Fig. 2.

the rings and that with this lost the complex becomes more and more difficult to form and also less and less stable. This is in agreement with observations at this laboratory that 3,3'-dicarboxy-2,2'-bipyridyl gives no complex with ferrous iron.[13]

We intend to inspect the ultraviolet absorption of the bases themselves as a further check on the postulates above.[14]

Acknowledgment.—We wish to thank Professor J. O. Kraehenbuehl of the Electrical Engineering Department of the University of Illinois for the curves with the General Electric recording spectrophotometer and Miss Ruth M. Johnston for special measurement of unstable solutions on the Beckman spectrophotometer.

Summary

1. The ferrous complexes of 3,3'-dimethyl-2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl and 5,5'-dimethyl-2,2'-bipyridyl have been prepared and their absorption spectra have been studied.

2. An explanation is offered for the much smaller molecular extinction coefficient of 3,3'-dimethyl-2,2'-bipyridyl ferrous complex compared with the other two and that of the 2,2'-bipyridyl complex.

3. The ferrous complexes of 4,4'-dimethyl-2,2'-bipyridyl and 5,5'-dimethyl-2,2'-bipyridyl conform to Beer's law over the range 0.00003 to 0.0002 mole/1000 g. of solution.

This is very probably due to the crowding of the methyl groups in the base and the resulting noncoplanarity of the pyridine rings. It seems reasonable to assume that the stabilities of the complexes are dependent on resonance between

(13) F. P. Richter, Ph. D. Thesis, University of Illinois (1941).

(14) For some recent work in this direction see: W. H. Rodebush, and I. Feldman, THIS JOURNAL, **68**, 896 (1946).

The Measurement of Potentials at the Interface between Vitreous Silica and Solutions of Thorium Chloride and Lanthanum Chloride

BY LLOYD A. WOOD[1] AND LAWRENCE B. ROBINSON[2]

Earlier papers[3] have described the improved apparatus for the measurement of streaming potentials and have reported the measurement of the zeta-potential of vitreous silica in contact with pure water, and with potassium chloride and barium chloride solutions. Herein are reported measurements with thorium chloride and lanthanum chloride solutions.

Experimental

Thorium chloride was prepared by the method described by Jones and Frizzell,[4] yielding a white

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(3) (a) Grinnell Jones and L. A. Wood. J. Chem. Phys., **13**, 106 (1945); (b) L. A. Wood, ibid., **13**, 429 (1945); (c) THIS JOURNAL, **68**, 437, (1946); (d) L. A. Wood and L. B. Robinson, J. Chem. Phys., **14**, 251 (1946).

(4) Grinnell Jones and L. D. Frizzell, ibid., **8**, 986 (1940).

hygroscopic solid of high purity. Professor Grinnell Jones kindly supplied a sample of lanthanum chloride which he had carefully purified.[5] The apparatus for producing and measuring the streaming potentials has been previously described,[3a] and consisted essentially of two Pyrex reservoirs connected by means of a vitreous silica capillary. The connections were made with ground joints sealed with paraffin wax which had been washed repeatedly, while melted, with boiling conductivity water. The solutions were forced through the capillary by nitrogen pressure, the gas having been passed in succession through tubes of soda lime and moist glass wool to remove carbon dioxide and dust. Silver–silver chloride electrodes were located at either end of the capillary to make possible the measurement of the stream-

(5) Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 602 (1934).

ing potentials and the electrical resistance of the capillary. The necessity for the latter measurement has frequently been overlooked by previous investigators, thus introducing a possible source of error into their measurements.[3a] The experiments were always carried out with duplicate sets of apparatus for two reasons: (1) The variety of data in the literature shows little consistency, and it is frequently observed that the identical or nearly identical experiments by different investigators have yielded different results. It is also found that there is a marked variation of the zeta-potential of the silica surface on standing in contact with the solution, during which time the potential appears to be approaching some equilibrium value.[6] Therefore, if measurements are made simultaneously with two different sets of apparatus over a period of time, one serves as a check against the other in approaching an equilibrium potential, even though the initial potentials may be quite different. It is reasonable to assume, when both reach and maintain the same potential, that this is the equilibrium zeta-potential. (2) The second reason is that a disparity between the two equilibrium zeta-potentials furnishes in itself information about the reproducibility of the measurements.

