ADSORPTION AND COLLOIDAL PROPERTIES OF RADIOACTIVE ELEMENTS IN TRACE CONCENTRATIONS

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Contents

I. Introduction

Radioactive elements in aqueous solutions are present in trace or very low concentrations. It is well known that under these conditions phenomena often occur, which do not occur in solutions of electrolytes at common concentrations. For example, the radioactive component disappears from the solution owing to adsorption on walls, or its chemical properties are changed because of conversion from the ionic to the colloidal state. This can happen when the solubility product has been exceeded or as a result of adsorption on foreign particles, or by coprecipitation with other ions, where the radioactive element can acquire properties of the other prevailing microcomponent. These effects are important for the physical-chemical characterization of elements in trace concentration as well as for their separation from solution. It will become clear from the present review that by adjusting the conditions leading to the formation of radiocolloids, better separation can result, and, on the other hand, by neglecting colloid formation a decreasing separation effect of individual methods may result. Even biological processes are affected by the formation of radiocolloids,[1,2] because the rate of diffusion of colloidal particles is lower than that of ions, resulting in a decrease in the rates of reactions.

The topic of trace concentrations is connected with adsorption and colloid formation, and hence the study of chemistry of trace radioelements in solution deals mainly with their adsorption on the surfaces of various materials and with the conditions of their transition into the colloidal dispersion. For this purpose some methods current in colloid chemistry are used, *e.g.*, ultracentrifugation, ultrafiltration, dialysis, electrophoresis, and self-diffusion. Radioactive sols have been treated in general in the monographs by Whal and Bonner,[3] Haissinsky,[4] and Starik.[5] In the present review the results of studies dealing with the radionuclide behavior in trace concentrations are reviewed according to the methods used with regard to their adsorption, physical-chemical properties, and methods of their separation.

The results of papers are summarized in tables according to applied methods. The individual authors have, however, worked under different conditions: dissimilar electrolytes, ionic strength, another experimental arrangement. The obtained results were not presented in the same way, and therefore their values are not always mutually comparable. The values are given in the tables under conditions when the studied phenomenon became maximally evident, *i.e.*, when the formation of the radiocolloid or the adsorption reached the maximum. When the concentrations of trace elements are presented, the fact must be taken into consideration in most cases that some of these radionuclides are always present in extremely low concentrations as nonradioactive ones, as they are introduced into the solutions from chemicals or by means of their elution from the glass walls of the vessels. In the most papers, the results have been presented in percentage, and for this reason, the tables are arranged from these values. Those results expressed in a different way are discussed in the text. Most authors have plotted their results in graphs, and therefore the majority of the presented values were read from them.

II. Methods for the Study of Radioactive Elements in Solution

A. CENTRIFUGATION, ULTRACENTRIFUGATION, FILTRATION, AND ULTRAFILTRATION

Results obtained by these methods are given in Table I. The influence of various factors such as ageing time of solutions, change of pH, and the presence of nonaqueous solvents and electrolytes on the formation of radiocolloids was studied

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Table I

Separation of Radionuclides by Centrifugation, Ultracentrifugation, Filtration, and Ultrafiltration

Radioelement	*Concn, M*[a]	*pH*	*Method of separation*[b]	*Separation, %*	*Notes*[c]	*Ref*
^{111}Ag	Trace	11.0	UC	100	24,000 g, t	6
^{111}Ag	Trace	7.0	F	47	fp, t	6
^{111}Ag	$<10^{-6}$	8.0	F	55	fp, t	11
^{241}Am	10^{-9}	7.8	C	85	2500 rev/min, gr	28
^{241}Am	10^{-9}	7.0–11.0	UF	98	cm, gr	27
^{199}Au	$<10^{-8}$	2.0–7.0	F	60	fp, gr	10
^{199}Au	$<10^{-8}$	5.0	UC	96	25,000 g, t	10
^{7}Be	$<10^{-9}$	11.8	UC	90	25,000 g, gr	12
^{7}Be	$<10^{-9}$	11.0	F	80	fp or glass frit, gr	12
Eu	1.4×10^{-7}	6.0–13.0	UF	95–100	cm, gr	22
^{155}Eu	10^{-9}	7.4	UC	98	65,000 g, gr	24
^{155}Eu	10^{-8}	6.9	UC	98	65,000 g, gr, non-radioactive	24
^{203}Hg(II)	10^{-6}	4.0	UF	78	Membrane filter, pores 5 mμ, gr	23
^{203}Hg(II)	10^{-6}	12.0	UF	80	Membrane filter, gr	23
^{203}Hg(II)	3×10^{-8}	3.8	C	58.7	3600 rev/min (1300 g), t	23
^{140}La	Trace	6.0–14.0	F	98	fp, gr	13
^{95}Nb	10^{-11} g-atom/l.	3.0–6.0	UF	100	cm, gr	31, 50
^{95}Nb	10^{-10}–10^{-11}	4.0–6.0	UF	100	cm, gr	60
^{95}Nb	10^{-11} g-atom/l.	2.0	C	10	2000 g, gr	31, 50
^{233}Pa	10^{-10}–10^{-11}	6.0	C	80	cm, gr, 3000 rev/min	33
^{233}Pa	10^{-10}–10^{-11}	5.0–12.0	UF	96	cm, gr	33
^{233}Pa	10^{-12}–10^{-13}	6.0–10.0	UF	96	cm, gr	32
Po	Trace	3.0	C	56	2500–3000 rev/min, t	25
Po	10^{-13}	5.8	C	23	3000 rev/min, gr	51
Po	Trace	6.0	UF	93	Ultrafilter "ultra-fein," t	25
Po	10^{-10}	8.0–12.0	UF	90	cm, gr	50
Po	10^{-9}	4.3	UF	70	cm, gr	51
^{210}Po	8.3×10^{-11}	7.0	F	~100	Molecular filter, t	17
^{210}Po	5×10^{-14}	7.0	F	82	Molecular filter, t	17
^{210}Po	5×10^{-15}	7.0	F	65	Molecular filter, t	17
Pu(IV)	2×10^{-5}	3.0–12.0	UF	97	cm, gr	80
Pu(IV)	2×10^{-5}	5.0–9.5	C	95	3000 rev/min, gr	80
Pu(IV)	1.96×10^{-5}	11	UF	100	cm, gr	21
^{239,238}Pu(IV)	4×10^{-10}	2.8	C	44	3000 rev/min, gr	34
^{239,238}Pu(IV)	4×10^{-8}	3.1	C	25	3000 rev/min, gr	34
^{239,238}Pu(IV)	1×10^{-6}	8.0	C	80	3000 rev/min, gr	34
^{147}Pm	10^{-10}	9.0	UF	90	cm, gr	55
^{106}Ru^{II}NO	3.3×10^{-6}	9.0	C	30	14,000 g, gr	16
^{106}Ru^{II}NO	3.3×10^{-6}	9.0	UF	87.5	Membrane ultrafilter (pore size <5 mμ)	16
^{106}Ru(III)	3.3×10^{-6}	9.0	C	30	14,000 g, gr	16
^{106}Ru(III)	3.3×10^{-6}	9.0	UF	65.0	Membrane ultrafilter (pore size <5 mμ)	16
Ru(IV)	10^{-7}	8.0–12.0	UF	80	Fresh solution, gr	15
Ru(IV)	10^{-7}	8.0–12.0	UF	100	Solution after 2 hr, gr	15
^{103}Ru(IV)	10^{-7}	6.8	UF	90	cm, fresh solution, gr	14
^{103}Ru(IV)	10^{-7}	6.8	UF	100	cm, solution after 24 hr, gr	14
^{125}Sb	10^{-7}	1.0–8.0	F	15–30	fp, t	11
^{125}Sb	10^{-7}	1.0–8.0	UC	5–20	25,000 g, t	11
^{43,47}Sc	10^{-9} g-atom/l.	8.5	F	85.7	fp, t	111
Th	Trace	6.9	UF	57	Ultrafilter "ultra-fein," t	25
Th	Trace	10.0	C	17.6	2500–3000 rev/min, t	25
^{65}Zn	10^{-6}	9.0	UC	80	25,000 g, gr	8
^{95}Zr	10^{-11}	3.0–5.5	UF	92	cm, gr	99
^{95}Zr	10^{-10}–10^{-11}	4.0–10.0	UF	92	cm, gr	60
Zr	10^{-9}	4.0–10.0	UF	95	cm, gr	50
^{95}Zr	10^{-11} g-atom/l.	2.8–11.0	UF	90–96	cm, gr	54
^{95}Zr	10^{-10}–10^{-11}	4.0–10.0	C	95	3000 rev/min, gr	60
Zr	10^{-9}	3.8	C	48	2000 g, gr	50

