Another factor which tends to cause the early current to be smaller than predicted by eq. 2 is the fact that the area of the actual drop is smaller than that of a complete sphere by the area of the capillary lumen. However, this effect is relatively small. The area of the lumen of capillary no. 1 is 3.0×10^{-5} cm.^{2}. At a drop time of 3.2 sec., if one assumes that the drop is spherical after the first 0.03 sec. and that m is equal to its average value, the area of the drop at 0.03 sec. is computed to be 1.2×10^{-3} cm.^{2}, or forty times the lumen area. Actually because m is smaller than the average value, the drop area probably is somewhat smaller than this. Even so it does not seem that the area of the lumen can amount to more than about 5% of the drop area even as early as 0.03 sec. and it rapidly becomes an even smaller fraction as the drop grows, until at the end of the drop life at 3.2 sec. it amounts to only 0.1%.

Laitinen and Kolthoff[20] demonstrated that the current observed with a *solid* spherical electrode is larger than corresponds to diffusion control because when the diffusion layer becomes thick the density gradients within it produce convective stirring which disturbs the diffusion gradient. With the dropping electrode, at a normal drop time of about 3 sec., this effect is greatly minimized because the diffusion layer does not have time to grow very thick. However, it is to be expected that at very long drop times it will become significant and cause the slope of the $i_t/t^{1/6}$ *versus* $t^{1/6}$ curve to be larger than predicted by eq. 2 during the late life of the drop. This is probably the reason why the final slopes of curves 4 and 6 in Fig. 5 tend to be somewhat greater than those of curves 2 and 3. This same effect very probably is also the cause of Smith's[21] observation that current-time curves at extremely long drop times (several minutes) correspond approximately to a second order parabola $i_t = kt^{1/2}$.

CAMBRIDGE 38, MASS.

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[20] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3347 (1939).

[21] G. S. Smith, *Nature*, **163**, 290 (1949).

[CONTRIBUTION NO. 120 FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Studies in Low Concentration Chemistry. III. The Radiocolloidal Properties of Yttrium-90

BY GEORGE K. SCHWEITZER, BERNARD R. STEIN AND WM. MORRISON JACKSON

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Yttrium-90, the daughter of strontium-90 has been removed in the carrier-free form from its parent by utilization of the radiocolloidal properties of yttrium in low concentration solutions. Using solutions of yttrium-90, the effects of coagulation time, *p*H, the presence of various electrolytes and the presence of non-aqueous solvents upon the ease of removal of yttrium-90 from its solutions by filtration have been investigated. Also the ability of the radiocolloids to reform after an initial removal, as well as the efficiencies of various grades of filter paper in removal of the activity, has been studied. The results are in agreement with previous observations on this and other elements.

Introduction

This paper constitutes the third[1] in a series of articles dealing with the radiocolloidal properties of low concentration radionuclides in solution.

Kurbatov and Kurbatov[2] used yttrium-86 in solution as a means of investigating the radiocolloidal properties of this element. Employing filtration as a separation method, they determined the effects of *p*H, ammonium chloride concentration and yttrium concentration on the percentage yttrium that could be filtered from the solution. As the *p*H of an approximately 10^{-11} g./l. solution of yttrium was increased, the percentage filterable increased. Experiments with higher concentrations of yttrium indicated a similar behavior. At a *p*H of 7.0, the percentage yttrium filtered from a solution in the concentration range 3×10^{-2} to 10^{-5} g./l. coincides with the percentage yttrium removed from very low concentration solutions. As the concentration of ammonium chloride is increased in both 0.159 mg./l. and 10^{-11} g./l. yttrium solutions, the percentage yttrium filtered decreases.

This investigation is a continuation of work on yttrium to determine other factors which influence the formation and properties of the radiocolloidal aggregates.

Experimental

Materials.—All inactive chemicals employed were of analytical reagent grade. Only triply distilled water which was preserved in carbon dioxide-free air was used.

