

The above work was carried out in 0.8 *N* sulfuric acid, and under these conditions ferric ion is not reduced in the absence of formic acid. The conclusion is that each of the formate radicals produced in reactions 2 and 4 is capable of reducing ferric ions. In view of this fact and the dependence of reciprocal of rate linearly on the ferric ion concentration, step 7 or an equivalent one must occur.

Evidence for step 8 as a termination one is obtained from a kinetic analysis of the data. Step 8 must be added to the other reactions 1-9 in order to obtain the correct relationship between initial rate of oxidation and initial oxygen pressure.

Ratios of rate constants k_8/k_3 and k_9/k_2 may be calculated independently from the straight lines in Figs. 3 and 4 by application of equation (17). The rate of initiation ($4k_a + k_b$) equals the rate of ferric ion formation in the absence of formic acid. This may be derived from eqs. 1a, 1b, 5, 5a, 6 and 9. (In the absence of formic acid the hydrogen atom from (1a) reacts with oxygen to form the hydroperoxy radical.) The empirical equations for Figs. 3 and 4 are equations 17 and 18, respectively

$$1/r_0 = 1.65 + 0.575/(O_2)_0 \quad (\text{oxygen curve}) \quad (17)$$

$$1/r_0 = 1.75 + 117/(\text{HCOOH})_0 \quad (\text{formic acid curve}) \quad (18)$$

Subscript 0 indicates initial conditions. Units are millimole, liter and hour. Under the experimental conditions employed $(\text{Fe}^{++})_0 = 0.5 \text{ mN}$ and $4k_a + k_b = 0.0216 \text{ mN Fe}^{+++}/\text{hr.}$; so equation (18) becomes

$$1/r_0 = 23 \left(\frac{k_8}{k_3(O_2)_0} + \frac{k_9}{k_2(\text{HCOOH})_0} \right) \quad (19)$$

From equations (17), (18) and (19) one obtains the values shown below for the ratio of rate constants

	Fig. 3	Fig. 4	Average
k_8/k_3	0.025	0.09	0.06
k_9/k_2	7.2	5.1	6.2

Owing to the limited solubility of oxygen in the solution, the values obtained from Fig. 3 are probably less accurate than those obtained from Fig. 4.

The steady state concentration of hydrogen peroxide may be calculated for a characteristic run using equation (12). Barb, Baxendale, George and Hargrave¹¹ measured k_6 and report a value of 53 moles l.⁻¹ sec.⁻¹. At a dosage rate of 0.875 $\times 10^{20}$ e.v./l. hr. and a ferrous ion concentration of $0.5 \times 10^{-3} \text{ M}$, r is found to equal $336 \times 10^{-6} \text{ M Fe}^{+++}/\text{hr.}$ Under these conditions the steady state concentration of hydrogen peroxide is found to be $1.76 \times 10^{-6} \text{ M}$. Since the rate of oxidation decreases rapidly as ferric ion is formed, hydrogen peroxide concentration will be highest at the beginning of the irradiation. At this low concentration, hydrogen peroxide is not expected to react with the free radical species formed but must disappear primarily through reaction (6). The appreciable "after irradiation effect" found at ferrous sulfate concentrations of 10^{-4} molar may be explained by the attainment of steady state concentrations of 7×10^{-6} molar hydrogen peroxide.

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Studies in Low Concentration Chemistry. I. The Radiocolloidal Properties of Lanthanum-140¹

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A separation of carrier-free lanthanum-140 from barium-140 has been made, based upon the radiocolloidal properties of lanthanum-140 in basic solution. By use of separated lanthanum-140 in solution, the effects of pH and sodium nitrate concentration upon radiocolloidal formation were investigated. The per cent. of lanthanum that could be removed was found to increase, independent of coagulation time beyond 3.0 min., but dependent on sodium nitrate concentration, to a maximum of almost 100% as the pH is increased. After the attainment of the maximum, changes in pH and/or salt concentration had little effect upon the per cent. removal. Other electrolytes were added in varying amounts to lanthanum-140 solutions of constant pH. Per cent. removal decreased as the concentration of carbonate or citrate increased. Coagulation increased as the oxalate concentration increased up to 0.05 *N* and then decreased above this concentration.

