

ULTRAFILTRATION OF SOLUTIONS OF YTTRIUM IN TRACE CONCENTRATIONS*

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The behaviour of ⁹¹Y in trace concentrations ($\sim 10^{-11}$ – 10^{-12} mol l⁻¹) in aqueous solutions was studied by applying the technique of ultrafiltration over a cellophane diaphragm. The fraction of ⁹¹Y retained by the ultrafilter generally increases with increasing pH, from low values in the strongly acidic range over a local maximum at pH ~ 4 followed by a not very pronounced local minimum at pH ~ 5 to 7 to the highest values at pH > 9 . It is concluded that yttrium in aqueous solutions in the concentrations mentioned occurs at pH < 3 predominantly in ionic forms, at pH 3 to 9 predominantly as positively and negatively charged pseudocolloids and to a lesser extent also in ionic forms, and at pH > 9 to 11 in the form of a true colloid of the hydroxide ⁹¹Y(OH)₃. In addition to the predominant forms, molecular forms of yttrium are present in a rather low fraction, too. The retention of ⁹¹Y by the filter paper during the filtration of very dilute aqueous solutions over paper filters was proved to be due to adsorption.

Kurbatov and Kurbatov¹ and later Schweitzer and coworkers²⁻⁸ applied the technique of filtration of aqueous solutions of the yttrium radionuclide in trace concentrations over filter paper and assumed "radiocolloids" of yttrium to be retained mechanically by the paper. Starik and coworkers^{9,10}, however, proved this idea to be incorrect. The technique of ultrafiltration of radionuclides in trace concentrations in aqueous solution over collodium diaphragms was used by Schubert and Conn¹¹ and over cellophane by Starik and coworkers⁹.

The aim of this work is to study the behaviour of yttrium in trace concentrations in aqueous solutions by applying the technique of ultrafiltration over cellophane and, based also on the works¹⁻¹⁴ and our previous papers¹⁵⁻¹⁸, to build up a complete image of the chemical forms of yttrium in minute concentrations in aqueous solutions.

EXPERIMENTAL

The chemicals, solutions of the radionuclide, and apparatus and procedures used for the determination of the activities and pH values of the solutions have been described¹⁵.

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The filter diaphragm used for the ultrafiltration of the radionuclide solutions was represented by a circular cellophane foil, diameter 30 mm, thickness 0.027 mm, and pore diameter of the μm order (as determined by the bubble pressure measurements¹²). The diaphragm was placed between two perfectly ground perforated circular perspex disks equipped with rubber gasket. A thread sleeve was used to tighten the filter and simultaneously to connect it with a perspex cylinder vessel above the filter, inner diameter 35 mm. The working volume of the cylinder was 50 ml and the working overpressure of nitrogen applied was 0.4 MPa.

During the application of the Kurbatov-Kurbatov method¹, 50 ml of the radionuclide solution was filtered repeatedly over one filtration paper immediately after checking the pH and measuring the initial volume activity A_0 . After filtration, the volume activity A_z was determined under the same conditions as the initial activity A_0 . The percentage activity retained by the filter, K_{zi} , was then calculated according to the formula

$$K_{zi} = 100(A_0 - A_z)/A_0 \quad (1)$$

The average value of percentage retained activity, K_z , for a selected pH of the solution was calculated from three to five determinations of K_{zi} . The K_{zi} values lay in the range of $K_z \pm 9\%$.

During the application of the ultrafiltration technique, the working volume of the cylinder was filled with the solution and its pH value was checked and initial volume activity A_0 was determined. The nitrogen overpressure was set and the filtrate was sampled at preselected time periods; the activities of the samples, A_t , were determined under the same conditions as the activity A_0 . The pH values were checked in 2 h periods. The percentage activities N_i retained by the cellophane filter for the various measurements were determined by employing the formula (1) (substituting A_t for A_z). The average value N for a time period and a pH was calculated from three to five values of N_i . The N_i values lay in the range of $N \pm 12\%$.

RESULTS AND DISCUSSION

The percentage of the radionuclide retained during the filtration according to Kurbatov¹ increases with each repetition of the filtration over one filter (Fig. 1), the highest

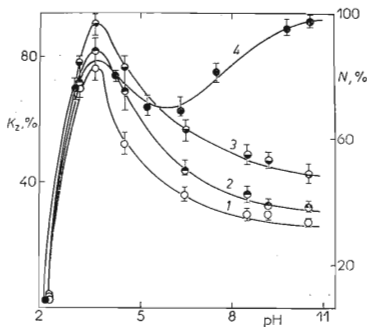


FIG. 1

Activity Fraction Retained During the Filtration of Aqueous Solutions of ^{91}Y in Minute Concentrations in Dependence on pH
1—3 Activity K_z retained by the filter paper during the application of the Kurbatov method: 1 one filtration, 2 two filtrations, 3 three filtrations; 4 activity N retained by the cellophane diaphragm after 9 h of ultrafiltration.

