

The Electrical Potential at the Interface between Vitreous Silica and Solutions of Barium Chloride

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Citation: *The Journal of Chemical Physics* **14**, 251 (1946); doi: 10.1063/1.1724127

View online: <http://dx.doi.org/10.1063/1.1724127>

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Barrer using 5.0A for the mean free path in the case of the permanent gases. Even if these estimated values of d are doubled, ΔS^\ddagger is only reduced by about 3 e.u. This large value of ΔS^\ddagger , if it were all due to the diffusing molecule, would correspond to more than its entropy of solution. Since this is not possible, the medium must share in the entropy change. Thus the data on the diffusion of water vapor corroborate the conclusions reached by Barrer for permanent gases: that activation energy is shared in part or

wholly in various degrees of freedom of the polymeric system.

ACKNOWLEDGMENT

The experimental data reported here were obtained in the course of work sponsored by the National Research Council and the Research and Development Branch of the Office of the Quartermaster General. It is a pleasure to acknowledge the assistance of Miss Helen Luben in the experimental work.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 14, NUMBER 4

APRIL, 1946

The Electrical Potential at the Interface between Vitreous Silica and Solutions of Barium Chloride

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(Received February 18, 1946)

The zeta-potential of vitreous silica in contact with several solutions of barium chloride has been determined by the measurement of streaming potentials. Solutions of seven concentrations between $10^{-6} M$ and $10^{-2} M$, inclusive, were studied, and the zeta-potential was found to decrease in a regular manner with increasing concentration. It is evident that there is no maximum in the curve of the zeta-potential *vs.* concentration, as most experimenters have reported.

IT is the purpose here to report measurements of the zeta-potential of vitreous silica in contact with solutions of barium chloride. The zeta-potential is not directly measurable, but is obtained conveniently from measurement of streaming potentials arising from the flow of the solutions through vitreous silica capillaries. The physical significance of the streaming potential measurements and their relation through Helmholtz's equation to the zeta-potential have been critically examined elsewhere.¹ The apparatus and technique for obtaining the necessary reliable streaming potential data for the computation of zeta-potentials have been described previously,² together with measurements of the zeta-potential of silica in contact with dilute potassium chloride solutions. Added interest is lent to this investigation by the fact that the data obtained make

possible a test of Langmuir's interpretation³ of the Jones-Ray effect⁴ observed with barium chloride.

EXPERIMENTAL

The apparatus and experimental technique employed in this investigation have been described previously² and no important changes have been made. Duplicate sets of streaming potential apparatus with capillaries of different diameters were operated concurrently so that observations with one could be corroborated with the other. Previous work has demonstrated that initial measurements of the zeta-potential are not usually reliable, because the surfaces of the capillaries sometimes require many days to attain equilibrium with the solution. It has not

¹ L. A. Wood, *J. Am. Chem. Soc.* **68**, 432 (1946).

² Grinnell Jones and L. A. Wood, *J. Chem. Phys.* **13**, 106 (1945).

³ I. Langmuir, *Science* **88**, 430 (1938); *J. Chem. Phys.* **6**, 894 (1938).

⁴ Grinnell Jones and W. A. Ray, *J. Am. Chem. Soc.* **59**, 187 (1937); **63**, 288 (1941); **63**, 3262 (1941); **64**, 2744 (1942).

TABLE I. Examples of data obtained with $1.00 \times 10^{-3} M$ BaCl_2 (thirteenth day).

Flow	P cm	E milli- volts	R ohms $\times 10^{-6}$	κ ohms $^{-1}$ cm^{-1} $\times 10^6$	$E\kappa/P$ $\times 10^4$	ζ milli- volts
Capillary I						
$L \leftarrow L'$	24.90	33.2	87.71	266.4	3.55	-34.2
$L \rightarrow L'$	24.70	34.0	87.87	265.9	3.66	-35.4
Capillary II						
$L \leftarrow L'$	24.50	33.1	327.9	265.1	3.58	-34.6
$L \rightarrow L'$	24.10	32.8	326.8	266.0	3.62	-35.0

TABLE II. Summary of measurements with $1.00 \times 10^{-3} M$ BaCl_2 .

