of both von Wogau and Meyer. Using the data of Weischedel, Cohen and Bruins, and those furnished by the polarographic method, the authors found the relation, $D\sqrt{M}$ = constant, to be invalid for the diffusion of metals in mercury.

It appeared to the authors that if the values of the diffusion coefficients were to give reliable indications of compound formation, a more fundamental approach to the problem was necessary. From kinetic theory it is known that the diffusion coefficient is related to the mean free path of the diffusing particles whether they be atoms or molecules and that mean free path depends on the dimensions and velocity of the particles. In Fig. 1 the diffusion coefficients obtained by Weischedel, Cohen and Bruins and the authors are plotted against the radii of the metal atoms.[21] It would be expected that copper would diffuse at about the same rate as zinc since these metals have approximately the same atomic radius and atomic weight. However, copper diffuses much more slowly than does zinc, a fact which indicates that copper does not exist in dilute mercurial solution in monatomic form but in all probability in molecules of a copper-mercury compound. Since bismuth has about the same atomic weight as lead but a much smaller atomic radius (1.46 *vs.* 1.74 Å.), it would be expected that bismuth would diffuse more rapidly than lead. However, this is not the case and the existence of molecules of a bismuth-mercury compound in dilute mercurial solution is indicated.

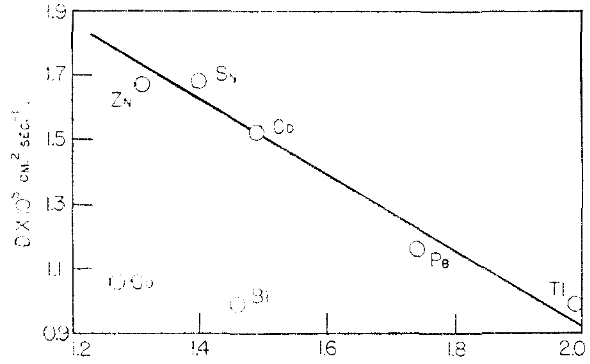

Fig. 1.—Relation between diffusion coefficients of metals in mercury and radius of metal atoms.

ADDED IN PROOF.—After the completion of the present paper, the authors' attention was directed to a paper by Turner and Winkler[22] in which these authors, using the equation of Strehlow and von Stackelberg[23] for the anodic diffusion current of a dropping amalgam electrode, reported the values 1.52×10^{-5} and 1.28×10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficients of cadmium and lead in mercury.

Acknowledgment.—The authors express their thanks to E. I. du Pont de Nemours & Co., Inc., and the Wisconsin Alumni Research Foundation for financial assistance to one of them (W. C. C.). The authors are also grateful to James C. Huber of the University of Wisconsin for his work on bismuth amalgams.

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[21] Handbook of Chemistry and Physics, 31st ed., 1949, p. 2680–2682.

[22] R. C. Turner and C. A. Winkler, *Can. J. Chem.*, **29**, 469 (1951).

[23] H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[CONTRIBUTION NUMBER 111 FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

Studies in Low Concentration Chemistry. II. The Radiocolloidal Properties of Silver-111

BY GEORGE K. SCHWEITZER AND JAMES W. NEHLS

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A method has been devised for the separation of carrier-free silver-111 from irradiated palladium foil based on the formation of radiocolloids in basic solution. The effects of coagulation time, *p*H, method of removal and the presence of nonaqueous solvents on the formation of these radiocolloids have been determined, and the ability of the radiocolloids to reform after an initial removal has been studied. The results obtained agree with previous observations on radiocolloids of other elements.

Introduction

It has been known for a number of years that certain radioactive isotopes of the heavy elements form radiocolloids. Radiocolloids may be defined as the agglomerates which form in very low concentration solutions (10^{-8} M and less) and which can be detected by virtue of their radioactivity. Recently, many other elements, including a number of lighter ones, have been shown to exhibit radiocolloidal behavior.[1]

Reasoning from the previous work on other elements, it seemed possible that silver would form radiocolloidal aggregates under suitable conditions. This paper describes the investigations which were carried out to test this possibility.

Experimental

Materials.—All inactive chemicals used were of analytical reagent quality. All water was triply distilled and preserved in carbon dioxide-free air.

Radioactivity Apparatus.—Measurements of the radioactivities of samples were made using a conventional Geiger counting apparatus. All radioactivities were counted for a sufficiently long time to give a maximum standard deviation of 1%.

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[1] G. K. Schweitzer and W. M. Jackson, U. S. Atomic Energy Commission Document ORO-48, 28 pp. (1951); to be published. A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 142–148.