increment being obtained in the alkaline region on the third filtration. In fact, the increase of the retention on repeated filtration itself rules out the assumption¹ that the filter paper could catch mechanically colloidal forms of the radionuclide. Comparing the dependences measured with the dependence of the adsorption coefficient on pH for adsorption of ^{91}Y on a filter paper of the same sort in the same aqueous medium¹⁵, we can see a qualitative similarity, particularly in the positions of the maxima at pH 4 to 5. Evidently the cause of retention of the radionuclide during the filtration according to Kurbatov and Kurbatov is to be sought in the adsorption on the paper, particularly on the active carbonyl groups —COO^- whose presence in cellulose has been proved^{13,14}. Some differences between the dependences are natural, as the adsorption of ^{91}Y as studied in¹⁵ occurred in static conditions, whereas the adsorption appearing during the application of the Kurbatov–Kurbatov technique occurs in dynamic conditions. At any rate, the agreement between the two dependences is better than that found on comparing the curves obtained by the Kurbatov–Kurbatov method with the curve obtained from ultrafiltration (Fig. 1). Starik and coworkers^{9,10} have shown that the colloidal particles of the hydroxide in question are about 3 orders of magnitude smaller than the size of the pores of the filter paper used by Kurbatov and Kurbatov, hence they cannot be retained mechanically. On the other hand, retention of colloidal forms of trivalent metals and metals of higher valency in minute amounts by cellophane, whose pore size is of the μm order, is feasible.

The fraction of ^{91}Y retained by the cellophane diaphragm in dependence on the duration of ultrafiltration (Fig. 2) of a strongly acidic solution (pH 1.9) exhibits first an exponential decrease; after 6–9 h this decrease is rather slow. This can be explained so that the noncolloidal, *i.e.* molecular (small-size) and particularly the

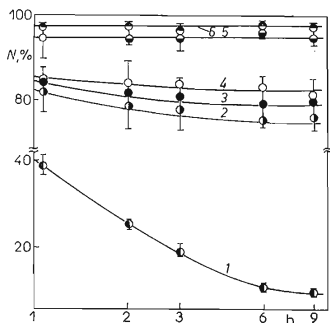


FIG. 2
Activity Fraction Retained by Cellophane Diaphragm From Aqueous Solutions of ^{91}Y in Minute Concentrations in Dependence on Logarithm of the Filtration Time Period
pH 1 1.9; 2 3.0; 3 4.2; 4 7.5; 5 9.8; 6 10.6.

ionic forms prevailing in the strongly acidic solution, adsorb first on the pores of the cellophane and only after saturating it they can pass the material. On the other hand, in the basic region, pH 9.8 to 10.6, the colloidal forms predominate absolutely (95% and more), the process of saturation of the filter is therefore not observed at all. A slight tendency to saturation is seen at pH 3.0 to 7.5, which can be ascribed to the occurrence of a rather high fraction (15–25%) of noncolloidal forms of ^{91}Y . After six to nine hours of ultrafiltration the filter is sufficiently saturated, thus the N values yield on the whole a true image of the fraction of the colloidal form in the solutions. The fraction of ^{91}Y retained by the cellophane filter, hence also the fraction of the colloidal form of ^{91}Y , in dependence on pH after nine hours of filtration is shown in Fig. 1. A rapid increase appears with pH increasing up to pH ~ 3 , the fraction approaching 80%. Regarding the finding¹⁵ that true colloids of the hydroxide $^{91}\text{Y}(\text{OH})_3$ cannot be present in aqueous solutions of pH $< 9-11$ we infer from the dependence mentioned that in the range of pH 3 to 9, about 70 to 80% of yttrium (concentration $\sim 10^{-11}$ to 10^{-12} mol l⁻¹) occurs in the form of positively and negatively charged pseudocolloidal particles¹⁴. The content of the colloidal form rises additionally and for pH 9.8 to 10.6 attains 95% and more – here it is true colloid of the hydroxide $^{91}\text{Y}(\text{OH})_3$. The maximum on the curve $N = f(\text{pH})$ (Fig. 1) at pH ~ 3.5 is obviously related with the maximum of adsorption of positively charged (predominantly cationic) forms of yttrium on negatively charged sorbents observed¹⁵ at pH 4 to 5. This higher adsorption (occurring also on the negatively charged particles of the silicic acid gel washed out of the walls of glass vessels) results in an enhanced formation of bulk adsorption pseudocolloids, found during centrifugation investigations¹⁸, with the maximum at pH 4 to 5, too. The existence of the maximum of positively charged forms of ^{91}Y and minimum of negatively charged forms of that nuclide at pH 5 to 6 has been also confirmed in the work¹⁷. The mild saddle-shaped minimum at pH 5 to 7 is analogously related to the decrease of adsorption of cationic forms of ^{91}Y on solid negatively charged impurities in the aqueous solution, which act as the nucleus (inactive carrier) of the adsorption pseudocolloid. This assumption is corroborated by the decrease of adsorption of ^{91}Y in traces on glass and on filtration paper at pH > 4.1 , found previously¹⁵.

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