TRACES OF YTTRIUM AND LANTHANIDES RADIONUCLIDES IN AQUEOUS SOLUTIONS. I.

ADSORPTION OF TRACE AMOUNTS OF YTTRIUM

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Adsorption of yttrium ^{91}Y from aqueous solutions on filter paper, glass, and teflon has been studied in the concentration range $\sim 10^{-11} - 10^{-12}$M of ^{91}Y at pH 1·5–11·5 and at the temperature 25°C. The relative adsorption coefficients show a maximum at pH 4–5 in the case of paper and glass and at pH 5–6 in the case of teflon. The maximum of ^{91}Y adsorption on paper is substantially decreased in the presence of 0·01M-NaCl. The observed maxima are not directly connected with the formation of the true colloid hydroxide $^{91}Y(OH)_3$ in the solution, the existence of which in the studied solutions is possible only at pH $> 9-11$. At pH $< 9-11$ yttrium ^{91}Y can probably be present in the solution only in the form of ions or pseudocolloids. Molecular forms of yttrium contribute but little to the total activity of yttrium ^{91}Y in the whole pH range studied.

Studying the problem of the forms of yttrium Y^{3+} that exist in trace amounts in the aqueous solutions, Kurbatov and Kurbatov[1] filtered solutions of traces of ^{85}Y through filter paper and they assumed that only the colloidal hydroxide $^{85}Y(OH)_3$ would be retained. The filtration method has been further developed by Schweitzer and coworkers[2-5]. Starik[6,7] proved that the colloidal particles of the hydroxide are by about three orders of magnitude smaller than the pores of the filter paper used so that traces of yttrium can probably be retained on the paper by adsorption. The same is valid also for the cationic forms of yttrium that can be adsorbed by the ion exchange mechanism on the carboxylic groups that were proved to exist in cellulose[10,11]. Therefore, the retention of yttrium traces in filter paper cannot be taken as a proof for the existence of colloidal forms of yttrium in solutions.

The aim of this series of papers is to contribute to the solution of the problem of the forms of those rare-earth radionuclides that are important in the mixtures of fission products of uranium ^{235}U and plutonium ^{239}Pu, in aqueous solutions and in trace amounts. In this paper the trace amounts of yttrium ^{91}Y in aqueous solutions are studied by the method of adsorption on filter paper, glass and teflon.

EXPERIMENTAL

Hydrochloric acid, sodium hydroxide, and sodium chloride (of the analytical grade), triply distilled water (distilled once in a metal apparatus and twice in a glass apparatus) of pH 6·3 were used. Solutions of yttrium ^{91}Y in 1·5M-HCl of the "radiochemical purity" contained impurities the activity of which did not exceed 1% of the total activity (5 Ci/l, *i.e.* $\cong 10^{-6}$M-^{91}Y) and inactive impurities (Fe, Cr) of concentrations $<0{\cdot}006$ g/l. They were used without any isotopic carrier. The stock solution was diluted by water to concentrations of $^{91}\text{Y} \sim 10^{-11}-10^{-12}$M. The acidity of solutions was adjusted by small amounts of HCl or NaOH. After the preparation the solutions used for experiments were "aged" for 24 h at the temperature of (25 ± 0·1) °C. They were kept in polyethylene flasks with a dust-proof cover which protected them also against carbon dioxide from the air. The paper Schleicher-Schüll ("Blue Ribbon"), the foil of polytetrafluoroethylene (teflon) and the cover glass plates "Micro" (for the microscope technique) of the sodium glass were used as sorbents in the adsorption experiments. The paper was washed in the Büchner funnel, 3 times by water and 3 times by ethanol (96%), teflon and glass samples were washed 3 times by the pure, distilled trichloroethylene and 3 times by ethanol. All sorbents were dried at 105°C. The activities were measured by the GM tube for β-particles with the end-window (4·1 mg/cm^2) (counter Frieseke-Hoepfner, model FHZ — 15b). The acidity was measured by the pH-meter PHM-31-Copenhagen. In the adsorption experiments 300 ml of the radionuclide solution were transferred into a 500 ml polyethylene flask in which 5—7 samples of sorbents were fixed so that they could not touch each other. For the whole adsorption period the samples in a closed flask were put into a desiccator filled with soda lime and kept at a constant temperature of (25 ± 0·1) °C. The sorbent samples were then taken out of the solution, three times rinsed in 5 ml of ethanol (96%) in the Büchner funnel and dried at 105°C. After taking out the sample the pH values of the solution were measured in at least three aliquots. In the case that this value differed by more than ±0.1 pH unit from the pH value obtained before the adsorption, the whole experiment was rejected from further evaluations. This precaution had to be done in 1·6% of all experiments. From the remaining solution 3 aliquots of 0·5 ml were taken, transferred on the filter paper discs (of the diameter of 16 mm) placed in the central cavities of three standard aluminum measuring plates, and dried at 105°C. The sorbent samples were also placed on similar plates with cavities corresponding to the shapes of samples. The activities of sorbent samples (A_s) and the activities of three solution samples (the average value A_r) were measured under identical conditions. The relative adsorption coefficients for the individual sorbent samples were calculated from the relation: $K_i = 100\, A_s\, v/A_r p$, where v is the volume of the measured solution in ml and p is the geometric surface of the sorbent sample in cm^2. The mean value (K_a) of the relative adsorption coefficient was usually calculated from 5—7 values of K_i. The scatter of K_i values did not exceed ±13% of K_a.