Separation of Silver-111.—One-half gram of neutron-bombarded palladium foil was obtained from the Oak Ridge National Laboratory. This contained about 10 millicuries of silver-111, a radionuclide of half-life 7.5 days emitting a 1.0 mev. beta.[2] A small piece of the palladium foil (about 1 cm.^{2}) was dissolved in 5 ml. of aqua regia. To this solution was added 25 ml. of concentrated sodium hydroxide solution dropwise. The heavy, dark brown precipitate that formed after the addition of a small amount of base dissolved upon further addition. Presumably hydrous palladium oxide is precipitated which then dissolves in an excess of base.[3] This basic solution was then filtered through a fine glass frit with the aid of suction. The frit was then washed with a small amount of distilled water to remove the excess solution. The filtrate and wash solution were discarded. Five ml. of 0.01 *N* nitric acid was slowly pulled through the frit. This solution was sampled, and a half-life determination showed it to contain silver-111, as did absorption measurements with aluminum and lead absorbers. No palladium could be detected in the solution by use of the dimethylglyoxime spot test reaction[4] which is sensitive to 0.05 μg. at a concentration of one part per million.

Preparation of Samples.—A small amount of the active silver solution was placed in a beaker, 0.01 *N* nitric acid was added to increase the volume, other substances which were called for in the specific experiment were added, and then the *p*H was adjusted with dilute sodium hydroxide solution. All *p*H measurements were made with a Beckman model G *p*H meter.

The solution was then filtered through Whatman No. 50 filter paper, or was centrifuged at 24,000 times gravity in a Misco Electric Micro Centrifuge for 30 min. From the radioactivities of 0.100-ml. samples which were taken before and after filtration or centrifugation, the amount removed could be calculated. The 0.100-ml. samples were measured with a 0.100-ml. micropipet, placed on metal planchets, evaporated to dryness, and then counted.

Results

Coagulation Time.—The effect of the time allowed between the adjustment of *p*H and filtration upon the removal of silver-111 was investigated, and the data are plotted in Fig. 1. On the basis of these results a coagulation time of 60 min. was allowed for all succeeding samples.

***p*H Studies.**—Figure 2 illustrates the results obtained as the *p*H of the silver-111 solution is varied.

Electrolyte Effects.—Table I shows the results obtained when 0.001 *N* nitric acid solutions of silver-111 were made up to various concentrations with different electrolytes, and then adjusted to a *p*H of 7.0 with sodium hydroxide solution.

TABLE I

ELECTROLYTE EFFECTS AT *p*H OF 7.0

Concn. of added electrolyte, *N*	Removed by filtration, %						
	NaCl	NaBr	NaI	Na-NO$_3$	NaClO$_4$	KC-lO$_4$	Na-CN
0.0001	39	36	40		37	37	37
.001	34	34	39	38	37	35	38
.01	32	33	36	36	34	36	33
.1	35	35	41	34	32	31	30
1.0	37	37	43	32	29	30[a]	24
Above 1.0 *N*	38[b]	41[c]	47[d]	21[e]	23[e]		16[f]

[a] 0.8 *N*. [b] 6.0 *N*. [c] 8.2 *N*. [d] 7.3 *N*. [e] 10.0 *N*. [f] 5.0 *N*.

Solvent Effects.—Figure 3 indicates the effect of the composition of the solvent upon the per cent. of radiocolloid filtered.

Reformation Studies.—Experiments were performed to test whether any considerable amount of radiocolloid would reform upon aging after that initially formed was removed by filtration or centrifugation. Samples 0.01 *N* in nitric acid were prepared and adjusted to the proper *p*H with sodium hydroxide solution. After standing for 60 min., the samples were filtered and the percentage removed was calculated. The filtrate was then allowed to stand for 60 min., filtered, and the total percentage removed calculated. This was repeated for two more 60-min. intervals. The results indicated that only a small amount of silver (5 to 10%) is removed by filtrations following the initial one at *p*H values of 2.0, 7.0 and 10.0. Other samples were prepared by adjusting the 0.01 *N* nitric acid solution to the proper *p*H with sodium hydroxide solution. These were centrifuged for 30 min., the percentage removed then being determined. After standing for 30 min., these same samples were again centrifuged, and the total percentage radiosilver removed was determined. Similar determinations were made except that the second time period, instead of 30 min., was lengthened to 24 hours. Only a very small percentage (2 to 5%) of the silver was removed by the second centrifugation in both cases at *p*H values of 2.0, 7.0 and 10.0.