Introduction

Certain carrier-free radionuclides in solution have been shown to behave more like colloids than like true solutes. These particles have been called radiocolloids. Unlike ordinary colloids, the solubility product apparently is not exceeded.²

(1) This work constitutes Contribution No. 107 from the Department of Chemistry, The University of Tennessee. The authors wish to thank the United States Atomic Energy Commission for the Research Grant that made the research possible.

(2) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 142-148; M. Haissinsky, "Les Radiocolloids," Hermann et Cie, Paris, 1934; G. K. Schweitzer and M. Jackson, "Radiocolloids," U. S. Atomic Energy Commission Document ORO-48.

Over fifteen elements have been shown to form radiocolloidal aggregates in solution. The study of the radiocolloidal behavior of lanthanum has been limited to dialysis experiments and the measurement of diffusion coefficients. Schubert and Conn³ found that all of the lanthanum-140 in a fission product mixture was dialyzable in water, 0.01 *M* hydrochloric or 1.0 *M* nitric acid, while less dialyzed in 0.1 *M* phosphoric acid, 0.1 *M* hexafluosilicic acid or 0.1 *M* oxalic acid. The diffusion coefficient of lanthanum-140, corrected for viscosity effects, was found to be faster in nitric acid than in uranyl nitrate solutions.

(3) J. Schubert and E. E. Conn, *Nucleonics*, **4**, No. 6, 2 (1949).

The present research was undertaken to study further the radio-colloidal properties of carrier-free lanthanum-140.

Procedure

Materials.—Two millicuries of barium-lanthanum-140 as the nitrates in acid solution was obtained from the U. S. Atomic Energy Commission, Oak Ridge, Tennessee. The activities were reported to be carrier-free indicating that the total amount of lanthanum present was about 10^{-11} mole. Barium-140 with a half-life of 12.8 days⁴ decays to lanthanum-140 by β -emission. The lanthanum-140 with a half-life of 40 hours,⁵ then decays by the emission of a 1.41 Mev. beta and a 2.00 Mev. gamma to stable cerium-140.

The inactive chemicals used in these experiments were Merck and Co., Inc., reagent grade sodium hydroxide, sodium hydrogen carbonate, sodium nitrate, ammonium oxalate, Baker C. P. reagent barium nitrate, diammonium monohydrogen citrate, ammonium nitrate and du Pont C. P. reagent nitric acid and ammonium hydroxide. All solutions were prepared from freshly distilled water.

Apparatus.—All radioactivity measurements were made with standard counting apparatus. The liquid samples were evaporated on glass planchets and were mounted in an open type Tracerlab SC-10 radioassay sample holder. The counting tube was a Tracerlab TGC-2 tube of the end-window type having a window surface density of 1.7 mg./cm.² This tube was connected to a Tracerlab P-4 pre-amplifier, and a scaling circuit, mechanical register, and a high voltage source, the latter three being contained in a Tracerlab Sc-2A 64 scalar. Measurements of pH were made with a Beckman Model H pH Meter. All glassware was coated with Beckman Desicote to minimize adsorption of the radiocolloids.

Separation of Lanthanum-140.—One-tenth of the 2-millicurie shipment (about 0.2 ml.) was diluted to 15 ml. with water. About 1.0 ml. of this solution was pipetted into 50 ml. of 1.0 N nitric acid and then saturated carbonate-free sodium hydroxide solution was added until the resulting solution was strongly basic. This was filtered, with suction, through a fine fritted glass filter. The very highly active material which remained on the glass frit was removed by allowing 50 ml. of 1.0 N nitric acid to slowly filter through. A 0.100-ml. portion of the acid filtrate was removed, placed on a glass planchet, and evaporated to dryness. The activity of this material was measured at varied time intervals during a period of 5 days. The resulting decay curve indicated that a small amount of barium-140 still remained.

The process of making the acid filtrate basic, filtering and then removing the activity with acid was repeated. A decay curve showed that barium-140 could still be detected. The procedure was repeated still a third time; the acid filtrate contained pure lanthanum-140 as indicated by a decay curve showing a half-life of 40 hours.

Stock solutions of carrier-free lanthanum-140 were prepared by eluting the activity with 0.01 N nitric acid and with 1.0 N nitric acid.