Table I (Continued)

Radioelement	*Concn, M*[a]	*pH*	*Method of separation*[b]	*Separation, %*	*Notes*[c]	*Ref*
U(UO_2^{2+})	10^{-8}	4.5–6.5	UF	98	cm, gr	53
U(UO_2^{2+})	5×10^{-4}	5.0	UF	81	cm, gr	53
^{90}Y	10^{-8}	7.0	UC	100	25,000 g, t	11
^{90}Y	10^{-8}	8.0	UC	100	25,000 g, gr	9
^{90}Y	Trace	7.0	F	95	fp, gr	7

[a] Molar concentrations except where noted. [b] C, centrifugation; UC, ultracentrifugation; F, filtration; UF, ultrafiltration. [c] gr, value from the graph; t, value from the table or text; fp, filter paper; cm, cellophane membrane.

by centrifugation and filtration methods.[6-13] It was found, for example, that ^{90}Y forms filterable aggregates with maximum filtration at pH 7, depending on the porosity of the filter. The presence of other electrolytes led to increased removal of ^{90}Y.[7,11] In the case of ^{198}Au it was found that radiocolloids are formed at concentrations lower than 10^{-8} *M* over a wide region of pH values.[10] Filtration of ^{140}La revealed that colloids are formed from slightly acidic through neutral to alkaline region of pH.[13] Filtration and centrifugation were used to study the colloidal properties of ^{7}Be.[12] Some radionuclides did not show colloidal behavior; *e.g.*, colloidal properties were not found for Zn.[8]

Colloidal radioruthenium was separated by ultrafiltration and centrifugation.[14,15] Starik and Kositsyn have shown that Ru(IV) at 10^{-7} *M* concentration and pH 5.0 yields a sharply increased filterable fraction, which decreases beyond the neutral region.[14] In another work[16] ultrafilters with various sizes of pores were used for the study of Ru(III) and $Ru^{II}NO$, and it was found that the system is formed of particles of various sizes rather than being monodisperse. The behavior of Po in solution was studied by filtering through molecular filters.[17,18] The element was found to be in the colloidal form within a wide range of pH, with the maximum yield in the neutral region and in absence of complex electrolytes. Chamié and Haissinsky[19] studied the ageing of Po colloids; the fraction of Po separable by centrifugation increased with the age of the solution. King[20] treated Np and Pu by centrifugation and found that in slightly acidic medium and at trace concentrations, radiocolloids of Pu but not of Np are formed. Lindenbaum and Westfall[21] studied colloidal properties of Pu by ultrafiltration as a function of pH, time of adjusting the pH, and relative concentrations of Pu and complexing ions. Polymerization of Pu increased with increasing pH and could be suppressed by the addition of a large excess of citrate ions. The colloidal state of europium was studied[22] by ultrafiltration through a cellophane filter. The state of Hg(II) in trace concentration was studied by centrifugation as well as by ultrafiltration. It was found that a radiocolloid was formed in solutions aged at pH 2–7 and 12–14 by adsorption or coprecipitation with foreign particles. In fresh solutions at pH 0–2 $HgCl_2$ existed in molecular form, but at pH 4–13 hydrolysis took place, leading to molecular mercury(II) hydroxide.[23] Ichikawa and Sato[24] compared the behavior of radioactive and nonradioactive Eu during centrifugation at extremely low concentrations, but no difference was found. The colloidal states of Po and Th were studied by centrifugation and ultrafiltration, and it was found that two groups of particles are present in the solutions with dimensions of the order 30–40 and 1 $\mu\mu$, respectively. The coarsely dispersed particles represent the radioelement adsorbed on impurities; the fine particles are composed of radioelement alone.[25] By the method of ultrafiltration or centrifugation the colloidal properties of UX_1,[26] ^{241}Am,[27,28] ^{95}Zr,[29] ^{95}Nb,[30,31] Pa,[32,33] and Pu[34] were determined.

B. ION EXCHANGE AND SORPTION ON SORBENTS

The results are summarized in Table II. Adsorption of cations by ion exchangers is governed by the law of active mass action; an increased concentration of electrolyte depresses the adsorption of trace cation.[35,36] In the case of radiocolloid

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Table II

Ion Exchange and Sorption of Radionuclides

Radioelement	*Concn, M*	*pH*	*Sorbent*	*Sorption, %*	*Notes*[a]	*Ref*
^{241}Am	10^{-8}–10^{-9}	1.2–1.8	Cation exchanger	92	gr	42
^{241}Am	10^{-8}–10^{-9}	8.0–10.0	Anion exchanger	80	gr	42
^{199}Au	$<10^{-8}$	1.0	Norit A carbon	97 ± 2	10 mg, t	10
^{131}I(I$^-$)	10^{-7}	1.0–3.0	Norit A carbon	95	200 mg, gr	39
^{131}I(I$^-$)	10^{-7}	1.0	Clay	20	200 mg, gr	39
^{95}Nb	Trace		Amberlite IR-1	85	0.7 *M* uranyl nitrate, gr	1, 37
^{95}Nb	Trace		Amberlite IR-1	71	0.1 *M* uranyl nitrate, gr	1, 37
^{32}P(PO$_4^{3-}$)	$<10^{-7}$	1.9–7.2	Clay	100	200 mg, gr	39
^{32}P(PO$_4^{3-}$)	$<10^{-7}$	9.2–11.5	Norit A carbon	100	200 mg, gr	39
^{35}S(SO$_4^{2-}$)	10^{-8}	2.7	Norit A carbon	40	200 mg, gr	39
^{35}S(SO$_4^{2-}$)	10^{-8}	2.5	Clay	94	200 mg, gr	39
^{35}S(SO$_4^{2-}$)	10^{-7}	4.0	Charcoal	98	400 mg, gr	40
^{35}S(SO$_4^{2-}$)	10^{-7}–		BaCrO$_4$, PbCrO$_4$, PbO, Pb, Ag$_2$S, HgS, ZnS, Hg(COOH)$_2$	>90	1000 mg, t	40
^{125}Sb	10^{-7}	5.0	Norit A carbon	95	10 mg, t	11
^{46}Sc	Trace		Charcoal	5	1 mg, gr	40
^{89}Sr	Trace		Amberlite IR-1	53	0.1 *M* uranyl nitrate, gr	1, 37
^{89}Sr	Trace		Amberlite IR-1	0	0.7 *M* uranyl nitrate, gr	1, 37
Pu(IV)	2×10^{-5}	2.7	Silica gel	94 ± 1	t	80
^{233}U	10^{-6}	5.0–9.0	Iron(III) oxide	100	gr	100
^{95}Zr	Trace		Amberlite IR-1	45	0.1 *M* uranyl nitrate, gr	1, 37
^{95}Zr	Trace		Amberlite IR-1	70	0.7 *M* uranyl nitrate, gr	1, 37
^{90}Y	10^{-8}	6.0	Norit A carbon	90	10 mg, gr	9
^{90}Y	10^{-8}	8.0	Norit A carbon	94	10 mg, gr	9
^{90}Y	10^{-5}	6.0	Norit A carbon	80	10 mg, gr	9
^{90}Y	10^{-5}	11.0	Norit A carbon	90	10 mg, gr	9

[a] gr, value from the graph; t, value from the table or from the text.

adsorportion, electrolyte either does not influence or increases adsorption.[35,36] Sorption of traces of ^{95}Zr and ^{95}Nb increases with increasing concentration of electrolyte, the respective mechanism being not an ion exchange and being irreversible.[37]