Time days	No. ^a	Capillary I			Capillary II		
		$\kappa \times 10^6$	ζ mv	Av. devia- tion	$\kappa \times 10^6$	ζ mv	Av. devia- tion
2	18	266.7	-37.0	1.1%	268.7	-33.0	2.7%
3	18	266.2	-35.7	0.6	268.0	-33.6	1.2
4	18	266.8	-35.7	0.6	268.2	-33.6	1.2
5	18	267.9	-34.9	0.3	268.2	-33.5	0.9
6	18	267.8	-34.7	0.6	268.3	-33.6	1.2
7	30	266.3	-34.3	0.6	267.6	-33.9	0.6
8	24	267.9	-34.1	0.6	268.0	-33.8	0.3
9	18	267.9	-33.9	0.6	267.9	-34.2	1.2
10	12	268.4	-34.7	0.6	268.2	-34.0	2.1
11 ^b	6	267.0	-34.7	0.7	266.2	-42.1	0.7
12	6	267.2	-34.4	0.3	266.6	-37.1	0.5
13	12	266.3	-34.6	1.7	265.3	-34.8	0.3

^a "No." denotes the number of individual measurements constituting the series summarized. Since each measurement was duplicated with Capillary II, the same number of measurements was made with each capillary. Four individual measurements are given in Table I.

^b A new sample of the solution was placed in each set of apparatus preceding this measurement.

been found possible to control the previous treatment of the surfaces so that the potentials are immediately reproducible, and the practice in this laboratory has been to study the variation of the zeta-potential with time until it was reasonably certain that the equilibrium potential was reached. The two capillaries were adjudged to have reached equilibrium when they reached the same value and remained unchanged for several days, but in general it was necessary to be satisfied with somewhat less than this ideal behavior. With solutions of barium chloride the approach to a constant value was much more rapid than with any of the solutions which have been studied in this laboratory at the date of writing, including potassium chloride, thorium chloride, and lanthanum chloride.

The capillary surfaces were prepared for measurements with solutions of a given concen-

TABLE III. Examples of data obtained with $1.00 \times 10^{-4} M$ BaCl_2 (fourteenth day).

Flow	P cm	E milli- volts	R ohms $\times 10^{-6}$	κ ohms $^{-1}$ cm^{-1} $\times 10^6$	$E\kappa/P$ $\times 10^4$	ζ milli- volts
Capillary I						
$L \leftarrow L'$	25.20	626.3	833.3	28.04	6.97	-67.3
$L \rightarrow L'$	24.90	623.2	826.5	28.27	7.08	-68.4
Capillary II						
$L \leftarrow L'$	24.50	680.7	3225	26.95	7.49	-72.3
$L \rightarrow L'$	24.26	660.7	3145	27.64	7.53	-72.7

tration by immersing them in hot nitric acid (redistilled) for a day or more. Then steam and hot water from a silica condenser was drawn through them for about an hour, in order to remove the nitric acid, followed by a final rinse while hot with about 20 cc of the solution about to be measured. This cleaning treatment was given the capillaries preceding a change in the concentration of the solution. It was found effective in establishing conditions for eventual agreement of the zeta-potential of the two capillaries within a few millivolts.

In obtaining streaming potential measurements, the experimental procedure was to apply a measured pressure difference, P , between the two reservoirs at either end of the connecting capillary, and while the solution was flowing through the capillary, the following measurements were made in rapid succession: the electrical resistance, R , of the capillary was measured, then three measurements of the streaming potential, E , and of the pressure, P , were made, followed by a second resistance measurement. Then the direction of flow was reversed under approximately the same pressure, and the above procedure was repeated. These measurements were usually repeated two or three times with somewhat different pressures. No dependence of the quantity $E\kappa/P$ on the pressure was ever observed.

In presenting the data obtained, it is impractical to give all of the large number of individual measurements, but in order to furnish examples of the experimental data, a representative example, selected at random, of the data obtained with each capillary will be given for each solution. Then a table summarizing the results of each series will be given. The measurements are

TABLE IV. Summary of measurements with $1.00 \times 10^{-4} M$ BaCl₂.