Measurement of Radioactivity.—All radioactivities were measured with a Nuclear Model 163 Scaler connected to a Nuclear Neher–Pickering quenching unit and a Nuclear D-34 mica end-window Geiger tube. This tube was mounted in a Tracerlab SC-9 manual sample changer. All radioactivities were counted for times long enough to give a maximum standard deviation of 1%.

Separation of Yttrium-90.—Two millicuries of an equilibbrium mixture of strontium–yttrium-90 as the chlorides in acid solution was obtained from the Oak Ridge National Laboratory. The yttrium-90 is the short-lived daughter (half-life 61 hr.)[3] of strontium-90, a β-emitter with a half-life of 19.9 yr. The yttrium-90 is a β-emitter of 2.18 mev. energy decaying to stable zirconium-90. Since no yttrium was added in the separation process, the yttrium-90 was assumed to be present in carrier-free form.

To the approximately 0.5 ml. of radioactive solution obtained from Oak Ridge, there were added 25 ml. of water and 5 ml. of concentrated hydrochloric acid. Five ml. of this resulting solution was taken, adjusted to a *p*H of 13.0 with concentrated carbon dioxide-free sodium hydroxide solution and filtered slowly through a very fine glass frit.

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[1] G. K. Schweitzer and W. M. Jackson, THIS JOURNAL, **74**, 4178 (1952); G. K. Schweitzer and J. W. Nehls, *ibid.*, **74**, 6186 (1953).

[2] J. D. Kurbatov and M. H. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942).

[3] W. Meyerhoff, *Phys. Rev.*, **74**, 621 (1948); R. I. Powers and A. F. Voigt, *ibid.*, **79**, 175 (1950).

The frit was then washed with 1.0 *N* sodium hydroxide and then with water which had been adjusted to a *p*H of 9.0 with sodium hydroxide solution. One-hundredth *N* hydrochloric acid was slowly pulled through the glass frit, the filtrate was then brought to a *p*H of 13.0 with the sodium hydroxide solution, and the filtration, washing, and elution with acid were repeated. The resulting filtrate was shown to contain only yttrium-90 as evidenced by a half-life determination and absorption measurements. No strontium could be detected by the sodium rhodizonate spot test which is sensitive to 0.45 γ of strontium in 0.05 ml.,[4] nor could any silica be detected.

Sample Preparation.—All samples were prepared in 10-ml. beakers. Three or four ml. of the radioyttrium solution 0.01 *N* in hydrochloric acid was placed in a beaker, 0.01 *N* hydrochloric acid was added to increase the volume, other substances which were called for in the specific case were added and the *p*H was adjusted with dilute sodium hydroxide or ammonium hydroxide solution. All *p*H measurements were made with a Beckman model G *p*H meter. A 0.100-ml. portion of the prepared solution was then removed with a micropipet, was deposited on a 1-in. metal planchet, dried under an infrared lamp and its radioactivity was determined. Following this, the solution was filtered through Whatman No. 50 filter paper. The filtrate was sampled; the 0.100-ml. portion was deposited on a metal planchet, dried, and its radioactivity was measured. From the activities of the two samples, the percentage yttrium removed was calculated.

Results

Coagulation Time.—The effect of the time allowed between the adjustment of the *p*H and filtration of a 0.1 *N* hydrochloric acid solution upon the percentage yttrium removed was determined. Data were collected at *p*H values of 4.5 and 9.0 at intervals of five minutes for total periods of 120 min. The percentage removed shows a slight initial rise in the first 25 or 35 min. followed by a slow decrease, the activity removed attaining a constant value after 55 or 60 min. On all succeeding samples, a standing time of 60 min. was allowed.