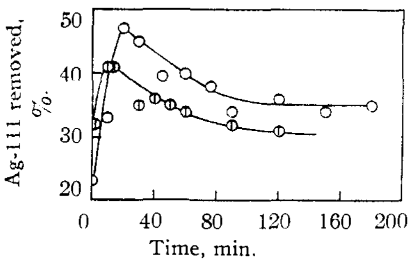

Fig. 1.—The effects of time and temperature at a *p*H of 7.0: ○, at 25°; ⊖, at 60°.

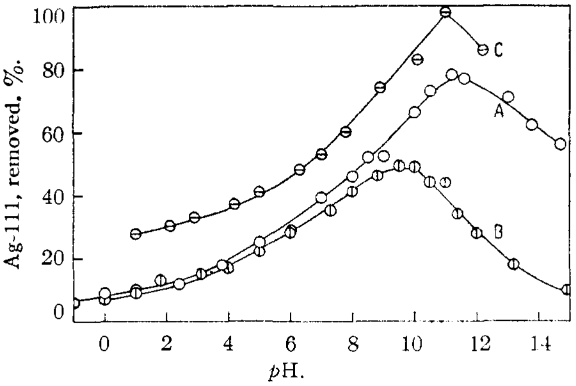

Fig. 2.—The effects of *p*H and the reagent used for neutralization upon the removal of Ag-111: A, NaOH used for neutralization, samples filtered; B, NH$_4$OH used for neutralization, samples filtered; C, NaOH used for neutralization, samples centrifuged.

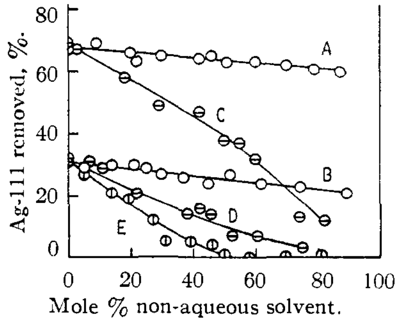

Fig. 3.—The effect of the presence of a non-aqueous solvent in the water upon the removal of Ag-111: A, ethanol at a *p*H of 10.0; B, ethanol at a *p*H of 6.0; C, 2-methylpropanol-2 at a *p*H of 10.0; D, 2-methylpropanol-2 at a *p*H of 6.0; E, 1,4-dioxane at a *p*H of 6.0.

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(2) E. P. Steinberg, reported in Plutonium Project Report CC-1331, p. 23 (Feb. 1944); G. T. Seaborg and I. Perlman, *Rev. Modern Phys.*, **20**, 611 (1948).

(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XV, Longmans, Green and Co., London, 1936, pp. 633, 656.

(4) F. Feigl, "Qualitative Analysis by Spot Tests," 3rd Eng. ed., Elsevier Publishing Co., New York, N. Y., 1946, p. 106.

Filtration Efficiency.—Various grades of Schleicher and Schuell filter papers[5] were employed to investigate the efficiencies with which they retained the radiocolloidal aggregates at *p*H values of 7.0 and 10.0. Papers having low relative retentivities retained much smaller amounts of silver than those with high retentivity values. In general, the harder grade of papers removed more activity than did the softer or more porous types.

Miscellaneous Experiments.–Duplicate samples of a 0.01 *N* nitric acid solution of silver-111, which had been made 1.0 *N* in sodium bromide, were adjusted to a *p*H of 7.0 with sodium hydroxide solution. One sample was exposed to strong sunlight for 60 min., the other being kept in the dark for a like time period. Thirty-seven per cent. radiocolloid was filtered from the former, 36% from the latter. A repeat experiment gave 39% for the light exposed sample and 37% for the one remaining in the dark.

A sample of the 0.01 *N* nitric acid solution was adjusted to a *p*H of 7.0 with sodium hydroxide solution. After standing 60 min., 36% radiocolloid was filtered out. The *p*H of a second sample was adjusted to 7.0, then hydrogen sulfide was bubbled through for 30 min. The sample then stood for 60 min., after which 43% of the activity was filtered out. The *p*H of a third was adjusted to 7.0, hydrogen sulfide was bubbled through for 30 min., and *p*H was readjusted to 7.0. After standing for 60 min., 51% of the activity was removed by filtration.