Electrolyte or ion exchangers act by their groups as coagulants, and ion exchangers also act as adsorbents. The capacity of an ion exchanger for adsorption of radiocolloids is lower than the capacity for ion exchange. ^{95}Zr and ^{95}Nb were not only in the colloidal state, but partly also in the ionic form, the ratio of both forms depending on the conditions under which the solutions were prepared. Colloidal hydroxides of Ru(III) and Ru$^{\text{II}}$NO were adsorbed from aqueous solutions on ferrous hydroxide.[38] The separation was highly efficient, and the sorption passed through a maximum in a slightly alkaline region of pH. Schweitzer and Jackson[39] studied whether adsorption is of primary importance for colloid formation. Adsorption of ^{45}Ca, ^{22}Na, ^{134}Cs, ^{35}S(SO$_4^{2-}$), ^{131}I(I$^-$), and ^{32}P(HPO$_4^{2-}$) on clay and charcoal was carried out.[39] The radionuclides listed did not show colloidal behavior after adsorption, so the authors concluded that adsorption is not a primary factor in radiocolloid formation. Also Y, Sc, and Sn were adsorbed on the charcoal.[9,40] Sorption of Ce^{3+} on vermiculite increases with increasing concentration of sodium nitrate.[41] At trace concentrations in solutions of sodium nitrate, Ce^{3+} is found in the colloidal state.[41] Starik and Ginzburg studied the colloidal behavior of Am by ion exchange on exchangers.[42] Adsorption on a cation exchanger was highest at pH 1–3.5 and with increasing pH decreased owing to the formation of hydrolytic products. On an anion exchanger, adsorption peaked at pH values higher than 7 and was explained by physical adsorption of colloidal particles on the surface of the anion exchanger.

Adsorption isotherms for inhomogeneous microcomponents including ions, associates, and colloidal particles, under the conditions when the degree of saturation of sorbents is very low, are derived in several papers.[43–48] It is concluded that each microcomponent has its own independent distribution coefficient.[45] A plot of the overall distribution coefficient *vs.* pH is characterized by a peak, the location of which depends only on the nature of the radiocolloid.[46] The relations derived include also a correction factor for the influence of a neutral electrolyte and of complexing agents.[47] A neutral electrolyte does not lead to desorption, does no influence hydrolysis or the change of pH, and does not lead to complex formation. It can cause coagulation of particles which may, however,

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not result in sedimentation but in increasing the number of particles with the same sorption behavior. As an example of a regular peak in the pH dependence of sorption of colloidal particles, the authors mentioned sorption of Ru(III) on manganese(IV) hydroxide. The peak was at approximately pH 5.5.[46]

C. ADSORPTION ON SURFACES

The results are presented in Table III. The course of adsorption in trace concentrations on glass, polyethylene, and various metals was studied both for elucidation of the sorption mechanism proper and to reveal the state of the microcomponent in the solution. Adsorption of radionuclides on glass was used for discrimination of colloids between the so-called true colloids, *i.e.*, formed only from radioactive material and the pseudocolloids, *i.e.*, formed by adsorption of radionuclides on foreign impurities present.[49–52] It is supposed that primary impurities in solutions are colloidal particles of silicic acid. If any particular radionuclide shows colloidal properties in a certain pH interval, its adsorption on glass in the same pH interval is studied. If maximum adsorption on glass does not fit the peak of colloidal properties, then colloids are considered as true, not being formed by adsorption. The amount of colloidal Po found by electrochemical exchange with copper electrode amounted to 95% at pH 9, and to 20% at pH 4.8 whereas adsorption on glass was, at the same pH values, 1.5 and 8%, respectively.[50] Maximum adsorption of Po takes place at the pH value at which colloidal properties are only slightly pronounced, and hence adsorption is of little importance for the formation of Po colloid, which is therefore a true colloid. On the glass surface there is a layer of colloidal silicic acid which determines the adsorption properties of the glass. In slightly acidic and slightly alkaline solutions the surface of glass is negatively charged. By adsorption on glass colloidal behavior of Ru(III), Ru(IV),[14] $U^{II}O_2$,[53] Zr(IV),[54] Pm(III),[55] Tl(III), Tl(I),[56] and Co[57] was studied.

On the other hand, other papers show that SiO_2 is transferred into solution by the action of water in the monomeric form so that it should not exert any influence on the pseudocolloidal behavior of trace radionuclides.[58,59] Davydov[22] studied the state of Eu (as 1.4×10^{-7} *M* nitrate) on glass in the range of pH between 2 and 13. Starting with the pH value of 5, adsorption on glass increased, and beyond pH 11 a decrease of adsorption was observable. Within the pH values 5.8–10.5 Eu existed as a pseudocolloid and only at a pH higher than 12 did it form true negatively charged colloids. Also the nature of the colloid of ^{95}Zr–^{95}Nb at 10^{-10}–10^{-11} *M* concentration was studied by adsorption and desorption on glass.[60] Adsorption as a function of pH has a maximum, which is a result of irreversible adsorption of hydrolyzed forms of Zr and Nb on colloidal impurities of silicic acid, which means that the formation of pseudocolloids is involved.

The adsorption of gold on glass from highly diluted solutions was investigated.[61] On the glass surface exist groups such as $\equiv$Si—O—Si$\equiv$ and $\equiv$Si—OH, the latter functioning as adsorption centers for Au(III) and H^+ ions. Adsorption of Au increases with increasing pH, but beyond pH 2 Au(III) ions hydrolyze and $Au(OH)_3$ is formed with a positive surface charge and is adsorbed. By further increasing the pH, colloidal particles adsorb OH^- ions, and change their charge, with the result that adsorption is depressed. Adsorption and desorption of Mn on glass were studied as a function of Mn concentration, pH, composition of the solution, and time.[62] Adsorption is explained on the basis of ion exchange of Mn^{2+}, and electrostatic and physical adsorption of colloidal $Mn(OH)_2$. Adsorption and desorption of Au and Fe on polyethylene as a function of concentration, pH, composition of the solution, and time were studied.[63,64] Adsorption of traces of Au in the form of hydrolytic products took place by a physical mechanism.[63] Iron was present at pH 2–5 as Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2{}^+$, and over pH 5 as colloidal ferric hydroxide, which was adsorbed on polyethylene. Over pH 10 $Fe(OH)_4{}^-$ anions were formed.[64] The sorption capacity of polyethylene for colloidal iron was high. Adsorption of ^{203}Hg, ^{59}Fe, ^{198}Au, and ^{54}Mn on various materials was studied; the mechanism of adsorption was analogous.[65–69]

Belloni, Haissinsky, and Salama[70] studied the adsorption of microamounts of ^{147}Pm, ^{144}Ce, and ^{106}Ru on Pt, Au, Ag, steel, glass, and poly(vinyl chloride). The adsorption of Pm and Ce was reversible, but that of Ru was irreversible. Temperature led to increased adsorption. Adsorption of Pm and Ce obeyed Langmuir's isotherm, whereas for Ru adsorption was governed by Henry's law. Concurrent action of H^+ ions was observed; with increasing concentration of H^+ ions adsorption was lowered, and the decrease of adsorption after the peak was explained by the formation of colloidal, weakly adsorbed micelles. Adsorption of Pm and Ce was conditioned by electrostatic attraction; adsorption of Ru took place according to the same mechanism. Ru can replace Pt, and therefore its adsorption was partly irreversible.