In order to start with a clean surface, the capillary surfaces were cleaned each time the apparatus was dismantled for changing the solution, by prolonged heating in nitric acid. The following data may be considered to demonstrate the efficacy of this treatment in removing thoriums ions, which are known to be particularly tenaciously held by glass surfaces: (1) The observed zeta-potential of silica in contact with pure water (specific conductance: 0.3×10^{-6} ohms^{-1} cm.$^{-1}$) was -177 millivolts. (2) Then 10^{-3} M thorium chloride was caused to flow through the capillary for four hours. After washing the capillary with water and steam, the zeta-potential with pure water was -89 millivolts. (3) The capillary was then washed with hot saturated potassium chloride solution (in an attempt to displace adsorbed thorium ions by potassium ions), followed by water and steam, and the observed zeta-potential with pure water was -69 millivolts. (4) The capillary was washed with hot concentrated nitric acid, followed by water and steam, and the zeta-potential with pure water was found to be -172 millivolts. The difference between potentials (1) and (4) is within the limit of error for measurements with pure water, so it may be concluded that the nitric acid essentially restored the original potential to the capillary surface.

Results

Thorium Chloride.—Streaming potential measurements were made with thorium chloride solutions over an extended period of time, in an effort to obtain a reliable value for the equilibrium zeta-potential. In general both with thorium

(6) See (3c) for a discussion of this.

chloride and with lanthanum chloride solutions, it was found that there was poor agreement between the initial zeta-potentials of the two capillaries, and that marked changes in the magnitude of the potential took place on standing a few days. In order to show examples of the data obtained and the general nature of the variations to be expected, some examples of individual streaming potential measurements are given in Table I. The zeta-potentials are computed from the equation of Helmholtz

$$\zeta = 4\pi\eta E\kappa/DP$$

in which η is the viscosity coefficient, E the streaming potential, κ the specific conductance of the liquid in the capillary, D the dielectric constant, and P the pressure which produces the flow. The values used for the various fundamental constants have been stated previously.[3b] The particular data given were selected from those obtained during the period when the systems were believed to be nearest the equilibrium potentials. The difference between the pairs of values, as, for example, between the zeta-potentials given for capillary II with the 10^{-3} M solution, was usually the result of a small asymmetry of the silver-silver chloride electrodes, and such errors would nearly cancel one another in averaging the potentials.

TABLE I

EXAMPLES OF INDIVIDUAL STREAMING POTENTIAL MEASUREMENTS

Capillary	Direction of flow	P, cm.	E, millivolts	R, $\Omega \times 10^{-6}$	κ, Ω^{-1}cm.$^{-1}$ $\times 10^6$	ζ, millivolts
(1.08×10^{-3} M ThCl$_4$, 26th day)
I	→	25.26	42.9	33.13	705.2	+115.7
I	←	24.96	42.0	33.13	705.2	+114.6
II	→	24.66	42.0	123.0	706.7	+116.3
II	←	24.50	40.6	123.0	706.7	+113.2
(1.08×10^{-4} M ThCl$_4$, 47th day)
I	←	26.06	428.0	235.3	99.3	+157.5
I	→	25.80	432.6	235.3	99.3	+160.9
II	→	27.42	448.5	862.1	100.8	+159.3
II	←	27.50	455.6	862.1	100.8	+161.4
(1.00×10^{-5} M ThCl$_4$, 38th day)
I	→	25.68	2798	1531	15.21	+160.6
I	←	25.30	2753	1536	15.21	+159.9
II	←	25.22	2555	5612	15.49	+151.6
II	→	25.10	2565	5621	15.46	+152.6
(1.00×10^{-6} M ThCl$_4$, 9th day)
I	←	16.45	5830	17,540	1.36	+ 46.6
I	→	16.15	5520	17,540	1.33	+ 43.9
II	←	19.10	4856	46,500	1.87	+ 45.9
II	→	18.50	4766	45,500	1.91	+ 47.5