A portion of the silver-111 solution was adjusted to a *p*H of 10.0 with sodium hydroxide. One and one-half ml. of this solution was placed in a small glass centrifuge tube, 0.5 ml. of a saturated solution of sucrose was added, and the tube was allowed to stand for 15 min. Three such runs indicated that 69, 70 and 72% of the activity had plated out on the walls of the tube. The plated activity, in each case, was stripped from the tube walls with 1.0 *N* nitric acid. Determinations of the activities of the original and stripping solutions showed that all the activity could be accounted for in every instance.

Discussion

Numerous experiments showed that the average deviation between samples run under the same conditions was about 3% removal.

Separation of silver-111 from palladium is made possible by complex formation of palladium ions in strongly alkaline solution, while the silver apparently coagulates. A similar method has been employed for the separation of magnesium-27 from aluminum.[1] Maximum separation is obtained at a *p*H of 11.0 by centrifugation. Several filtrations must be performed successively in order to remove as much activity as centrifugation yields.

Variation in the length of time allowed to elapse between adjustment of *p*H and filtration of the sample brings out an interesting phenomenon. There is a very rapid increase in the amount removed for the first 20 min., then a slow drop as shown in Fig. 1. After the first 60 min., there is effectively a leveling off indicating that time has no appreciable effect beyond this point. Similar results were obtained by the Kurbatov's in studies on yttrium[6] and zirconium.[7] The initial rise, drop and leveling off are accelerated by heating the solution. At 60° the maximum is reached at 10 min. and there is no further effect after 30 min. However the total amount of activity removable at the higher temperature is slightly less.

The curves showing the effect of *p*H on the amount of activity removed, Fig. 2, all have the same shape, which is approximately that of the probability curve. This is similar to the reported results on polonium.[8] It should be noted that a higher percentage of activity was consistently removed when centrifugation was used instead of filtration. This seems to discount the theory that radiocolloids are an adsorption phenomenon for that theory would predict that more activity should be removed by filter paper with its large surface area. The difference in removal between the two methods is almost uniform, being about 15% all along the curve. It is also interesting to note how the amount of activity removed varies when different types of filter paper are used. Hardened papers retain slightly more than others of the same relative grade, but in all types the amount appears to be a function of the porosity, the more porous papers retaining less activity. This again indicates that adsorption is not the principal factor because the more porous papers probably have the largest surface areas.

When ammonium hydroxide is used to adjust the *p*H of the samples instead of sodium hydroxide, the maximum amount removed is much lower and drops off more rapidly with further increase in *p*H. This is probably due to the formation of an ammino–silver complex.

When electrolytes containing anions with which silver forms insoluble salts are added to the carrier-free silver solution there is a slight decrease in removable activity until the concentration of the added electrolyte is about 0.01 *N*, but then the amount removed increases upon further addition so that in solutions 1.0 *N* and above more activity can be removed than was possible with no electrolyte present. With other electrolytes there is a continual decrease, the drop becoming more marked the higher the salt concentration. However, with electrolytes containing anions with which silver forms complexes the decrease is very sharp, and even less activity can be removed than with other added salts. Other investigators have obtained similar results: Chamie and Korvezee with polonium,[9] Werner with bismuth,[10,11] Kurbatov with thorium,[12] and Schubert and Conn with niobium.[13]

It was noticed by some previous workers[14–16] that aggregates were formed only when polar molecules were present in the system. Harrington[15] attempted to explain radiocolloid formation in gases on the following basis: Ions and recoil atoms present as a result of the ionizing effect of radiations and of radioactive disintegrations tend to remain together on collision and polar molecules have a tendency to be adsorbed on such groups. An aggregate once formed would continue to grow until removed from the system. Presumably then, the presence of polar molecules is necessary for the formation of radiocolloids in gaseous mix-

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(5) Schleicher and Schuell Co., "High Quality American Filter Papers, Catalog No. 70," Keene, N. H., 1951.

(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. Haissinsky, *Compt. rend.*, **194**, 275 (1932).

(9) C. Chamie and A. Korvezee, *ibid.*, **192**, 1227 (1931).

(10) O. Werner, *Mikrochemie*, [2] **4**, 360 (1931).

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

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

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

(14) E. L. Harrington, *Phil. Mag.*, [7] **6**, 685 (1928).

(15) E. L. Harrington and O. A. Gratias, *ibid.*, [7] 11, 285 (1931).