Preparation of Samples.—All samples were prepared in 30-ml. glass-stoppered weighing bottles. A small volume (about 10 ml.) of the stock solution, either 0.01 or 1.0 N in nitric acid, was taken for each sample. Salts were added if the experiment called for it, the pH was then adjusted by the addition of saturated sodium hydroxide solution, and then the sample was stoppered and allowed to stand for 60 minutes.

Whatman No. 50 filter papers in funnels were washed with a solution containing no lanthanum-140, but otherwise identical to the active solution being used. Excess wash solution was removed by suction. The previously prepared active solution was then thoroughly stirred and divided into two equal portions. A sample of each portion was taken for counting and then the two portions were filtered through the prepared papers. The filtrates were then sampled.

Each sample for counting was prepared by pipetting 0.500 ml. of the solution into a glass planchet and evaporating.

(4) G. T. Seaborg and I. Perlman, *Revs. Modern Phys.*, **20**, 620 (1948).

(5) K. E. Weimar, M. I. Pool and J. D. Kurbatov, *Phys. Rev.*, **63**, 67 (1943).

The per cent. activity removed was determined by counting the dried samples which had been taken before and after filtration.

Results

Coagulation Time.—Studies of the per cent. lanthanum-140 removed as a function of the time interval between the adjustment of pH and filtration were made. The results obtained for adjustment to a pH of 3.0 using lanthanum-140 solutions originally 0.01 and 1.0 N in nitric acid indicated that from 3 to 300 min. the per cent. lanthanum removed from the solution is independent of time. However, less lanthanum could be removed from the solutions originally 1.0 N in nitric acid.

pH Effects.—The effect of varying pH upon the removal of lanthanum-140 was determined under several different sets of conditions. The results as shown in Fig. 1 were obtained by starting with an active solution 1.0 N in nitric acid and adjusting the pH with carbonate-free sodium hydroxide.

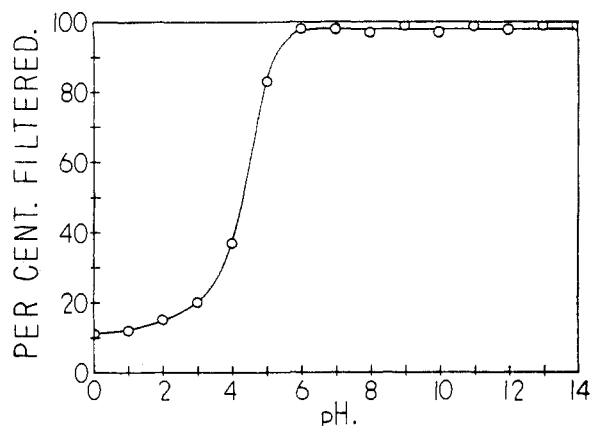


Fig. 1.—Per cent. lanthanum-140 filtered vs. pH obtained by neutralizing a solution 1.0 N in nitric acid with carbonate-free sodium hydroxide solution.

Each point represents an average of at least 3 determinations. Figure 2 shows the results obtained when a 0.01 N nitric acid solution was employed and pH adjustment was brought about by using sodium hydroxide. Considerable difficulty in duplicating results was encountered at pH values above 4.0. Curve B resulted from repeated determinations without any attempt to control the absorption of carbon dioxide from the air or the introduction of carbonates through the sodium hydroxide used for adjustment of the pH. Curve A was obtained when carbonate-free so-

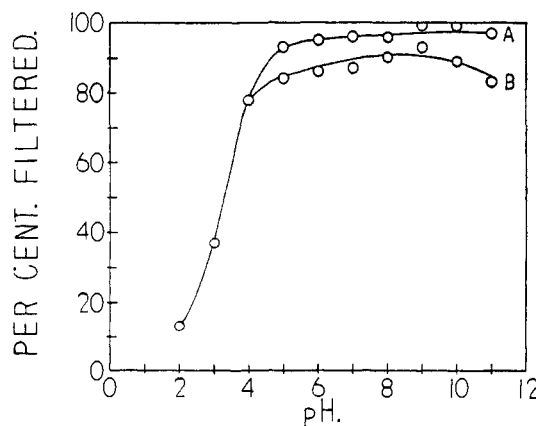


Fig. 2.—Per cent. lanthanum-140 filtered vs. pH obtained by neutralizing solutions 0.01 N in nitric acid with sodium hydroxide solution: curve A, special precautions taken against the introduction of carbonate and absorption of carbon dioxide; curve B, no special precautions taken to exclude carbonates or prevent carbon dioxide absorption.