RESULTS AND DISCUSSION

The time dependences of the ^{91}Y adsorption on paper (Fig. 1) show that the sorption equilibrium cannot be achieved even after 24 h of adsorption. It was, however, impossible to prolong further the adsorption time without using a buffer solution. The dependence of $K_a = \text{f(pH)}$ at various adsorption times (Fig. 2) has a similar shape. Therefore the adsorption time of 1 hour has been chosen for all experiments. For all sorbents the dependence of $K_a = \text{f(pH)}$ has a distinct maximum of adsorption the peak of which is in the weakly acidic region. Certain differences have been observed between these dependences for the hydrophylic sorbents with properties of a weak catex (paper, glass) and those for the hydrophobic, typically molecular sorbent (teflon, Fig. 3). The curves for paper and glass are rather similar whereas the curve for teflon lies by about one order of magnitude lower. The maxima for paper and glass are at pH 4 – 5, for teflon at pH 5 – 6.

The increasing adsorption of ^{91}Y on sorbents with a catex character in the pH region $< 4{\cdot}1$ can be explained by the decreasing competition between H^+ ions and cationic forms of ^{91}Y (*e.g.*, $^{91}\text{Y}^{3+}$, $[^{91}\text{YOH}]^{2+}$, $[^{91}\text{Y(OH)}_2]^+$, that predominate in this pH region) on the negatively charged active groups of the catex ($-\text{COO}^-$ in the case of paper and $\equiv\text{SiO}^-$ in glass). However, it should be assumed that along with the cationic forms also traces of the other forms of yttrium ^{91}Y coexist in the region of maximum adsorption. The adsorption of these forms on a catex is much worse and their abundance in the solution increases with the increasing pH and also with the increasing hydrolysis. Moreover, in the region of the maximum of the curve $K_a = \text{f(pH)}$ these forms of ^{91}Y predominate over the before-mentioned cations and their positive charge can decrease (or their negative charge can increase) with the hydrolysis and with the polymerization of the hydrolytic products so that the adsorption on the negatively charged catex decreases. The presence of cationic forms of ^{91}Y should be, however, anticipated almost in the whole acidic region. This assumption is corroborated by the substantial decrease of the ^{91}Y adsorption in the 0·01M

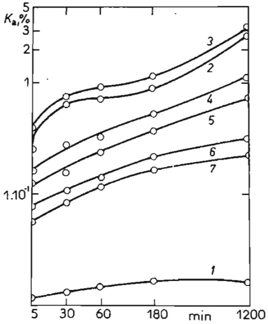

FIG. 1

The Dependence of the Logarithm of the Relative Adsorption Coefficients K_a of ^{91}Y Traces on Filter Paper on the Adsorption Time *t* at Various pH Values

pH: *1* 1·5; *2* 3·5; *3* 4·1; *4* 5·5; *5* 6·1; *6* 8·6; *7* 9·5.