In order to illustrate the data plotted in Fig. 1, a few typical averages of series of the individual measurements illustrated above are given in Table II. The "Time" is the number of days the solution had been in contact with the capillary,
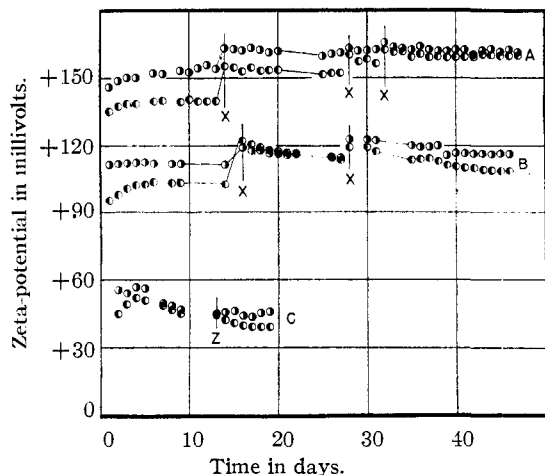
Fig. 1.—Variation with time of the zeta-potential of vitreous silica in contact with solutions of thorium chloride: A, 10^{-4} M; B, 10^{-3} M; C, 10^{-6} M ThCl$_4$. "X" denotes that the capillary was warmed before the group of measurements so designated. Before the measurements marked "Z," a fresh sample of solution was placed in the apparatus: measurements with capillary I, ◐; with capillary II, ◑.

and the "No." refers to the number of the individual measurements as in Table I which constitute the averages given. The "Average deviation" is that of the individual measurements from the mean value of the zeta-potential found with a given group of measurements.

TABLE II

EXAMPLES OF AVERAGE ZETA-POTENTIALS OBTAINED

Time. days	No.	$\kappa \times 10^6$ (Ω^{-1} cm.$^{-1}$)	ζ (mv.)	Av. deviation	$\kappa \times 10^6$ (Ω^{-1} cm.$^{-1}$)	ζ (mv.)	Av. deviation
				Capillary I			Capillary II
			(1.08 × 10^{-3} M ThCl$_4$)				
16	12	705.5	+122.7	0.6%	706.5	+119.1	1.3%
20	12	704.9	+117.4	1.6	706.7	+116.0	1.6
22	12	705.2	+116.4	2.7	706.7	+115.9	1.3
26	12	705.1	+115.0	0.5	706.4	+114.4	1.2
			(1.08 × 10^{-4} M ThCl$_4$)				
1	10	98.40	+135.4	0.4	99.09	+146.2	0.6
18	12	98.62	+153.2	0.7	99.52	+162.4	1.2
32	12	99.18	+162.5	0.7	100.83	+165.5	1.3
40	12	99.36	+159.2	1.2	100.96	+162.5	1.0
47	12	99.20	+158.6	1.0	100.83	+161.2	0.5
			(1.00 × 10^{-5} M ThCl$_4$)				
1	12	14.45	+129.5	1.4	13.17	+111.4	5.8
14	12	15.37	+164.7	0.5	14.76	+133.7	0.7
30	18	15.01	+159.0	0.4	15.37	+150.2	0.2
38	18	15.16	+160.8	0.6	15.50	+151.3	0.7
			(1.00 × 10^{-6} M ThCl$_4$)				
2	18	1.28	+ 45.0	2.0	1.31	+ 55.7	0.5
7	24	1.33	+ 48.7	1.6	1.73	+ 49.7	2.6
9	12	1.39	+ 45.2	2.6	1.87	+ 46.9	1.0
13	18	1.28	+ 44.3	2.5	1.70	+ 44.9	1.1

The measurements with solutions of thorium chloride are summarized in Figs. 1 and 2. Each point in the illustration represents an average zeta-potential as given in Table II. The usual disparities between the zeta-potentials of the two
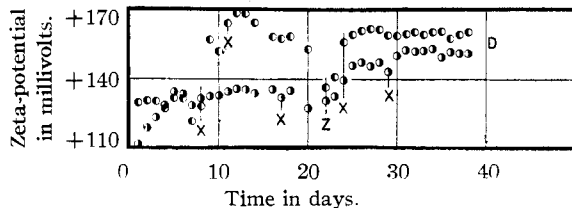

Fig. 2.—Variation with time of the zeta-potential of vitreous silica in contact with 10^{-4} M thorium chloride (see legend for Fig. 1 for explanation).