(16) C. Chamie, *J. chim. phys.*, **29**, 242 (1932).

tures. Chamie[16] extended these considerations to include the necessity of a polar solvent for the formation of radiocolloids in a liquid medium. The results obtained here with mixed solvent systems bear out this proposal. As can be seen from Fig. 3, non-aqueous solvents decrease the activity which can be removed from the solution. In fact, the amount removed is almost a linear function of the composition. The lower the dipole moment of the solvent the greater is the repressing effect. Small fractions of dioxane produce large decreases whereas there is practically no effect even in high concentrations of ethanol. Bouissieres found that ethanol and acetone cut down the formation of radiocolloids of polonium.[17]

The studies on reformation indicate that once the initially formed radiocolloidal aggregates are removed from the solution further grouping is not too pronounced. This is shown particularly by the centrifugation results. The apparent reformation in the filtered samples is probably due to relations in sizes of the aggregates and the pores of the paper. The small particles not retained by the first filtration are likely to grow and be caught in a second filtration even though no new groups are formed. At first glance this seems to contradict Harrington's theory since new aggregates should be formed as a result of the disintegration of silver atoms in the filtrate but it may be that sufficient time was not allowed for this process to become appreciable.

Exposure of a sample of silver solution containing added bromide ion to strong sunlight produces no change in the amount of activity removable compared to a sample kept in the dark. This seems to indicate that either the silver in the solution is already in the metallic state or that photo-reduction of silver does not occur at such a low concentration in solution.

Bubbling hydrogen sulfide through the silver solution greatly increases the amount of activity which can be removed. This agrees with both the results from added electrolytes whose anions form insoluble silver salts and the results on other nuclides.[18,19]

As shown by the above experiments, addition of sugar to a basic solution of the carrier-free silver indicates that the silver mirror test is valid even when there is not enough silver present to form a visible mirror.

Acknowledgment.—The authors wish to thank the United States Atomic Energy Commission for the research grant which made this work possible.

(17) G. Bouissieres, R. Chastel and L. Vigneron, *Compt. rend.*, **224**, 43 (1947).

(18) M. Guillot, *ibid.*, **190**, 1553 (1930).

(19) M. Guillot, *J. chim. phys.*, **28**, 14 (1931).

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Influence of Acidity Function and Water Concentration on the Rate of Hydrolysis of *p*-Nitrobenzophenone Diethylketal in Aqueous Ethanol

BY WARREN W. KAEDING AND LAWRENCE J. ANDREWS

RECEIVED JUNE 23, 1952

The kinetics of hydrolysis of *p*-nitrobenzophenone diethylketal in solutions of hydrochloric acid in aqueous ethanol have been investigated. The rate of ketone formation is dependent on the water concentration of the solvent and on the acidity function of the medium. These observations are consistent with a proposed reaction mechanism in which the ketal oxonium salt reacts with a water molecule in the rate-determining step. An alternate mechanism in which the oxonium salt dissociates to yield a carbonium ion which then reacts with a water molecule cannot, however, be rejected on the basis of the present evidence.

The rate of hydrolysis of benzophenone diethyl ketal in 0.02 *M* solutions of hydrochloric acid in aqueous ethanol does not, as one might expect, increase uniformly with increasing water concentration of the medium.[1] The reaction proceeds at a minimum rate when the solvent contains approximately 15 mole per cent. water. It has been assumed tentatively, therefore, that this reaction, like other acid-catalyzed reactions in aqueous ethanol,[2,3] is dependent in rate on the acidity function of the medium.

Since acidity function values for 0.1 *M* hydrochloric acid solutions are known,[4] a further investigation of the kinetics of ketal hydrolysis at this higher acid concentration has been undertaken to demonstrate quantitatively the dependence of the reaction rate on both the acidity function and water concentration of the medium. Both the *p*-chloro and *p*-nitro derivatives of benzophenone diethylketal were considered as potentially less reactive substitutes for the parent ketal for use in kinetic studies at the higher acid concentration.

p-Chloro- and *p*-nitrobenzophenone dichlorides were prepared, and a series of measurements of the kinetics of ethanolysis of the dichlorides were undertaken to assist in establishing procedures for their conversion to ketals. On the basis of these measurements, which are described in detail in the Experimental section, it was decided that only the *p*-nitro substitution deactivated the benzophenone nucleus to the degree required for a convenient rate study of ketal hydrolysis in 0.1 *M* acid solutions. Kinetic measurements of the ketal hydrolysis were therefore restricted to *p*-nitrobenzophenone diethylketal, which was conveniently prepared by ethanolysis of the corresponding dichloride in the presence of sodium carbonate.

(1) L. J. Andrews and W. W. Kaeding, THIS JOURNAL, **73**, 1007 (1951).

(2) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1982 (1948).

(3) J. D. Roberts and W. Watanabe, THIS JOURNAL, **72**, 4689 (1950).

(4) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).