Time days	No. ^a	Capillary I			Capillary II		
		$\kappa \times 10^6$	ζ mv	Av. deviation	$\kappa \times 10^6$	ζ mv	Av. deviation
9 ^b	18	27.80	-67.6	0.4%	27.38	-72.3	0.4%
10	12	27.80	-67.2	0.3	27.28	-72.2	0.3
11	18	27.88	-67.1	0.4	27.62	-73.2	0.3
12	24 ^c	27.98	-67.7	0.4	27.71	-73.9	1.9
13	18	27.87	-67.4	0.4	27.26	-72.5	1.8
14	18	28.09	-67.7	0.4	27.43	-72.9	0.8
15 ^d	12	27.85	-66.8	0.7	27.06	-72.0	2.2

^a See footnote (a) in Table II.^b Preceding these measurements were earlier series. The first sample of the solution was found to give higher values for κ , so it was thought probable that it had inadvertently become slightly contaminated. Therefore a new sample of the solution was placed in the apparatus on the eighth day. The zeta-potentials determined with the first sample were somewhat lower than those above.^c As a result of experimental difficulties, only 18 measurements were obtained for Capillary II in this series.^d Following the preceding series, both capillaries were warmed to see whether any change in the zeta-potential would result. When there was no change, the measurements were discontinued.

discussed in the chronological order in which they were made, except for those with $10^{-6} M$ and $10^{-2} M$, which are discussed at the end. The temperature was $25^\circ\text{C} \pm 0.03^\circ$ in every instance. The values for the fundamental physical constants are taken from the tabulation of Birge,⁵ except the data for the dielectric constant and viscosity coefficient, which were assumed to be the same as for pure water, as given by Dorsey.⁶ The zeta-potential, ζ , is obtained from the equation of Helmholtz:^{1,7}

$$\zeta = (4\pi\eta E\kappa)/(DP),$$

in which η is the viscosity coefficient, κ is the specific conductance of the liquid in the capillary, and D is the dielectric constant, the other quantities being defined above.

Measurements

The behavior of the capillary surface with the $10^{-3} M$ BaCl₂ was unusual in that there was little variation and almost perfect agreement. Two individual measurements with each capillary are given in Table I. The large reservoirs at either end of the capillaries were identified as L and L' , and the direction of flow is indicated

⁵ R. T. Birge, Rev. Mod. Phys. 13, 233 (1941); Am. J. Phys. 13, 63 (1945).⁶ N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940), pp. 187 and 364.⁷ H. Helmholtz, Wied. Ann. 7, 337 (1879).TABLE V. Examples of data obtained with $1.00 \times 10^{-5} M$ BaCl₂ (eighth day).

Flow	P cm	E millivolts	R ohms $\times 10^{-4}$	κ ohms ⁻¹ cm ⁻¹ $\times 10^6$	$E\kappa/P \times 10^4$	ζ millivolts
Capillary I						
$L \rightarrow L'$	23.80	7420	6983	3.346	10.43	-100.8
$L \leftarrow L'$	23.50	7330	7113	3.285	10.25	-99.0
Capillary II						
$L \rightarrow L'$	23.20	6735	24,390	3.564	10.35	-100.0
$L \leftarrow L'$	23.10	6395	24,390	3.564	9.87	-95.3

TABLE VI. Summary of measurements with $1.00 \times 10^{-5} M$ BaCl₂.

Time days	No. ^a	Capillary I			Capillary II		
		$\kappa \times 10^6$	ζ mv	Av. deviation	$\kappa \times 10^6$	ζ mv	Av. deviation
2	18	3.523	-94.3	1.1%	3.697	-90.4	2.3%
3	12	3.521	-97.3	2.0	3.668	-90.4	1.4
4	24	3.489	-97.4	1.4	3.706	-90.5	2.5
5	18	3.462	-98.3	3.1	3.688	-92.8	3.7
6	6	3.290	-96.8	2.8	3.477	-88.8	5.1
7 ^b	24	3.299	-100.8	0.9	3.574	-97.3	1.7
8	18	3.292	-99.3	0.7	3.556	-96.7	2.1
9	18	3.306	-97.7	0.8	3.478	-93.6	2.2
10	18	3.400	-99.7	1.5	3.681	-97.3	2.3

^a See Note (a) of Table II.^b Preceding the measurements on the seventh day, the solution in both sets of apparatus was mixed by forcing all the solution into reservoir L and bubbling a small amount of nitrogen through it.

accordingly. It is believed that the precision of all the measurements is 0.5 percent or better. The two potentials given for each capillary are the first measurements of two successive series of three, as described above, carried out on the thirteenth day of observation. Ten other similar measurements were made on that day with each capillary. All the measurements made with this concentration of BaCl₂ are summarized in Table II. It was observed that the zeta-potential of Capillary I was initially -37.0 millivolt and on long standing decreased slightly to about -34 millivolt. The zeta-potential of Capillary II was -33 millivolt initially, and this increased slightly to about -34 millivolt on standing. When a fresh solution was substituted after the measurements on the tenth day, the potential of Capillary I appeared to be undisturbed, while that of the other capillary was considerably increased. Because the potential of Capillary II soon returned to about -34 millivolt, it was presumed that the equilibrium had been upset for some unknown reason but that it was soon

TABLE VII. Examples of the data obtained with $5.00 \times 10^{-4} M$ BaCl_2 (fifth day).