capillaries initially are clear evidence of the unreliability of many measurements in the literature. It is reasonable to interpret the subsequent variation as an approach to a reproducible equilibrium potential, but the discouraging slowness of the change raises the question of whether it is worth while to pursue the measurements until it is reached. In an effort to speed up the change, the capillaries were heated while the solution was flowing through them, prior to the measurements marked X, with some success. In Fig. 1, curve B, are summarized the measurements with 1.08 × 10^{-3} M thorium chloride. The most probable equilibrium value of the zeta-potential was considered to be +114 millivolts, the average of the potentials on the 26th and 27th days. The subsequent measurements substantiated this conclusion, the zeta-potentials on the final day being +109.2 and +116.4 millivolts. With 1.08 × 10^{-4} M thorium chloride, as summarized in curve A, the zeta-potentials were essentially constant from the 38th to the 47th days, giving averages of +159.5 and +161.8 millivolts for capillaries I and II, respectively. The mean of these and most probable equilibrium potential was +161 millivolts. The measurements with 1.00 × 10^{-5} M thorium chloride are summarized in Fig. 2. The variations were more irregular than with the above two solutions, and the closest approach to a stationary equilibrium potential was observed from the 31st to the 38th days, with average potentials of +159.9 and +151.8 millivolts for capillaries I and II, respectively, over that period. The mean of these, +156 millivolts, was considered the most probable equilibrium zeta-potential for this solution. The measurements with 1.00 × 10^{-6} M thorium chloride are summarized in Fig. 1, curve C. After irregular variation, the potentials of the two capillaries attained a potential of +46 millivolts on the ninth day. A fresh solution was substituted, and the first measurements, obtained with the previously aged surface, showed substantial agreement at about +45 millivolts, which was accepted as the most probable equilibrium zeta-potential.

Lanthanum Chloride.—In order to illustrate the data obtained, pairs of streaming potential measurements obtained with each capillary on the last day of measurements with each solution are given in Table III. In Table IV are given summaries of the data obtained on four days with each

solution. The data from the two days near the beginning are intended to illustrate the initial variation, and the data from the two days near the end of the measurements are intended to demonstrate the relative constancy and reproducibility at that time. The "No." represents the number of individual streaming potentials which constitute the average for each capillary.

TABLE III

EXAMPLES OF INDIVIDUAL STREAMING POTENTIAL MEASUREMENTS

Successive measurements made on last day of observation

Capillary	Direction of flow	P, cm.	E, millivolts	R, $\Omega \times 10^{-6}$	Ω^{-1}cm.$^{-1}$ $\times 10^{6}$	ζ, millivolts
		(1.00 $\times$ 10^{-3} M LaCl$_3$)				
I	←	26.48	11.4	58.31	400.7	+16.7
I	→	26.24	12.5	58.31	400.7	+18.4
II	←	25.93	9.8	216.6	401.2	+14.7
II	→	25.73	11.7	216.6	401.2	+17.6
		(2.50 $\times$ 10^{-4} M LaCl$_3$)				
I	←	33.92	13.7	224.8	103.9	+ 4.1
I	→	33.65	13.2	224.8	103.9	+ 3.9
II	←	33.08	4.1	837.5	103.8	− 1.2
II	→	33.27	3.0	837.5	103.8	− 0.9
		(1.00 $\times$ 10^{-4} M LaCl$_3$)				
I	→	32.91	111.0	540.5	43.23	−14.1
I	←	32.35	100.1	540.5	43.23	−12.9
II	→	32.27	110.7	2105	41.29	−13.7
II	←	32.13	109.6	2105	41.29	−13.6
		(5.00 $\times$ 10^{-5} M LaCl$_3$)				
I	→	36.38	213	1005	23.25	−13.2
I	←	35.84	200	1005	23.25	−12.5
II	→	35.56	241	3711	23.42	−15.3
II	←	35.51	255	3711	23.42	−16.2
		(1.00 $\times$ 10^{-5} M LaCl$_3$)				
I	→	33.36	1971	4815	4.85	−27.7
I	←	33.06	1957	4805	4.86	−27.8
II	→	32.74	1927	17,010	5.11	−29.1
II	←	32.40	1936	17,000	5.11	−29.5

The results of the measurements with lanthanum chloride are shown in Figs. 3 and 4. Curve A represents the zeta-potentials with 1.00 $\times$ 10^{-3} M lanthanum chloride; curve B, with 2.50 $\times$ 10^{-4} M; curve E with 5.00 x 10^{-5} M; and the curve D, with 1.00 $\times$ 10^{-5} M. Each point again represents the average zeta-potential computed from about twelve streaming potential measurements. Preceding the measurements marked X, the capillary was warmed, resulting usually in an abrupt change of the zeta-potential. Preceding the measurements marked Y, the capillary was rinsed with hydrochloric acid, following a suggestion of Jones and Stauffer[7] to remove a possible deposit of lanthanum hydroxide, formed by hydrolysis. This cleaning procedure caused the zeta-potential to change abruptly, and measurements were then

(7) Grinnell Jones and R. E. Stauffer, THIS JOURNAL, **62**, 33 (1940).

