric hydroxide, though considerable at pH 6-10, is short of the adsorption of yttrium.

This interpretation of the adsorption is substantiated by the negative effect of an indifferent electrolyte in the mentioned range of pH and by the concentration dependence of the adsorption (Fig. 4). It is known that indifferent electrolytes generally suppress the ion-exchange adsorption of trace elements<sup>10,11</sup> and at pH < 9 they reduce the portion of the pseudocolloids of yttrium<sup>9</sup>. As can be seen from Fig. 2, the suppression of the adsorption by the electrolyte becomes less marked as pH increases. This fact suggests that with an increase in pH the physical adsorption is enhanced<sup>8,13</sup>. The shift of the increase in adsorption to higher values of pH and its relative decrease with the increase in concentration of yttrium can be explained as due to a lower content of the pseudocolloids of yttrium<sup>9</sup> or to suppression of the ion exchange, caused by inhomogeneity of the adsorption sites on the surface of the glass. Like in other cases<sup>8,14,15</sup>, the sites that get occupied first are the most active (acidic) ones. At higher concentrations of yttrium the adsorption occurs on the less active sites, which participate in the ion exchange at higher pH values.

The mechanism of the sorption of yttrium is even more complex in the pH range 8 to 12, where the state of yttrium alters<sup>9</sup>. First there occurs a decrease in the size

of the pseudocolloidal particles of yttrium based on ferric hydroxide. When pH exceeds the value of 10 the colloidal ferric hydroxide dissolves and yttrium adsorbs on other impurities in the solution. These changes are not marked with fresh solutions but become very significant in the adsorption from old solutions, which decreases with the increase in pH (Fig. 1). The probability of an ion exchange of yttrium on glass decreases from pH 8 to pH 12, one of the reasons being the hydrolysis of yttrium ions<sup>16</sup>. By contrast, the physical adsorption is more operative in this region, which follows even from the reduced effect of the indifferent electrolyte on the adsorption (Fig. 2).

The percentage of the adsorption of yttrium in the pH range 8–12 passes through a maximum when increasing the yttrium concentration. This phenomenon is rather unusual and is evidently due to an altered state of yttrium in the solution. As was found previously<sup>9</sup>, starting from pH 8 the more concentrated solutions of yttrium ( $2 \cdot 10^{-6} \text{ M}$ ) contain colloidal particles of yttrium hydroxide, whose properties change with the age of the solution. This accounts for the sorption difference between the fresh and the old solutions at this concentration (curves 1 and 2, Fig. 4). Since the colloidal yttrium hydroxide adsorbs on glass more readily than the pseudocolloidal forms of the trace yttrium, its formation brings about an increase in the adsorption. If the concentration of yttrium is further increased the properties of the colloidal yttrium hydroxide may change and, in addition, the surface of the glass progressively approaches the state of saturation. This explains the decrease in the relative adsorption at pH > 8. Apart from this decrease, however, a considerable part of colloidal yttrium hydroxide is adsorbed on glass even at relatively high concentrations of yttrium ( $2 \cdot 10^{-6}$ ,  $1 \cdot 10^{-5} \text{ M}$ ). It seems that the sorption capacity of glass for colloidal yttrium hydroxide is higher than for the traces of colloidal hydroxides of  $\text{Fe}^{\text{III}}$  and  $\text{Mn}^{\text{III}}$ , which are adsorbed considerably less<sup>8,13</sup>.

The concentration of yttrium affects even the position of its maximum adsorption on the pH scale. Argument is still going on in the literature<sup>17,18</sup> as to which process causes the decrease in the adsorption at pH values higher than that of the maximum adsorption. The results of the present paper indicate that the decrease in the adsorption of yttrium with increasing pH is due to a change in properties of the particles of colloidal  $\text{Y}(\text{OH})_3$ , rather than to its formation. This change is probably given by the increase of the negative charge of these particles<sup>9</sup>.

The increase in the adsorption of yttrium at pH > 12, observed in both the fresh and the old solutions at every concentration of yttrium investigated, is obviously due to a change in the properties of the adsorbent. The state of yttrium in this region of pH may differ from one case to another<sup>9</sup>. The most probable reason of the increase in adsorption is the surface dissolution of glass in the alkaline solutions. As a result, the unsaturated bonds in glass become accessible, and even the negatively charged colloids may adsorb to a greater extent<sup>19–21</sup>. The slow dissolution of the surface of glass may also cause a slow increase in adsorption with time from the solution of pH 13 (Fig. 3).

The adsorption of yttrium on glass is always lower than on polyethylene<sup>6</sup>. This fact is surprising in that pH range and at those concentrations of yttrium where yttrium is present mainly in the form of ions. For it has been generally assumed that the adsorption of simple ions on hydrophobic organic polymers is lower than on glass<sup>22</sup>. In the pH range where yttrium exists mainly in the colloidal form our results agree with the finding<sup>12</sup> that trace colloids adsorb more on polyethylene than on glass.

The results of our study of the desorption of yttrium agree with the above interpretation of the sorption. Yttrium desorbs readily in 1M-HCl or a solution of disodium ethylenediaminetetraacetate, where all forms of yttrium are converted into cations  $Y^{3+}$  or the soluble complexes. The promptness of this desorption proves that yttrium is not bound to glass by chemisorption, whose bonds it would be more difficult to disrupt. It is of interest to compare the desorption of yttrium produced by 1M-NaOH with that effected by water alone. If the adsorption occurred at lower pH values the desorption by the hydroxide was invariably more efficient than that observed in water, whereas after adsorption at pH  $\sim 14$  it was the other way round. This fact is easy to explain by the idea that yttrium desorbed from glass by water cannot be re-adsorbed so readily as after the desorption by 1M-NaOH, since the leaching in water renders the glass surface less active for the adsorption<sup>10,11</sup>.

The results discussed above do not prove convincingly an interaction of the traces of yttrium and iron ( $3 \cdot 10^{-7}M$ ) in the adsorption on glass, since no data are available on the sorption of yttrium in the absolute absence of iron. More can be said, however, about the effect of  $3 \cdot 10^{-5}M$  iron (Fig. 2). Since at this concentration of iron yttrium is known<sup>9</sup> to co-precipitate with ferric hydroxide at pH  $\geq 5.5$ , the decrease in the adsorption of yttrium in the presence of iron in this region of pH is due to an insufficient capacity of glass for the colloidal carrier of yttrium, *i.e.* ferric hydroxide<sup>8</sup>. At pH  $< 6$  it is also necessary to take into account the possible competition between the yttric ions and the ionic products of the hydrolysis of ferric ions in the ion-exchange on glass. The phenomenon discussed is further evidence that the adsorption of the trace elements can be strongly affected by their interaction with the colloidal forms of other elements, also present in very low concentrations<sup>7</sup>.

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