Flow	P cm	E milli- volts	R ohms $\times 10^{-6}$	κ ohms $^{-1}$ cm^{-1} $\times 10^6$	$E\kappa/P$ $\times 10^4$	ξ milli- volts
Capillary I						
$L \leftarrow L'$	24.18	105.5	175.0	133.5	5.82	-56.3
$L \rightarrow L'$	23.86	103.9	175.0	133.5	5.81	-56.2
Capillary II						
$L \leftarrow L'$	24.66	104.4	650.1	133.7	5.66	-54.7
$L \rightarrow L'$	24.46	106.2	650.1	133.7	5.80	-56.1

TABLE VIII. Summary of measurements with $5.00 \times 10^{-4} M$ BaCl_2 .

Time days	No. ^a	Capillary I			Capillary II		
		$\kappa \times 10^6$	ξ mv	Av. devia- tion	$\kappa \times 10^6$	ξ mv	Av. devia- tion
2	18	133.2	-55.1	0.4%	131.9	-53.8	1.1%
3	18	133.4	-55.7	0.4	132.4	-52.7	1.3
4	24	133.0	-55.6	0.4	131.5	-55.0 ^b	1.3
5	24	133.6	-56.1	0.4	133.2	-55.2	1.3
6	18	133.6	-56.3	0.2	133.0	-55.0	1.6
7	30	133.7	-56.5	0.3	133.6	-55.2	1.6

^a See Note (a) of Table II.^b The increase in the potential of Capillary II on the fourth day may be attributed to the fact that, preceding these measurements, the solution in reservoir L' was forced into reservoir L to remix the solution in order to eliminate the electrode asymmetry and decrease the average deviation. Although this did not result, the disturbance of the double layer caused by flow of the solution through the capillary apparently had the effect of hastening the attainment of equilibrium.

reestablished. The accepted value for the zeta-potential with this solution was -34 millivolt.

With $10^{-4} M$ BaCl_2 the observations were somewhat less satisfactory. In Table III are given individual measurements to serve as examples of the measured quantities, selected as in Table I. It will be noticed that with both capillaries there was a slight asymmetry of the observed zeta-potentials, which was the result of asymmetry of the silver-silver chloride electrodes. Such asymmetries were common occurrences, particularly with the more dilute solutions, and were ascribed to slight differences in concentration which arose in the solutions. These differences may have been caused by some of the silver chloride dissolving from the electrodes or by the glass of the reservoir walls dissolving, or by the ingress of some other impurity. The asymmetries could usually be eliminated, or greatly diminished, by remixing the solution, which was done by forcing all the solution into one reservoir and bubbling a small amount of nitrogen through it

for stirring. Then half the solution was forced back through the capillary to the empty reservoir so that the measurements could be continued. However, with $10^{-4} M$ BaCl_2 the asymmetries were not large enough to make this necessary, as is evident from the "average deviations" from the mean of each series as given in Table IV, the summary of the measurements with this concentration. Earlier measurements were made, but it was found that the conductivity figures were high as compared with those observed with the fresh sample of the solution placed in the apparatus on the eighth day of observation. Therefore the measurements prior to the ninth day were discarded. The zeta-potential of Capillary II was always about 5 millivolts higher than that with Capillary I, and there appeared to be no tendency for them to converge. However, the two values were considered to be in close enough agreement so that further work was unwarranted. The accepted value for the zeta-potential was taken as -70 millivolt, the average on the thirteenth and fourteenth days, when it seemed that constant values had been reached.

In Table V are examples of the individual measurements with $10^{-5} M$ BaCl_2 . In the in-

TABLE IX. Examples of the data obtained with $2.50 \times 10^{-3} M$ BaCl_2 (second day).