Herczynska and Campbell[71] studied the deposition of ^{137}Cs, ^{32}P (as phosphate) on gold, platinum, and stainless steel as a function of pH and time of contact of the solution with metal. Maximum phosphate deposition on gold, platinum, and stainless steel took place at pH 3–4 and was explained by adsorption of H^+ ions in this pH range which

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Table III

Adsorption of Radionuclides on Surfaces of Various Materials

Radioelement	*Concn, M*^{a}	*pH*	*Material*	*Adsorption, %*	*Notes*^{b}	*Ref*
^{241}Am	10^{-9}	6.0	Lead	15	gr	84
^{241}Am	10^{-9}	5.9	Nickel	16	gr	84
^{241}Am	10^{-9}	6.0	Platinum	11.5	gr	84
^{241}Am	10^{-9}	6.0	Aluminum	9.5	gr	84
^{241}Am	10^{-9}	6.0	Gold	6.0	gr	84
^{241}Am	10^{-9}	6.8	Silica glass	60	gr	28
^{241}Am	10^{-9}	5.8	Silver	4	gr	84
^{241}Am	10^{-9}	5.8	Platinum	13	20% EtOH, gr	84
^{241}Am	10^{-9}	6.0	Nickel	19	20% EtOH, gr	84
^{241}Am	10^{-9}	6.0	Copper	17.5	20% EtOH, gr	84
^{241}Am	10^{-9}	3.0	Iron	40	20% EtOH, gr	84
^{241}Am	10^{-9}	5.5	Glass	2.9	90% EtOH, gr	84
^{241}Am	10^{-9}	4.4	Nickel	1.8	90% EtOH, gr	84
^{241}Am	10^{-9}	7.5	Copper	1.0	90% EtOH, gr	84
^{241}Am	10^{-9}	5.6	Platinum	1.4	90% EtOH, gr	84
^{198}Au	10^{-8}	10.8	Silicon	100	In <0.001 *M* NaCl, t	68
^{198}Au	10^{-6}	10.8	Silicon	100	In <0.001 *M* NaCl, t	68
^{198}Au	10^{-8}	10.8	Silicon	<1.7	In 0.1 *M* KCN + <0.001 *M* NaCl, t	68
^{198}Au	10^{-6}	10.8	Silicon	<0.3	In 0.1 *M* KCN + <0.001 *M* NaCl, t	68
^{198}Au	10^{-6}	3.5	Glass	15	gr	61
^{198}Au	10^{-7}	2.7	Glass	25.5	gr	61
^{198}Au	10^{-8}	2.4	Glass	46	gr	61
^{199}Au	$<10^{-8}$	2.0	Glass	32	gr	10
^{198}Au	10^{-9}	2.0	Glass	66	gr	61
^{198}Au	10^{-5}	3.5	Polyethylene	96	gr	63
^{198}Au	10^{-6}	3.9	Polyethylene	100	gr	63
^{198}Au	10^{-7}	3.5	Polyethylene	83	gr	63
^{198}Au	10^{-8}	1.8	Polyethylene	88	gr	63
^{242}Cm	1.5×10^{-12}	4.0–6.0	Platinum	100	gr	76
^{242}Cm	1.5×10^{-12}	5.3	Glass	84	gr	76
^{60}Co	10^{-8}	9.0	Glass	95	t	57
^{137}Cs	$\sim 10^{-7}$	7.0	Platinum	0.5	gr	71
^{137}Cs	$\sim 10^{-7}$	4.5	Stainless steel	3.3	gr	71
Eu	1.4×10^{-7}	7.0–11.0	Glass	48	gr	22
^{59}Fe	3×10^{-7}	5.2	Glass	48	gr	66
^{59}Fe	3×10^{-7}	10.8	Glass	54	gr	66
^{59}Fe	3×10^{-7}	6.3–9.2	Polyethylene	98–99	gr	64
^{203}Hg	3×10^{-8}	12.0	Polyethylene	94.8	In ≤0.001 *M* $NaNO_3$, t	65
^{203}Hg	3×10^{-8}	12.0	Polyethylene	92.6	In ≤0.001 *M* $NaNO_3$ 0.01 *M* NaCl, t	65
^{203}Hg	3×10^{-8}	12.0	Polyethylene	91.6	In 1 *M* $NaNO_3$, t	65
^{203}Hg	3×10^{-8}	13.0	Glass	38.1	t	69
^{52,54}Mn(II)	10^{-5}	12.1	Glass	17	gr	62
^{52,54}Mn(II)	10^{-6}	8.5	Glass	29	gr	62
^{52,54}Mn(II)	10^{-7}	9.5	Glass	49	gr	62
^{52,54}Mn(II)	$<5 \times 10^{-8}$	10.0	Glass	64	gr	62
^{52,54}Mn(II)	$\leqslant 3 \times 10^{-8}$	10.8	Silicon	100	In <0.001 *M* NaCl, t	68
^{52,54}Mn(II)	$\leqslant 3 \times 10^{-8}$	10.8	Silicon	0.37	In 0.1 *M* KCN + <0.001 *M* NaCl, t	68
^{95}Nb	10^{-11} g-atom/l.	2.0	Silicon	14	gr	31, 50
^{95}Nb	10^{-10}–10^{-11}	2.0	Silica glass	14	gr	50, 60
^{233}Pa	Trace	5.0	Silica glass	60	gr	50
^{233}Pa	Trace	4.0	Iron	38	gr	85
^{233}Pa	Trace	2.9	Nickel	24	gr	85
^{233}Pa	Trace	4.0	Copper	25	gr	85
^{233}Pa	Trace	3.4	Gold	6	gr	85
^{233}Pa	Trace	3.5	Platinum	4	gr	85
^{233}Pa	10^{-13}	2.0	Iron	60	20% EtOH, gr	84
^{233}Pa	10^{-13}	4.0	Platinum	12	20% EtOH, gr	84
^{233}Pa	10^{-13}	4.0	Nickel	16	20% EtOH, gr	84
^{233}Pa	10^{-13}	4.0	Copper	14	20% EtOH, gr	84

Table III (Continued)

Radioelement	*Concn, M*[a]	*pH*	*Material*	*Adsorption, %*	*Notes*[b]	*Ref*
^{233}Pa	10^{-13}	2.1	Iron	70	90% EtOH, gr	84
^{233}Pa	10^{-13}	2.1	Nickel	45	90% EtOH, gr	84
^{233}Pa	10^{-13}	4.0	Copper	12	90% EtOH, gr	84
^{233}Pa	10^{-13}	4.0	Platinum	8	90% EtOH, gr	84
$^{32}P(PO_4^{3-})$	10^{-10}	4.0	Platinum	53.0	gr	71
$^{32}P(PO_4^{3-})$	10^{-10}	3.0	Perspex	21.3	gr	71
$^{32}P(PO_4^{3-})$	10^{-10}	3.2	Gold	19.5	gr	71
$^{32}P(PO_4^{3-})$	10^{-10}	3.0	Stainless steel	60.0	gr	71
Po	10^{-10}	4.0	Glass	7	gr	51
Po	10^{-9}	9.0	Glass	2	gr	51
Po	5×10^{-13}	5.4	Silica glass	14	gr	52
^{238,239}Pu(IV)	10^{-6}	5.1	Glass	7.7	gr	34
^{238,239}Pu(IV)	4×10^{-8}	3.0	Glass	7.3	gr	34
^{238,239}Pu(IV)	4×10^{-10}	3.1	Glass	4.5	gr	34
^{238,239}Pu(VI)	5.2×10^{-9}	7.0	Platinum	84.0	gr	78
Ru(IV)	10^{-7}	6.0	Glass	35	gr	15
$U(UO_2^{2+})$	5×10^{-4}	7.0	Glass	56	gr	53
$U(UO_2^{2+})$	10^{-8}	7.0	Glass	60	gr	53
^{233}U(VI)	1×10^{-6}	5.1–6.0	Platinum	60	gr	77
^{233}U(VI)	4×10^{-9}	4.7–7.1	Platinum	87	gr	77
^{95}Zr	10^{-11} g-atom/l.	4.0	Silica glass	35	gr	54
^{95}Zr	10^{-10}–10^{-11}	3.1	Silica glass	74	gr	60

[a] Except where noted. [b] gr, value from the graph; t, value from the table or text.

constitutes favorable electrostatic conditions for attraction of an anion to the surface. The second adsorption maximum was within pH 7–9 and was ascribed to physical adsorption. The decrease of phosphate adsorption beyond pH 9 is explained by covering the surface with OH^- ions, which repel HPO_4^{2-} ions. For ^{137}Cs, maximum deposition occurs at pH 8–11 and is explained by covering the surface by OH^- ions, which produces electrostatically favorable conditions for adsorption of cations. The second peak at pH 5 is again ascribed to physical adsorption. A paper by Ichikawa and Sato[72] deals with the adsorption of carrier-free Eu from solutions on surfaces of some plastic materials and glass as depending on the change of pH and the concentration of electrolyte. The adsorption peaked at pH 4.5 and at 9.5. The results were interpreted as follows. Below pH 5 ions of Eu^{3+} and H_3O^+ compete for adsorption centers on the surface of material and the drop in concentration of H_3O^+ ions leads to increased adsorption of Eu. Ions of Ca^{2+} and Na^+ depress the adsorption of Eu. For pH values higher than 5, hydrolysis of Eu^{3+} takes place stepwise to $Eu(OH)^{2+}$, $Eu(OH)_2^+$, and $Eu(OH)_3$; ions formed with a lower charge are adsorbed to a lesser extent, hence the drop of adsorption between pH 5 and 9. In alkaline medium adsorption of Eu increases with increasing concentration of electrolyte. Eu is apparently in the colloidal state and the electrolyte causes its coagulation and adsorption.