***p*H.**—Figure 1 shows the results obtained as the *p*H values of various yttrium-90 solutions are varied. Curve A was obtained by neutralizing a 0.1 *N* acid solution with sodium hydroxide without taking any special precautions to exclude carbon dioxide from the samples. When care was exercised to prevent absorption of carbon dioxide by the samples and introduction of carbonates in the sodium hydroxide solution, curve B was obtained. Curves C and D resulted from the neutralization of 0.01 *N* solutions of yttrium-90 with carbon dioxide-free sodium hydroxide and carbon dioxide-free ammonium hydroxide, respectively, precautions being observed to prevent absorption of carbon dioxide from the air by the samples.

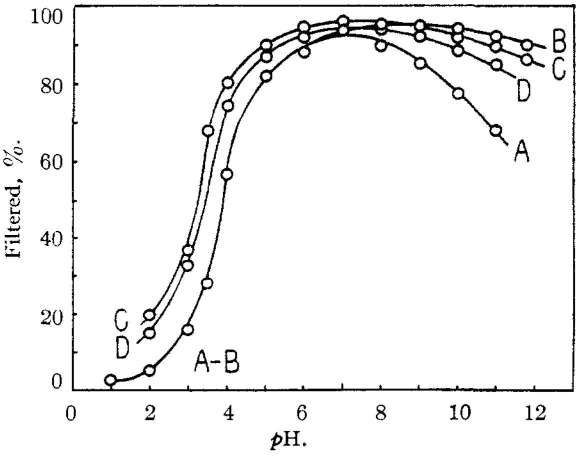

Fig. 1.—Percentage yttrium-90 filtered *versus* *p*H.

Electrolyte Effects.—Table I shows the results obtained when 0.01 *N* hydrochloric acid solutions of yttrium-90 were made up to various concentrations with different electrolytes and then adjusted to given *p*H values with carbon dioxide-free sodium hydroxide solution.

TABLE I

ELECTROLYTE EFFECTS

Concn. of added electrolyte, *M*	Percentage removed					
	*p*H 3.5					
	NaCl	Na-ClO_4	$(NH_4)_2$-C_2O_4	$(NH_4)_2$-HC_6-H_5O_7	NaH_2-PO_4	*p*H 9.0 $NaHCO_3$
0.0001	..	..	..	70	..	..
.001	..	..	..	44	72	88
.01	71	70	..	14	69	62
.05	68	67	57	8	..	36
.1	58	60	43	2	46	27
.5	44	36	16	0	..	12
1.0	23	20	14	0	9	6

Solvent Effects.—Table II lists the results obtained from studies designed to test whether the presence of a non-aqueous solvent decreases the percentage of filterable yttrium-90. All samples were run in quadruplicate and the values given are averages. Solutions originally 0.01 *N* in hydrochloric acid were employed.

TABLE II

SOLVENT EFFECTS AT A *p*H OF 5.0

Ethanol-water system		2-Methylpropanol-2-water system	
Mole %	Removed, %	Mole %	Removed, %
21	90	16	95
28	91	22	94
37	92	31	94
48	88	43	90
61	68	52	86
		60	78

Reformation Studies.—Studies were made to find whether any considerable amount of radiocolloid would reform upon aging after that initially formed was removed by filtration. Samples initially 1.0 *N* in hydrochloric acid were adjusted to a *p*H of 6.0 with sodium hydroxide. After standing 60 min., filtration through one Whatman No. 50 filter paper, removed 71% of the yttrium-90. After another 60-min. standing 14% more activity was removed by a similar filtration. Each of these values is an average of three separate determinations. For three other samples similar to these, after standing 60 min., filtration through two filter papers folded together gave an average removal of 87%.

Filtration Efficiency.—The values given in Table III illustrate the efficiencies of several grades and types of filter paper for retaining yttrium-90. Samples 1.0 *N* in hydrochloric acid were adjusted to a *p*H of 6.0 with sodium hydroxide, then were filtered through one filter paper. The relative retentivities of the filter papers, which were Schleicher and Schuell brand, as given in the second column of the table were obtained from the Schleicher and Schuell catalog.[5]

TABLE III

FILTRATION EFFICIENCY

Schleicher and Schuell filter paper	Relative retentivity	Removed at *p*H 6.0, %
604 ash low	15–25	29
597 ash low	35–50	35
602 ash low	90–98	76
589-1 H ash free	10–20	13
589-WR ash free	35–50	24
589-RR ash free	92–98	57
410 Hardened	10–20	23
497 Hardened	35–50	28
576 Hardened	96–99	60

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[4] F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 169.