Flow	P cm	E milli- volts	R ohms $\times 10^{-6}$	κ ohms $^{-1}$ cm^{-1} $\times 10^6$	$E\kappa/P$ $\times 10^4$	ξ milli- volts
Capillary I						
$L \rightarrow L'$	27.34	16.8	36.32	643.3	3.95	-38.2
$L \leftarrow L'$	27.00	16.9	36.29	643.8	4.03	-38.9
Capillary II						
$L \rightarrow L'$	28.00	13.6	134.91	644.3	3.13	-30.2
$L \leftarrow L'$	27.80	13.9	134.95	644.1	3.22	-31.1

TABLE X. Summary of measurements with $2.50 \times 10^{-3} M$ BaCl_2 .

Time days	No. ^a	Capillary I			Capillary II		
		$\kappa \times 10^6$	ξ mv	Av. devia- tion	$\kappa \times 10^6$	ξ mv	Av. devia- tion
1	12	645.0	-38.5	0.3%	643.8	-30.6	2.0%
2	6	643.7	-38.6	1.0	644.1	-30.7	1.6
5	6	642.6	-38.6	0.3	642.2	-30.0	0.3
7 ^b	6	634.2	-37.9	0.5	635.4	-31.2	0.3
8	12	641.2	-38.1	0.5	640.5	-31.8	2.5

^a See Note (a) in Table II.^b A new sample of the solution was placed in both sets of apparatus preceding these measurements.

TABLE XI. Measurements with $1.00 \times 10^{-2} M$ BaCl₂.^a

Flow	<i>P</i> cm	<i>E</i> milli- volts	<i>R</i> ohms $\times 10^{-6}$	κ ohms ⁻¹ cm ⁻¹ $\times 10^6$	<i>E</i> / κ / <i>P</i> $\times 10^4$	ζ milli- volts
A. Examples of the data obtained (fourteenth day)						
<i>A</i> → <i>B</i> ^a	37.23	3.4	13.65	2369	0.216	-2.1
<i>A</i> ← <i>B</i>	40.64	3.2	13.73	2356	0.185	-1.8
B. Summary of the data						
Time days	No. ^b	κ $\times 10^6$	<i>E</i> / <i>P</i> av.	ζ milli- volts	Average deviation millivolts	
1	4	2363	0.114	-2.6	0.62	
14	12	2365	0.081	-1.84	0.21	
15	12	2369	0.081	-1.86	0.17	

^a The apparatus used for these measurements is that described in reference 8.

^b The "No." is the number of measurements which were averaged to yield the figures reported. Two such measurements are given in A.

stances given, there is a slight asymmetry in the values from Capillary I, and a much larger asymmetry with Capillary II. These were observed to some extent in all the measurements, summarized in Table VI, and were responsible for the larger average deviations. Mixing the solutions prior to the measurements on the seventh day decreased the asymmetry with both capillaries, but did not entirely eliminate it with either set of apparatus. However, averaging the zeta-potentials causes the cancellation of a constant asymmetry so that the accuracy of the measurements is greater than that indicated by the average deviation. The accepted equilibrium zeta-potential value was -98 millivolt, the average of the measurements on the tenth day.

The next solution measured was the $5 \times 10^{-4} M$ BaCl₂, and examples of individual measurements are given in Table VII. In the examples there appeared to be no asymmetry with Capillary I, but there was a noticeable amount with Capillary II. This is also evident from the figures for the average deviations in Table VIII, wherein all the measurements with this concentration are summarized. Little or no variation with time was observed with Capillary I, but there was a slight increase in the zeta-potential with Capillary II. The accepted value of the zeta-potential was -55 millivolt.

Measurements were then made with $2.5 \times 10^{-3} M$ BaCl₂ (see Table IX), which were somewhat more difficult to obtain because of the low streaming potential and the difficulty of determining the zero point for the resistance

measurements with the direct current bridge. The relatively high conductivity of the solution resulted in considerable polarization of the electrodes when the bridge current was applied, causing the zero point to shift. However, the measurements of *E* and *R* are considered accurate to better than 1 percent. Essentially constant zeta-potentials were observed with Capillary I, all at about -38 mv, a higher value than was observed previously with a more dilute solution. (See Table X.) With Capillary II, the zeta-potential was about -31 millivolt most of the time, reaching -32 on the last day of observation. Substituting a fresh solution after the measurements of the fifth day brought about no appreciable change in the zeta-potential of either capillary. The accepted value was -35 millivolt, the average of the measurements on the eighth day. Reference is made below to the fact that this is higher than the potential to be expected from the measurements with more dilute solutions. These results were less gratifying than those with the other concentrations, in that the two capillaries acquired potentials relatively far apart, and the accepted value was not as concordant with the other measurements as might be desired.