The colloidal behavior of Y by adsorption on polyethylene was studied, and the formation of the colloid was explained by ion-exchange adsorption on suspended particles in the solution.[73] The kinetics of adsorption and the saturation value for yttrium were shown to be dependent on the surface treatment. Adsorption of ^{147}Pm from solutions on the metal surface was investigated.[74] Adsorption of cations from solution was dependent on the composition of the surface layer and took place on the oxide and hydroxide groups of the metal surface. Hydrolysis of adsorbing ions was also an important factor in its adsorption.[73,74] Adsorption of Pa on glass and other materials[75] (^{242}Cm, U^{6+}, Pu^{4+}, Pu^{6+}) on the surface of platinum was investigated.[76–79] The adsorption peak of Pa on glass in slightly alkaline medium was explained by the existence of positively charged pseudocolloids.[75] Adsorption of U^{6+} on Pt satisfied the validity conditions of Freundlich's isotherm.[77] Grebenshchikova and Davydov[80] studied the state of Pu(IV) in the pH region of 1.0–12.0 by adsorption and desorption from silica gel, and the results showed that Pu(IV) is in the collodial state in the interval of pH 1.4–12.0. Adsorption of ^{7}Be on glass, silica, fluorothene, and plexiglass is treated in the work of Sebastyanov and Rudenko.[81] Up to the value of pH 7.6 Be is in solution as Be^{2+} and $Be(OH)^+$ and at about pH 7.2 predominantly as $Be(OH)_2$. At higher pH values polynuclear complexes of Be(II) are present. Another paper[82] deals with adsorption of Cs, Tl, Ag, and Sr on polyethylene and fluorothene. Adsorption of ions Cs^+, Tl^+, Sr^{2+}, and Ag^+ increased in the sequence $Cs^+ < Tl^+ < Sr^{2+} < Ag^+$. Adler and Steigman[83] dealt with adsorption of UX_1 and Ra E on colloidal graphite. A dipping Geiger–Müller counter was coated with colloidal graphite, so that it served simultaneously as accumulator and detector. Adsorption took place through linear diffusion. Starik and Kositsyn[14] studied the adsorption of Ru(III) and Ru(IV)

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Table IV

Self-Diffusion Coefficients of Radionuclides

Radioelement	*Concn, M*[a]	*pH*	*Temp, °C*	*D*,[c] *cm²/sec*	*Radius, Å*	*Notes*[d]	*Ref*
^{144}Ce(III)	10^{-3}		20	0.469×10^{-5}		In 0.1 *M* HCl, t	87
^{144}Ce(III)	10^{-5}		25	0.612×10^{-5}		In 0.01 *M* HNO_3, t	88
^{144}Ce(III)	10^{-5} [b]	1.0	25	0.608×10^{-5}		t	90
^{144}Ce(III)	10^{-5}	2.0	25	0.612×10^{-5}		t	90
^{144}Ce(III)	Trace	3.0	25	3.17×10^{-6}	7.6	a, t	95
^{144}Ce(III)	Trace	5.8	25	1.04×10^{-6}	23.0	a, t	95
^{144}Ce(III)	Trace	7.0	25	7.52×10^{-7}	31.8	a, t	95
^{144}Ce(III)	Trace	10.0	25	6.51×10^{-7}	36.8	a, t	95
^{155}Eu	Trace	3.0	25	9.86×10^{-6}	2.4	a, t	95
^{155}Eu	Trace	5.8	25	1.47×10^{-6}	16.3	a, t	95
^{155}Eu	Trace	7.0	25	1.58×10^{-6}	15.2	a, t	95
^{155}Eu	Trace	10.0	25	1.33×10^{-6}	17.9	a, t	95
Np(V)	4×10^{-6} [b]	2.8	25	0.636×10^{-5}		t	90
^{212}(Pb + Bi)	Trace			1.8×10^{-7}	130	t	92
^{210}Po	Trace			3×10^{-9}	8000	t	92
^{147}Pm	Trace	3.0	25	4.87×10^{-6}	4.9	a, t	95
^{147}Pm	Trace	5.8	25	3.88×10^{-6}	6.2	a, t	95
^{147}Pm	Trace	7.0	25	3.09×10^{-6}	7.8	a, t	95
^{147}Pm	Trace	10.0	25	1.07×10^{-6}	22.4	a, t	95
Pu(IV)	1×10^{-5} [b]	1.8	25	0.385×10^{-5}		t	90
Pu(IV)	1×10^{-5} [b]	2.7	25	0.158×10^{-5}		t	90
Pu(IV)	10^{-5}		25	0.507×10^{-5}		In 1 *M* HNO_3, t	88
Pu(IV)	10^{-5}		25	0.469×10^{-5}		In 7 *M* HNO_3, t	88
^{106}Ru(IV)	10^{-6}	3.0	25	4.33×10^{-6}	5.6	a, t	94
^{106}Ru(IV)	10^{-6}	6.4	25	2.18×10^{-6}	11.1	a, t	94
^{106}Ru(IV)	10^{-6}	6.8	25	7.04×10^{-7}	34.1	a, t	94
^{106}Ru(IV)	10^{-6}	8.3	25	2.21×10^{-6}	10.9	a, t	94
^{106}Ru^{III}NO	10^{-6}	3.0	25	7.60×10^{-6}	3.6	b, t	94
^{106}Ru^{III}NO	10^{-6}	6.8	25	2.95×10^{-6}	9.3	b, t	94
^{106}Ru^{III}NO	10^{-6}	6.9	25	2.29×10^{-6}	11.9	b, t	94
^{106}Ru^{III}NO	10^{-6}	8.8	25	4.86×10^{-6}	5.6	b, t	94
^{90}Sr	10^{-5}	1.0	25	0.775×10^{-5}		t	90
^{90}Sr	10^{-5} [b]	6.0	25	0.779×10^{-5}		t	90
^{234}Th(IV)	10^{-5} [b]	1.0	25	0.479×10^{-5}		t	90
^{234}Th(IV)	10^{-5} [b]	2.0	25	0.510×10^{-5}		t	90
^{95}Zr	1×10^{-5}	7.5	25	0.050×10^{-5}	50	t	89
^{95}Zr	1×10^{-5}		25	0.351×10^{-5}	7.0	In 0.1 *M* HCl, t	89
^{95}Zr	1×10^{-3}		25	0.480×10^{-5}		In 1 *M* HCl, t	89
^{95}Zr	1×10^{-5}		25	0.480×10^{-5}		In 1 *M* HCl, t	89
^{95}Zr	1×10^{-7}		25	0.484×10^{-5}		In 1 *M* HCl, t	89

[a] Except where noted. [b] Concentration in g-ion/l. [c] D = self-diffusion coefficient. [d] t, value from the table or text; a, $\mu = 0.1$ (NaCl); b, $\mu = 0.1$ ($NaNO_3$).

on glass as a function of its state in solution. Maximum adsorption was found at a pH of about 5, where maximum colloidal Ru(IV) is formed. The method of adsorption on glass was also used to study microamounts of uranium in solution,[53] and the results showed that at pH 2.5–7.5 uranium in 10^{-8} *M* concentration is in the form of a pseudocolloid. The behavior of ^{241}Am (10^{-9} *M*) and ^{233}Pa (10^{-13} *M*) during adsorption from aqueous and water–ethanolic solutions on the surface of glass, fluorothene, lead, copper, nickel, aluminum, gold, and silver has been described.[84,85] The sorption of ^{241}Am and ^{233}Pa on the surface of the already mentioned materials from aqueous solutions follows a similar course and differs only in the position of the peak. In water–ethanolic solutions the behavior of both elements was quite different as to the pH dependence or the dependence on the nature of the sorbent. Skulskii and Glazunov[86] deduce the transition of parent isotope into the colloidal state from the lowering of the selectivity of adsorption of the daughter product, due to its incorporation into the colloidal form of the parent material. Adsorption of genetically bound radioisotopes ^{137}Cs and ^{137}Ba on polyethylene and fluorothene was studied, and it was found that the parent radioisotope forms a colloid with the tetraphenylboron anion.[86] The results were compared with those obtained by dialysis.[86]

D. SELF-DIFFUSION

The results are summarized in Table IV. The transition of radioactive ions into the colloidal state can be inferred from the slowing-down of their self-diffusion in solution. From

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the determined values of the self-diffusion coefficient and from the viscosity of the medium and assuming a spherical form, the radius of particles can be calculated from the relation

$$D = kT/6\pi\eta r$$

where D = the self-diffusion coefficient, cm^2/sec; k = the Boltzmann's constant; η = the viscosity of the medium, P; T = the absolute temperature; and r = the radius of particles, cm.