TABLE IV

EXAMPLES OF AVERAGE ZETA-POTENTIALS OBTAINED

Time. days	No.	Capillary I $\kappa \times 10^{6}$ Ω^{-1} cm.$^{-1}$	ζ, mv.	Av. deviation, milli-volts	Capillary II $\kappa \times 10^{6}$ Ω^{-1} cm.$^{-1}$	ζ, mv.	Av. deviation, milli-volts
		(1.00 $\times$ 10^{-3} M LaCl$_3$)					
1	12	400.1	+11.4	1.1	400.6	+ 9.6	2.1
4	12	400.5	+15.8	2.0	398.9	+16.1	2.1
6	12	400.3	+16.9	0.6	399.6	+15.8	0.9
7	12	400.7	+17.4	0.6	401.0	+16.1	1.2
		(2.50 $\times$ 10^{-4} M LaCl$_3$)					
1	4	102.2	+ 1.5	0.3	98.9	− 1.8	0.6
4	12	103.2	+14.0	.4	103.0	− 1.3	.6
17	12	104.2	+ 2.4	.3	103.3	+ 1.3	.4
20	12	103.9	+ 3.9	.1	103.9	− 0.9	.2
		(1.00 $\times$ 10^{-4} M LaCl$_3$)					
1	12	43.23	−16.7	0.2	42.05	−17.1	0.5
4	6	42.64	− 9.2	.8	41.24	−15.8	.1
12	12	43.13	−16.6	.5	42.11	−14.4	.1
16	12	43.02	−12.7	.9	41.46	−13.6	.1
		(5.00 $\times$ 10^{-5} M LaCl$_3$)					
1	4	22.22	− 8.1	0.8	22.15	−10.8	0.4
4	12	22.13	− 4.5	.2	22.07	− 7.3	.8
13	12	23.17	−13.7	.2	23.33	−15.6	.4
16	12	23.24	−12.9	.3	23.40	−14.6	.9
		(1.00 $\times$ 10^{-5} M LaCl$_3$)					
1	6	4.77	−34.9	0.6	5.08	−37.8	0.3
5	12	4.78	−26.8	.7	5.20	−36.2	.7
22	12	4.78	−27.8	.1	5.06	−29.2	.3
24	8	4.82	−27.5	.2	5.17	−29.2	.2

carried out until a reasonable constancy was reached. However, it was not thought worth while to continue them to the same lengths of time as had been done with the thorium chloride measurements.

The zeta-potential values selected as most probable were the averages for the final day of the observations in each instance, because it was thought that the diminishing variations observed preceding the final values indicated a close approach to equilibrium, and usually the two capillaries yielded values in substantial agreement. These zeta-potentials with the lanthanum chloride solutions are given in Table V.

TABLE V

Concn. moles/liter	Zeta-potential, millivolts	From curve	Difference between I and II, millivolts
10^{-3}	+17	A	1.3
2.5 $\times$ 10^{-4}	+ 2	B	4.8
10^{-4}	−13	C	0.9
5 $\times$ 10^{-5}	−14	E	1.7
10^{-5}	−28	D	1.7

The differences between the zeta-potentials obtained from capillaries I and II on the final day of observation are given in the last column, and only in the instance of the 2.5 $\times$ 10^{-4} M solution were the potentials more than two millivolts apart.

Discussion

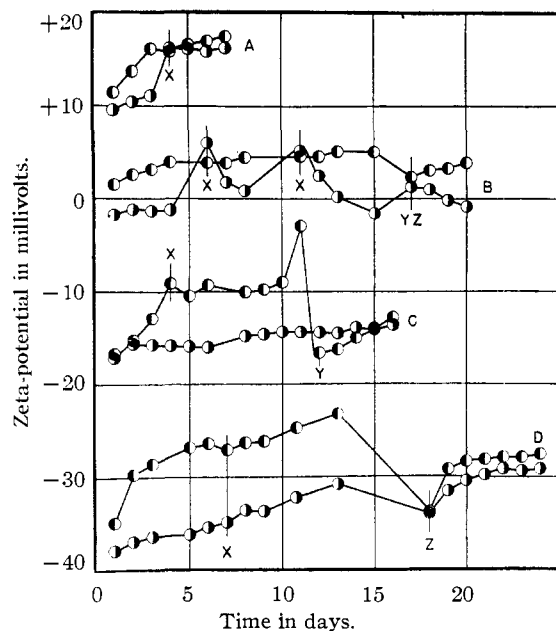The zeta-potentials reported here are plotted in Fig. 5 as functions of the logarithm of the con-