A few measurements were made with $10^{-2} M$ BaCl₂ in the simpler apparatus constructed for measurements with pure water previously described elsewhere.⁸ The greater ease of manipu-

TABLE XII. Measurements with $1.00 \times 10^{-6} M$ BaCl₂.^a

Flow	<i>P</i> cm	<i>E</i> milli- volts	<i>R</i> ohms $\times 10^{-6}$	κ ohms ⁻¹ cm ⁻¹ $\times 10^6$	<i>E</i> / κ / <i>P</i> $\times 10^4$	ζ milli- volts
A. Examples of the data obtained (third day)						
<i>A</i> ← <i>B</i>	18.52	10,007	14,790	2.187	11.81	-114.1
<i>A</i> → <i>B</i>	15.07	8,013	14,660	2.206	11.73	-113.3
B. Summary of the data						
Time days	No.	$\kappa \times 10^6$	<i>E</i> / <i>P</i> av.	ζ millivolts	Average deviation	
1	24	2.298	520.7	-115.7	0.6%	
2	24	2.415	504.3	-117.7	0.8	
3 ^b	36	2.250	527.3	-114.5	2.1	
4	24	2.310	513.0	-114.5	0.6	
5	22	2.315	523.0	-117.1	0.5	
6	12	2.339	504.7	-114.1	0.9	

^a The apparatus used for these measurements is that described in reference 8. Bright platinum electrodes were used instead of silver-silver chloride electrodes to avoid introduction of silver ions and additional chloride ions.

^b A new sample of the solution was placed in the apparatus preceding these measurements.

⁸ L. A. Wood, J. Am. Chem. Soc. 68, 437 (1946).

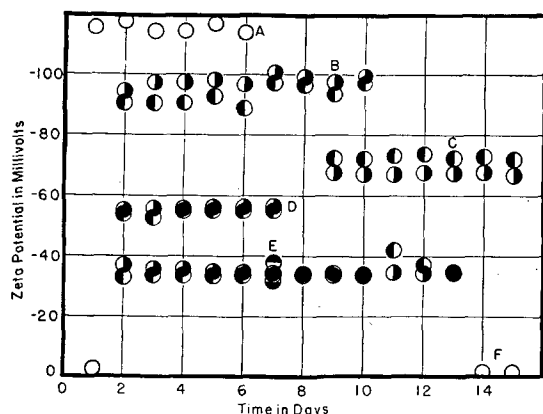


FIG. 1. Variation of the zeta-potential with time.

Data from all-silica apparatus: ○.
 Data from Capillary I: ●; data from Capillary II: ○.
 A: 10⁻⁶ M; B: 10⁻⁵ M; C: 10⁻⁴ M; D: 5 × 10⁻⁴ M; E: 10⁻³ M;
 F: 10⁻² M.
 Selected data for 2.5 × 10⁻³ M: ● for Capillary I; ○ for Capillary II.

lation of this apparatus, and the fact that the low streaming potential limited the accuracy of its measurement, rendered the use of this apparatus more desirable than the more elaborate apparatus employed in the above measurements. The results of the measurements with this concentration are given in Table XI. The conductance, κ , is calculated from R with the cell constant, (length)/(cross section), of 32,345. The summary of the data indicates that the zeta-potential with this solution is about -2 millivolt. While the percentage deviation is very large, because of the low streaming potential, the actual magnitude of the average deviation is comparable to that of the 10⁻³ M solutions.

Measurements were made with 10⁻⁶ M BaCl₂, using the same all silica apparatus. With such a dilute solution, it is particularly important to avoid the introduction of impurities either from the glass or the silver-silver chloride electrodes of the more elaborate apparatus suitable for use with less dilute solutions. Therefore the bright platinum electrodes were used, and since the liquid came in contact only with these and with the silica, this danger was avoided. However, the values obtained for the specific conductance were larger than would be expected, as can be seen from the data in Table XII. The water used in preparing the solutions was conductivity water which had been redistilled with a silica condenser, and should have had a κ of less than 0.5 × 10⁻⁶.