The diffusion coefficients of a number of radionuclides such as ^{140}Ba, ^{89}Sr, ^{140}La, ^{95}Zr, ^{95}Nb, ^{103}Ru, and ^{132}Te were determined by the diaphragm method.[1] The colloidal states of ^{95}Zr and ^{95}Nb were manifested by low values of their self-diffusion coefficients. The radii of the respective particles were about 8–10 Å. For determination of the self-diffusion coefficient a modified method of diffusion in a capillary with one open end was used and the self-diffusion coefficients of Ce^{3+}, Zr^{4+}, Sr^{2+}, Am^{3+}, Th^{4+}, Pu^{4+}, and Np^{5+} were determined.[87–90] The values were mostly of the order of 10^{-6} cm^2/sec. For Zr(IV) the value was as low as 10^{-7} cm^2/sec at pH 7.5, the corresponding radius of particles being 50 Å.[89] The molecular weight of colloidal Pu as determined from the self-diffusion coefficient by Ockenden and Welch[91] was 4×10^3. By means of the capillary method the radius of particles of Po and of ^{212}(Pb + Bi) was determined.[92,93] Colloidal properties of ^{7}Be were found by Schweitzer and Nehls[12] by the self-diffusion method; the radius of particles was 22 Å. In another work[94] the self-diffusion coefficients of Ru(IV) and $Ru^{III}NO$ were determined as a function of pH and ionic strength of the solution. The formation of colloidal hydroxides of Ru(IV) and $Ru^{III}NO$ was found. A plot of the self-diffusion coefficient against the square root of the ionic strength of the solution passed through a minimum.

The self-diffusion method in the capillary was used for the study of self-diffusion of ^{155}Eu, ^{147}Pm, and ^{144}Ce in trace concentrations.[95] A plot of the self-diffusion coefficient against the pH was characterized by slowing-down of the rate of self-diffusion in an alkaline medium. After 100 hr of ageing no substantial change of particle dimensions occurred so that a relatively stable colloid is involved. The simultaneous self-diffusion of the trace element couples of ^{85}Sr and Fe(III) and of ^{85}Sr and Mn(IV) indicated, with increasing pH value, the interaction of ^{85}Sr with Fe(III) and Mn(IV) which become evident from the decrease in the values of the coefficients of self-diffusion because the adsorption of ^{85}Sr on trace colloidal Fe(III) and Mn(IV) hydroxides took place.[96] However, in the self-diffusion method coprecipitation of other trace ions and adsorption on impurities with gradually increasing concentration of hydroxyl ions cannot be excluded so that the determined self-diffusion coefficient need not correspond to the investigated radioactive microcomponent only.[95,96] The pH dependence of self-diffusion of some radionuclides is illustrated in Figure 1.

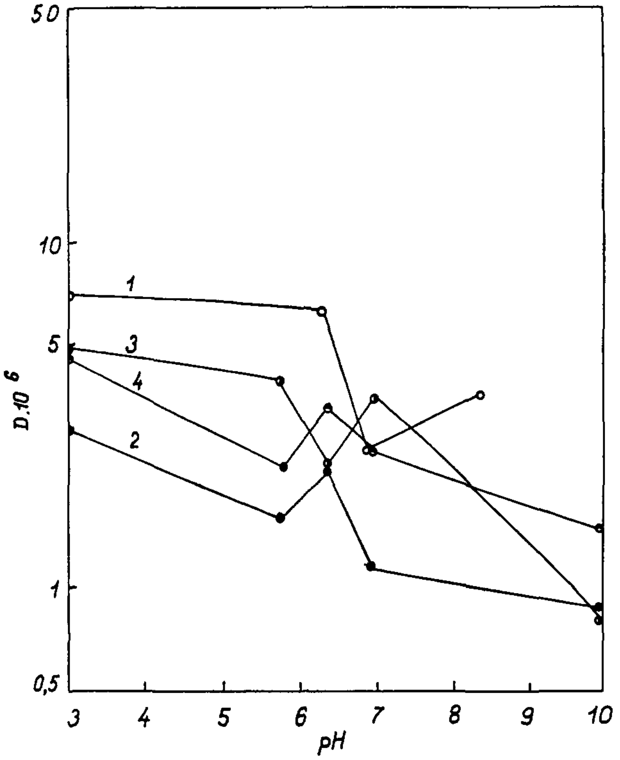

Figure 1. Self-diffusion coefficients of ^{106}Ru, ^{144}Ce, ^{147}Pm, and ^{155}Eu *vs.* pH.[94,95] Ionic strength μ = 0.01 (NaCl); D = self-diffusion coefficient, cm^2/sec: curve 1 for ^{106}Ru, curve 2 for ^{144}Ce, curve 3 for ^{147}Pm, curve 4 for ^{155}Eu.

E. DIALYSIS, ELECTROPHORESIS, AND OTHER METHODS

Results are shown in Tables V and VI. Dialysis of labeled manganese (5×10^{-8} *M*) and gold (10^{-7}–10^{-8} *M*) through a cellophane membrane and migration of trace manganese in an electric field as a function of pH, composition of solution, concentration of tracers, and time were investigated by Benes.[97] Formation of colloidal $Mn(OH)_3$ was found. At pH 0–8 manganese was present in the solution as Mn^{2+}, whereas above pH 8.5 a decrease of its dialysis was observed. Dialysis was used to study the state of Hg(II) in aqueous solutions.[23] Hg(II) diffused through the membrane, but the interpretation of results was rather difficult as dialysis was accompanied by intensive adsorption. The behavior of Ce^{3+} in solution was studied by paper electrophoresis and formation of radiocolloid was found.[98] Besides other methods, migration in an electric field was also used by Davydov[22] for studying the state of Eu. In a number of studies the sign change of the charge of the colloidal particles was investigated electrophoretically for Ru(III) and Ru(IV),[14] Am,[28] Zr,[30,54]

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Table V

Dialysis, Electrodeposition, and Foam Separation of Radionuclides

Radioelement	*Concn, M*	*pH*	*Method of separation*	*Separation, %*	*Notes*[a]	*Ref*
^{59}Fe	3×10^{-7}	9.2	Dialysis	1.2	cm, t	64
^{52,54}Mn	$<5 \times 10^{-8}$	10.0–12.0	Dialysis	10–0	cm, gr	97
^{233,231}Pa	Trace	3.0–3.4	Electrodeposition	>90	On gold-plated copper cathode, t	75
Po	2.7×10^{-13}–2.7×10^{-12}	1.3–2.1	Electrodeposition	100	On copper, t	105
^{106}Ru(IV)	1×10^{-6}	5.6	Foam	92	Dodecylamine, gr	104
^{106}Ru^{III}NO	1×10^{-6}	7.3	Foam	55	Dodecylamine, gr	104

[a] gr, value from the graph; t, value from the table or text; cm, cellophane membrane.