dium hydroxide was employed and special precautions were taken to avoid the introduction of carbon dioxide by absorption from the air. Immediately after adjustment of the pH, the samples were placed in small bottles (leaving only 10 to 12 cm.³ of air above the liquid) and were stoppered. After the period of standing, filtration and sampling were carried out as rapidly as possible. Given in Fig. 3 are the results obtained when an active solution 1.0 *N* in nitric acid was adjusted to various pH values with distilled ammonium hydroxide.

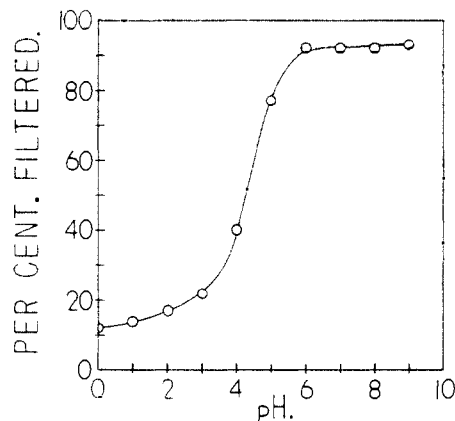


Fig. 3.—Per cent. lanthanum-140 filtered vs. pH obtained by neutralizing a solution 1.0 *N* in nitric acid with ammonium hydroxide.

Added Electrolyte Effects.—Sodium nitrate, sodium hydrogen carbonate, diammonium monohydrogen citrate and ammonium oxalate were used to investigate the effects of electrolyte concentration on the coagulation of lanthanum-140 at a given pH. All samples were prepared from a 0.01 *N* nitric acid solution of lanthanum-140. To this solution the proper amounts of electrolyte were added and then the pH was adjusted with sodium hydroxide. The effects are illustrated in Table I.

Discussion

The coagulation studies lead to the conclusion that from 3 to 300 min. the coagulation is independent of time. These data also indicate that, at a pH value of 3.0 as the concentration of the non-complexing electrolytes (nitric acid and sodium nitrate) increases, the per cent. removable decreases.

With increasing pH, coagulation increases until a maximum of almost 100% is reached, after which increase in pH produces no further change. Kurba-

TABLE I
EFFECTS OF ELECTROLYTES ON REMOVAL OF LANTHANUM¹⁴⁰

Added electrolyte concn. (N)	Removed by filtration, %				
	pH 4.0 NaNO ₃	pH 5.0 (NH ₄) ₂ HC ₂ H ₃ O ₇	NaNO ₃	pH 9.0 NaHCO ₃	(NH ₄) ₂ C ₂ O ₄
0.000	86	93	98	98	98
.001		47		88	
.005					34
.01	84	19	98	70	46
.025					74
.037				66	
.05		13			84
.1	70	9	95	58	59
.2					40
.25		6		49	
.5	34	5	96	31	
1.0	30	3	98		
2.5	28		95		

tov and Kurbatov report a similar behavior for yttrium,⁶ zirconium⁷ and thorium.⁸ Variation of the non-complexing electrolyte concentration has no effect upon coagulation beyond the point at which the maximum is attained. However, at pH values less than at the maximum, increased salt concentration results in a decrease in removal. Also the maximum is attained at a lower pH when the salt concentration is decreased. Similar effects have been noted by Kurbatov and Kurbatov with yttrium,⁶ zirconium⁷ and thorium.⁸

As one might expect, substances which complex with lanthanum decrease the radiocolloidal formation. Carbonate, whether absorbed from the air as carbon dioxide, or introduced, decreases the coagulation, as does citrate. Carbonate has the same effect upon radiocolloidal thorium.⁸ Citrate was found by Werner⁹ to decrease the coagulation of lead and bismuth radiocolloids. No previous work on the effect of oxalate concentrations has been reported, except that of Schubert and Conn³ which is in agreement with these researches.

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

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

(8) M. H. Kurbatov, *J. Phys. Colloid Chem.*, **54**, 1239 (1950).

(9) O. Werner, *Z. physik. Chem.*, **156A**, 89 (1931).