[5] Schleicher and Schuell Co., "High Quality American Filter Papers, Catalog No. 70," Keene, N. H., 1951, p. 6.

Discussion

Separation of yttrium-90 from its parent can be brought about by utilization of the fact that in strongly basic solutions, strontium-90 remains in solution while the yttrium seems to form aggregates which can be filtered out. Similar behavior has been observed in the cases of many other radionuclides in solution.[1,6]

When the time allowed for coagulation of the yttrium is increased at *p*H values of 4.5 and 9.0, there appears to be a slight initial rise in the per cent. removed during the first 25 or 35 min. followed by a slow decrease, the activity leveling off after approximately 100 min. Similar results have been reported, by other investigators for yttrium,[2] for zirconium,[7] and for silver.[1]

As the *p*H of the solution is increased up to a value of about 7.0, the percentage yttrium filtered increases to a maximum, after which a drop is observed as the *p*H is increased to about 12.0. This drop is quite pronounced when no precautions are taken to exclude carbon dioxide from the samples, but when such precautions are observed, the drop becomes very slight. These results, which were interpreted as indicative of complex formation by the introduced carbonate with the radiocolloidal yttrium, can be duplicated by the intentional addition of carbonate. By starting with a yttrium-90 solution more concentrated in hydrochloric acid, the *p*H curve is shifted toward higher *p*H values and toward lower percentage removal. Neutralization with ammonium hydroxide, precautions being taken against carbonate absorption, causes the drop following a *p*H of 7.0 to be more pronounced than that when neutralization is brought about by sodium hydroxide. Other studies[1,6,7] have yielded similar results.

The electrolyte effects as indicated in Table I bring out some interesting trends. As the concentration of a non-complexing electrolyte (such as sodium chloride or sodium perchlorate) is increased, the percentage yttrium removed decreases. Kurbatov and Kurbatov report a similar trend when ammonium chloride is employed.[2] A much more pronounced decrease in the removal of yttrium is realized when the concentrations of electrolytes such as ammonium oxalate, diammonium hydrogen citrate, sodium dihydrogen orthophosphate and sodium hydrogen carbonate increase. The decreases in the cases of the oxalate, the citrate and the carbonate are quite understandable since macro amounts of these yttrium salts are soluble in excesses of these anions; however, the phosphate data seem to be somewhat unusual since a macro amount of yttrium phosphate does not appear to dissolve to any great extent in an excess of the phosphate ion at a *p*H of 3.5.

No great effect on the percentage yttrium removed by the presence of ethanol or 2-methylpropanol-2 in the solution is realized until the mole per cent. non-aqueous solvent reaches a value of about 60. Around this point there seems to be a pronounced decrease in removal. These observations are similar to previous ones on silver radiocolloids.[1] No reason can be advanced as to why the decrease in removal is sudden and not gradational as the concentration of the non-aqueous solvent is increased.

The reformation studies indicate that no appreciable reformation occurs within 60 min. after part of the initially present radiocolloid is removed. The effects obtained appear to be simply the result of two filtrations as compared with one.

The amounts of activity removable by various grades of filter paper seem to follow the trend that one would expect. The retention of the radiocolloidal particles appears to be a function of the porosity of the paper within each type of paper.

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KNOXVILLE, TENN.

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(6) G. K. Schweitzer and W. M. Jackson, U. S. Atomic Energy Commission Document ORO-48, 28 pp. (1951); *J. Chem. Education*, **29**, 513 (1952).

(7) M. H. Kurbatov and J. D. Kurbatov, *J. Chem. Phys.*, **13**, 208 (1945).