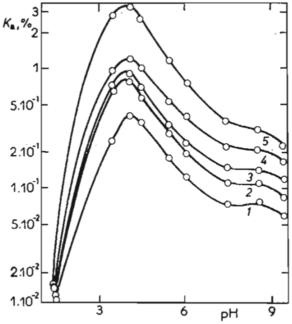

FIG. 2

The Dependence of the Logarithm of the Relative Adsorption Coefficients K_a of ^{91}Y Traces on Filter Paper on the Solution Acidity for Various Adsorption Times

Time, min: *1* 15; *2* 30; *3* 60; *4* 180; *5* 1200.

solution of NaCl (Fig. 4) due to the increasing competition with Na^+ ions. Certain increase of the ^{91}Y adsorption on paper in the neutral and basic regions due to the presence of Na^+ ions can be explained by "salting-out" of the non-ionic forms of ^{91}Y from the solution by these ions. Generally speaking, these forms can be either true colloids or adsorption pseudocolloids or molecules. It remains now to discuss which of these forms has to be considered under the given experimental conditions: *1.* The "salting-out" effect would first of all be observed for yttrium in the form of the true colloid hydroxide $^{91}Y(OH)_3$. The minimum pH value of the aqueous solution necessary for the precipitation of the true colloid hydroxide $Me(OH)_n$ from an aqueous solution of the molar concentration of the element $[Me^{n+}]$, in absence of foreign electrolytes, is given by the equation[6]:

$$pH_{min} = \frac{1}{n} \log P_{Me(OH)_n} - \log K_{H_2O} - \frac{1}{n} \log [Me^{n+}] , \qquad (1)$$

where $P_{Me(OH)_n}$ is the solubility product of the hydroxide $Me(OH)_n$ in the aqueous solution and K_{H_2O} the ionic product of water ($\approx 10^{-14}$). The published values[12-16] of the solubility product of $Y(OH)_3$ lie in the range from $5{\cdot}4 \,.\, 10^{-22}$ to $1{\cdot}06 \,.\, 10^{-24}$. In our experimental conditions the molar concentration of ^{91}Y was $\sim 10^{-11} - 10^{-12}$ so that Eq. (*1*) yields $pH_{min} = 9{\cdot}7 - 11{\cdot}0$. The region of existence of the true colloid hydroxide $^{91}Y(OH)_3$ is therefore very far from the adsorption maximum so that this

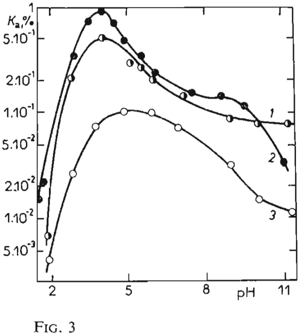

FIG. 3

The Dependence of the Logarithm of the Relative Adsorption Coefficients K_a of ^{91}Y Traces on the Solution Acidity

1 Glass; *2* filter paper; *3* teflon.

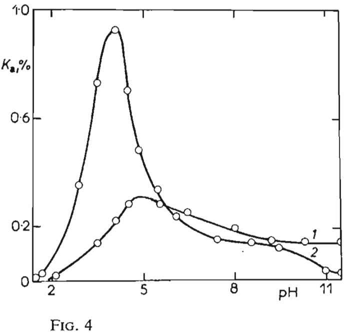

FIG. 4

The Dependence of the Relative Adsorption Coefficients K_a of ^{91}Y Traces on the Filter Paper on the Solution Acidity

1 In 0·01M-NaCl solution; *2* in absence of any foreign electrolyte in the solution.

maximum cannot be directly connected with the formation of this true colloid. *2.* Na^+ ions can "salt-out" also adsorption pseudocolloids. The pseudocolloidal forms of trace amounts of radionuclides of trivalent (and polyvalent) metals in aqueous solutions appear when the solubility product of the hydroxide of the respective radionuclide is not achieved and when a relatively high adsorption is observed[6]. It is therefore evident that in our experimental conditions the presence of the pseudocolloidal form of ^{91}Y in traces is very probable in the region of $pH < 9-11$, namely in the region of the adsorption maximum. *3.* Na^+ ions can "salt-out" even molecular forms[8,9] of the types $[^{91}Y(OH)Cl_2]^\circ$, $[^{91}Y(OH)_2Cl]^\circ$, or the monomers $[^{91}Y(OH)_3]^0_1$. The adsorption of ionic forms on teflon is excluded[8,9] because this sorbent has no electrical charge in the aqueous solution. It can be assumed that the dependence of $K_a = f(pH)$ in the ^{91}Y adsorption on this molecular sorbent (Fig. 3) reflects the adsorption of these molecular forms of ^{91}Y. It follows from these experiments that the abundance of molecular forms of ^{91}Y in the studied solutions is rather small.

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