Table VI

Sign of Charge of Radionuclides

Radioelement	*Concn, M*	*pH and sign of charge*	*Notes*[a]	*Ref*
Eu	1.4×10^{-7}	2.3–5.2 5.8–8.0 8.7–11.1 + ± −	t	22
Mn	$<5 \times 10^{-8}$	3.0–9.0 10.0 11.0 12.0 13.0 + ± − ± −	t	97
Pa	10^{-11}–10^{-10}	1.0–6.0 7.0–11.0 12.0–14.0 ± − ±	t	32
Pa	10^{-13}–10^{-12}	1.1–5.5 7.1 ± −	t	33
Po	Trace	1.1 2.1 2.9 3.9–4.1 5.1–11.1 12.5 12.9–13.9 − + ± + − ± −	t	102
Po	Trace	2.0–3.0 4.0–6.0 7.0–11.0 12.0 13.0–14.0 ± + − ± −	t	103
Pu(IV)	2×10^{-5}	1.0–7.5 8.5 10.1–11.4 + ± −	t	80, 101
Pu(IV)	7×10^{-7}	1.0–2.6 3.2–3.5 4.4–10.6 + ± −	t	101
Pu(IV)	10^{-8}	1.8 3.1–7.2 10.0–11.2 + ± −	t	34
Pu(IV)	10^{-6}	2.0–6.0 7.0–8.0 10.7–11.6 + ± −	t	34
Ru(IV)	10^{-7}	1.09–4.09 5.17 6.05–10.11 + ± −	t	15
Ru(IV)	10^{-4}	5.0–5.55 6.7–10.7 + −	t	14
Ru(IV)	10^{-5}	4.3–9.8 4.8–10.5 + −	gr	104
Ru^{III}NO	10^{-5}	6.5–10.7 −	gr	104

[a] gr, value from the graph; t, value from the table.

Mn,[97] Pa,[32,33] Y,[99] U,[53,100] Pu,[34,80,101] and Po[102,103] as a function of pH of the solution. For polonium the electrophoretic mobility of colloidal particles was also determined.[102] The mobility values of polonium varied from 1.7×10^{-4} to 9.3×10^{-4} cm^2/(V sec).[102] The charge and electrophoretic mobility of colloidal particles of Ru^{III}NO and Ru(IV) as a function of pH were determined.[104] From the dependence of electrophoretic mobility on pH the isoelectric point of colloidal hydroxide Ru(IV) was found to be at pH 4.8.[104] Mobilities of colloidal particles of Ru(IV) and Ru^{III}NO were of the order of 10^{-4} cm^2/(V sec).[104]

Starik and Ampelogova[105] describe the electrochemical deposition of traces of polonium on copper, Schweitzer and Bishop refer to the electrodeposition of traces of Zn on Pt,[8] and Samartseva reports electrodeposition of traces of Am and Cm on a Pt cathode.[106] The highest deposition of polonium on copper was at pH 1–3 and 13; at pH 8–11 there was minimal polonium deposition (colloid was formed).[105] For detection of radio colloids the radiographic method, isotopic exchange, and other methods were also used.[3,5,17] For example, it

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was found by autoradiography that part of the colloidal particles of Po contain about 700–2500 atoms of Po, but mostly the colloid is composed of less than 100 atoms.[17]

F. SEPARATION AND APPLICATION OF RADIOCOLLOIDS

The tendency of some radionuclides to form colloids can be used for their effective separation. Kirby,[107] for example, used sorption of the hydrolytic products of Y on Teflon, glass, and metals for their separation from Sr, which was washed out by water. In the presence of a carrier, conditions for Freundlich's isotherm were satisfied. Kurbatov and Kurbatov[108] separated the same nuclides by using agglomeration of Y. Similarly, the coagulation of colloidal Zr made its separation from Y_2O_3 target possible. The coagulated fraction was separated by filtration through paper.[109] Schweitzer and Nehls[6] also separated ^{90}Y from ^{90}Sr with the knowledge that ^{90}Sr remains dissolved in strongly alkaline solutions, whereas ^{90}Y forms aggregates which can be filtered off. ^{90}Sr and ^{90}Y were adsorbed on an NH_4-form Dowex 50-X4 column, and the radiocolloidal ^{90}Y was eluted with methanol or ethanol. The NH_4-form was chosen because its basicity facilitates the formation of radiocolloids.[110] Also the separation of ^{140}La from ^{140}Ba is based on the colloidal properties of La, which in colloidal form is filterable.[13] This colloid is formed from the slightly acidic up to the alkaline pH region. Duval and Krubatov[111] separated Sc from calcium target by filter paper; the maximum of adsorption of Sc was between pH 7 and 9. By paper electrophoresis radionuclides that were transformed into the colloidal state were distinguished from those which remained as ions. Elements such as ^{137}Ba, ^{90}Y, and ^{144}Ce formed colloids and did not migrate, whereas the velocities of ions of ^{137}Cs, ^{86}Rb, ^{24}Na, ^{42}K, and ^{131}I were in the range of 5–8 cm/hr.[112] Radioruthenium was separated from the aqueous phase by adsorption on ferrous hydroxide under conditions when mostly colloid is formed.[38] Also foam separation of Ru(IV) and $Ru^{III}NO$ by the surface-active compound dodecylamine was effective under conditions at which a part of the ruthenium was transformed into the colloidal state.[104] The presence of radionuclides in the molecular form was detected by extraction with trimethyl phosphate, as neutral complexes of the type $[M(NO_3)_p]^0$ were extracted more significantly.[103] The radiocolloids are often used in biological and medical research, and in medical diagnosis and therapeutics,[113–126] but in these cases the colloids are not predominantly used in trace concentrations. Among the radioisotopes applied in these fields to a considerable extent, we may mention, *e.g.*, Pu,[127–131] Au,[132–145] P,[146–149] Tc,[150–157] and others.[158–161]

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III. Analysis and Evaluation of Results

The reproducibility of the results was 10,[24] 15,[51] 15–20,[52] and 12.7%,[95] and the tables show that the results obtained by the individual authors sometimes differ. The validity of the published values need not be general, and in some cases they are valid only for the given system and experimental arrangement.

The chemistry of radioelements in trace concentrations is concerned partly with the study of the colloidal state of these elements and partly with adsorption of trace elements on various surfaces. The adsorption of trace elements on surfaces can be explained by common mechanisms: ion exchange, physical adsorption, and electrostatic attraction. The high adsorption of trace radioelements on the surface of various materials under certain conditions and during filtration is of practical significance and its neglect could lead to an erroneous interpretation of experimental data. Such conditions can be chosen, under which the adsorption does not take place or is negligible. As to radiocolloids, views on their formation and on the nature of the colloidal particles are not uniform. Starik expressed the opinion that radiocolloids can be formed only from radioactive material, even though in trace concentration, but the solubility product must be reached[5,49,50] (so-called "true colloids"). The transformation of a radionuclide into a true colloid is characterized by a lowering of its adsorption on negatively charged surfaces.[49] The second view is that radiocolloids are only adsorption entities formed by adsorption of the respective radionuclide on impurities accidentally present in the solution[2,4,5] (so-called "pseudocolloids"). Radiocolloids are also defined as agglomerates formed at microconcentrations of the order of 10^{-8} M and lower which can be identified by means of radiation.[2,26,109] Schweitzer and Jackson[39] state further that adsorption need not be of primary importance for their formation. Formation of true radiocolloids is possible only at concentrations greater than 10^{-5} M when adsorption on impurities can already be neglected.[101] This corresponds, however, to the range of common concentrations. According to Kirby[107] radiocolloid is an incorrect term and their classification on "true" and "pseudocolloids" is irrevelant. The term radiocolloid is ascribed to materials present in microconcentrations, the behavior of which differs from what can be expected for their behavior in a true solution.[20] Benes and Majer[162] have replaced the term "radiocolloid" by "trace colloid," since the former should denote that it was determined radiometrically. A trace element can be incorporated into the solid phase of another compound, can assume the properties of the compound present in an excess, and can lose its individual chemical properties. The concentrations of impurities of hydrolyzable elements such as Fe, Pb, Zn, Sr, and Mn in distilled water and chemicals is of the order of 10^{-9}–10^{-7} M,[163] so that the behavior of traces can hardly be explained without a knowledge of their interaction with impurities.[95,96,162] The mutual interaction between radioactive ion and trace colloidal hydroxides was found by the method of self-diffusion.[96]