Fig. 3.—Variation with time of the zeta-potential of vitreous silica in contact with solutions of lanthanum chloride: A. 10^{-3} $M;$ B, 2.5×10^{-4} $M;$ C, 10^{-4} $M;$ D, 10^{-5} M LaCl$_3$. "X" denotes that the capillary was warmed preceding the designated group of measurements. "Y" denotes that the capillary was rinsed with hydrochloric acid preceding the designated group of measurements. "Z" denotes that a fresh sample of solution was placed in the apparatus preceding the designated measurements: measurements with capillary I, ◐; with capillary II, ◑.
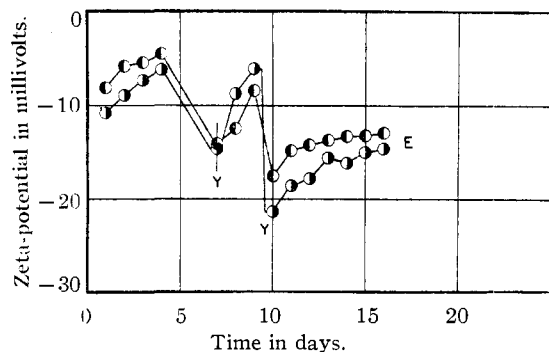

Fig. 4.—Variation with time of the zeta-potential of vitreous silica in contact with 5×10^{-5} M lanthanum chloride solution (see legend of Fig. 3 for explanation).

centration, along with the zeta-potentials obtained earlier for silica in contact with solutions of potassium chloride (curve A) and barium chloride (curve B). The line W is the zeta-potential of silica in contact with pure water,[3c] which should be approached by all of the solutions as dilution is increased. It is evident that the shape and position of the lanthanum chloride curve C are essentially those which might have been expected from the earlier data of A and B. The thorium chloride curve D is unlike the others, although it is
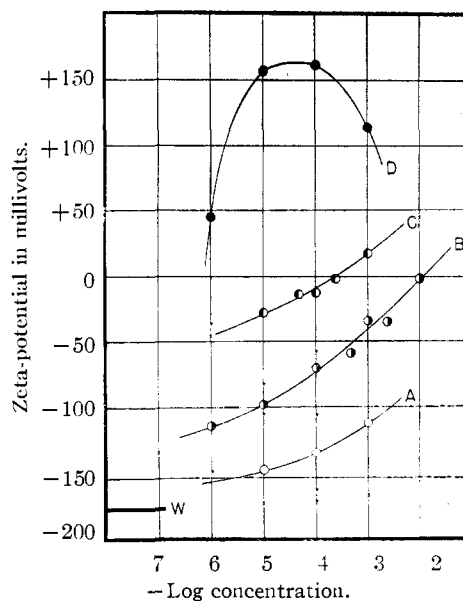

Fig. 5.—Comparison of experimentally determined zeta-potentials of vitreous silica in contact with various solutions: A, potassium chloride; B, barium chloride; C, lanthanum chloride; D, thorium chloride. The line W is the zeta-potential of the silica in contact with pure water.

possible that at higher concentrations A, B and C might also exhibit a maximum. Higher concentrations are at present outside the range of measurement of this apparatus. One reason, however, why the thorium chloride might be expected to give a different type of curve is that it hydrolyzes in dilute solutions, although not to the extent that thorium hydroxide precipitates. Measurements of the pH of thorium chloride solutions in this Laboratory indicate that at 10^{-5} M, there can be only a negligible amount of Th^{++++} in the solution, the first step of the hydrolysis having gone nearly to completion, although at 10^{-3} M 90% of the thorium is presumably in the form of this ion. The interpretation of the data on the hydrolysis is not completed, so that further comment ought not to be made.

Summary

Measurements of the zeta-potential of vitreous silica in contact with solutions of thorium chloride and lanthanum chloride have been made and are described. A comparison is made with earlier data obtained with potassium chloride and barium chloride solutions. The most probable equilibrium zeta-potentials were believed to be as follows

Concentration, moles/liter	LaCl$_3$, millivolts	ThCl$_4$ millivolts
10^{-3}	+17	+114
2.5×10^{-4}	+ 2	
10^{-4}	−13	+161
5×10^{-5}	−14	
10^{-5}	−28	+156
10^{-6}		+ 45