Schubert and Conn[1] and Schweitzer and Jackson[2] dealt with radiochemical behavior of some fission products, and according to these authors radiocolloidal behavior is manifested (1) by slowing down of diffusion, (2) by settling of radioactive components in the solutions by centrifugation or action of gravitational forces, (3) by coagulation or peptization by an electrolyte, (4) by anomalous course of adsorption on finely dispersed particles in the solution or on vessel walls, (6) by incomplete exchange or by not reaching the equilibrium between radioactive and nonradioactive isotope of the same element, (7) by incapability to diffuse through a membrane, permeable for ions, (8) by inhomogeneous distribution of radioactive material as found by autoradiography. Radioelements in highly diluted solutions can be present in four states: ionically dispersed, molecular, true colloidal, and adsorption-colloidal. Several forms can coexist in the solution, *e.g.*, colloidal and ionic dispersions.[5]

A study of the influence of the intrinsic radiation on the formation of the colloid showed that low radioactivity has no influence on the formation of radiocolloids.[24] Radioactive Eu formed the same colloid at radioactivity of 0.5 μCi/ml as nonradioactive Eu. With the exception of the level of radioactivity at which the composition of the solvent is considerably changed by radiation, the chemistry of stable and radioactive elements is the same. The same opinion also has been expressed by Kirby.[107]

In some studies conditions for the formation of true colloids of the given material were determined experimentally, and the solubility products were obtained from these results.[5,49] However, the solubility products cannot be obtained[164] from these data as radiocolloids are not in thermodynamic equilibrium; aggregation and peptization of micelles occur, on which adsorption and desorption of ions take place. Separation methods of phases also influence the formation of a colloid and the attainment of the state of equilibrium. The separation of a solid phase depends on the method used (centrifugation, dialysis, and electrochemical precipitation), the age of the solution, and the method of preparation of the solution. The data can be related only to the solubility of the compound but cannot be considered for the calculation of thermodynamic constants. It is necessary to take into consideration the possibility of coprecipitation with the other microcomponent. The stability of the composition of the precipitate depends not only on the pH of the solution but also on the ratio of ions M^{n+} and H^+. If at the same pH the concentration of the metal varies by an factor of 10^5 to 10^{10}, the measured solubility may be related to other compounds. In Starik's method for resolution of true colloids it is assumed that adsorption properties of macroscopic sorbents qualitatively agree with the properties of trace impurities of the same chemical composition, *e.g.*, in the dependence of adsorption on pH. However, this may not be generally true as we have to take into consideration a high sensitivity of adsorption at trace concentrations toward external factors, *e.g.*, the action of H^+ ions which compete with metal ions.[164]

These difficulties were corroborated when the solubility product of $Ce(OH)_3$ was determined[98] on the basis of a study of the colloidal behavior of Ce(III) in 10^{-11} M concentration by the method of filtration and paper electrophoresis.[98] Its value equaled 10^{-35}, while that presented in tables and obtained by the usual methods is 1.4×10^{-20}. The solubility of the amorphous form differs from that of the

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crystalline one and depends on the particular state in which the amorphous material exists.[165] In these systems the law of mass action cannot be used. The solid phase must be represented only by $Me(OH)_n$, which must be in an equilibrium with the dissolved forms.

$$Me(OH)_n(s) \rightleftharpoons Me(OH)_n(l) \rightleftharpoons Me_n^+ + nOH^-$$

The validity of the constant is verified by the check of its stability against a change of variables. Owing to hydrolysis and polymerization, polynuclear complexes Me–O–Me or $[Me(OH)^{(n-1)+}]_m$ and $Me_p(OH)_q$ are formed. The value of the solubility product cannot be applied over the whole range of hydroxide precipitation. From the value of pH at which precipitation begins, the solubility product cannot be derived; it is necessary to know which hydrolyzable form polymerizes and under which conditions. For example, the following reactions take place with Pu.

$$Pu^{4+} + 2H_2O \rightleftharpoons PuOH^{3+} + H_3O^+ \qquad K_1 = 0.025$$

$$Pu(OH)^{3+} + 2H_2O \rightleftharpoons Pu(OH)_2{}^{2+} + H_3O^+ \qquad K_2 \cong 0.025$$

$$Pu(OH)_2{}^{2+} + 2H_2O \rightleftharpoons Pu(OH)_3{}^+ + H_3O^+ \qquad K_3 = 3.3 \times 10^{-3}$$

$$Pu(OH)_3{}^+ + 2H_2O \rightleftharpoons Pu(OH)_4 + H_3O^+ \qquad K_4 = 7.2 \times 10^{-6}$$

A change in the concentration of OH^- at a constant concentration of Me^{n+} in solution results in the change of the composition of the forming precipitate, and the solubility product becomes an undefined quantity because we do not know the exact composition of the precipitate. The precipitate is formed with a varied ratio of OH^- and Me^{n+}, and the solubility product evaluated from the values of pH at which precipitation of hydroxides starts cannot be related to the whole interval of hydroxide precipitation.[101] Reaching the value of the solubility product need not necessarily mean that true colloid must be formed.[101] If the radioelement is hydrolyzed in the solution, colloidal forms are produced which are adsorbed with hydrolyzable forms on the impurities. In order to form true colloids without adsorption of hydrolyzable forms on the surface of impurities, the transformation into true colloids must be faster than adsorption. According to the theory of precipitation in solutions, a rather high oversaturation is required in order to form a new solid phase, so that a mere attainment of the solubility product need not be a satisfactory condition for the formation of a precipitate.[166] Here it must be taken into consideration that not the precipitation of the crystalline phase but the formation of colloidal particles is necessary, so that the degree of oversaturation need not be so large. The dimensions of particles of the formed solid phase depend on two factors: the rate of nucleation, W (in crystallization centers), and the growth rate of the crystal, Q.[167] The dispersion degree is proportional to the ratio of W/Q. All factors which speed up nucleation and slow down the crystallization make the formation of colloidal particles possible. In other words, the formation of colloidal particles depends on the oversaturation of the solution. If the total number of ions in solution is rather low, the nuclei cannot grow and a sol is formed. Its ageing depends on the Brownian movement and increases with temperature; for some colloids the ageing depends on their solubility; for those with higher solubility it is faster. Impurities and foreign ions accelerate ageing.[167] In the solutions of trace concentrations or microconcentrations, the number of ions of the radioactive component is rather low so that conditions for sol formation are from this point of view favorable. From the measurement of self-diffusion of colloidal hydroxides of Ru(IV), $Ru^{III}NO$, Ce(III), Pm(III), and Eu(III), no coagulation occurred after 100 hr of ageing, which means that a stable colloid is involved.[94,95] For Po, ageing also had no influence on the filtrable fraction.[17] With regard to the number of molecules, it is possible to form particles of colloidal dimensions from trace elements.[1] Formation of radiocolloids of Ru(IV), $Ru^{III}NO$, Ce(III), Pm(III), Eu(III), and others was detected by the self-diffusion method, but it cannot be proved whether the diffusing colloid is formed solely of radioactive microcomponent or of adsorption colloid with other nonradioactive microcomponents.[94,95]

Colloidal properties of Y are explained by its ion-exchange adsorption with particles suspended in solution,[78] whereas the formation of colloidal Hg[97] and Co(II)[57] is explained by adsorption or coprecipitation with foregin particles. Radiotracer zirconium formed colloids in nitric acid with precipitant phenylarsonic acid.[168] The tendency toward colloid formation is related to hydrolyzability and low solubility.[169,170] Radioactive materials are adsorbed on impurities which have no defined nature, and hence the behavior of the radiocolloid tends to be irreproducible.[20] With respect to the fact that the presence of various ions and colloidal particles in the solution cannot be excluded, the formation of a radiocolloid is more likely due to heterogeneous nucleation with submicroscopic particles, which pass into the solution from the walls of vessles and from chemicals, and by changing the pH at which precipitation took place. Because of differences in the chemical nature and mutual nonadsorbability, besides colloidal impurities there may exist also radiocolloids formed of radioactive matter only. Pseudocolloids, also can be formed from radionuclides, the hydroxide of which is soluble and does not have colloidal properties.[96] There exist often in parallel more forms of radiocolloids, which result in a more difficult separability, as each kind of such a radiocolloid has its own distribution coefficient[48] so that the attainment of their most effective separation is hindered.

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