The conductance of 10⁻⁶ M BaCl₂ should have added about 0.28 × 10⁻⁶ to this value of κ for the water, giving a total κ of less than 0.8 × 10⁻⁶. However, it will be noted that the measured resistance of the capillary containing this solution was about 14,000 megohms, which gives a κ approximately three times larger than 0.8 × 10⁻⁶. This could be explained in several ways: (1) the solution had become contaminated, (2) the extra conductance was the result of surface conductance, and (3) some path existed for the current other than through the solution. If (1) was the true reason, then the results are in error, but if either (2) or (3) was responsible for the high κ , then the value for the zeta-potential is correct, because the quantity required for the calculation of the zeta-potential is in reality the resistance between the ends of the capillary, which is the quantity measured.¹ The accepted value of the zeta-potential for this concentration is -115 millivolt, but it must be considered less certain than the values for the other solutions.

In order to show the relative constancy and concordance of the measurements, the zeta-potentials are plotted in Fig. 1 as functions of time, except for the 2.5 × 10⁻³ M solution which would have been so intermingled with the 10⁻³ M solution data as to be confusing. The data for the seventh day from Table X for the 2.5

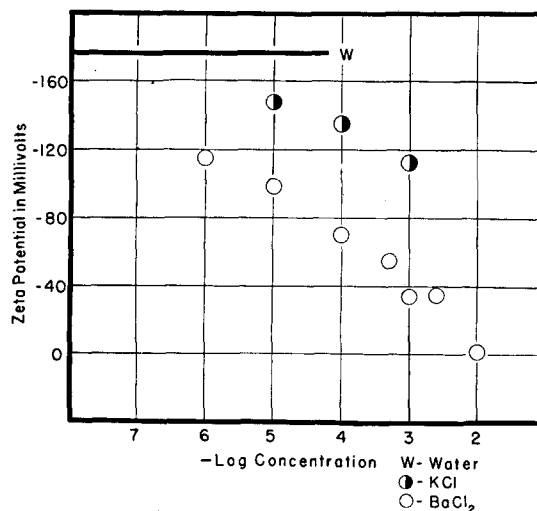


FIG. 2. Variation of the final zeta-potentials with concentration. Barium chloride: ○; potassium chloride: ●. The line W is the zeta-potential of silica in contact with pure water, which the curves described by the points should approach with dilution.

$\times 10^{-3} M$ solution are shown immediately below the letter *E*, however. The radius of each circle is 2.5 millivolts, and it is evident that in general the agreement between the values for the two capillaries was better than this.

DISCUSSION

In Fig. 2 are plotted the accepted values for the zeta-potential with each of the barium chloride solutions, together with the zeta-potentials observed earlier² with three solutions of potassium chloride. The abscissa represents the logarithm of the molar concentration of salt. The solid line *W* is the zeta-potential of silica in contact with pure water, known to be about -177 millivolt;⁸ both curves should approach this line as the concentration approaches zero and $\log c$ approaches $-\infty$. Attention is directed to the fact that neither with potassium chloride nor with barium chloride does there appear to be any maximum zeta-potential, and it cannot be considered probable that additional data would reveal a maximum. This substantiates the observations of Rutgers, Verlende, and Moorkens,⁹ who reached the same conclusion about the zeta-potential of glass in contact with these solutions.

Instead of going through a maximum, the zeta-potential for these two salts has been observed to decrease with increasing concentration in a more or less regular fashion. It has been noted above, however, that the 5×10^{-4} , 10^{-3} ,

$2.5 \times 10^{-3} M$ points are not entirely consistent, because it is evident either that the zeta-potentials for $5 \times 10^{-4} M$ and particularly for $2.5 \times 10^{-3} M$ BaCl_2 are too high, or that the potential for $10^{-3} M$ (and possibly $10^{-2} M$) are too low. It will be recalled that the order in which the solutions were measured was 10^{-3} , 10^{-4} , 10^{-5} , 5×10^{-4} , and $2.5 \times 10^{-3} M$, so that a considerable period of time intervened between the inconsistent measurements. These observations suggest that the effect may be the result of hysteresis, but it seems improbable that any such hysteresis effect could have survived the treatment with nitric acid and steam which was given the capillaries when the concentration was changed. It seems more reasonable to conclude that this is the result of the inability to control completely for a long time the condition of the surface of the capillary. The fact that the values for the $2.5 \times 10^{-3} M$ solution were 6 mv apart also indicates that the same equilibrium conditions did not prevail on each capillary surface with this solution. If the values for the 5×10^{-4} and $2.5 \times 10^{-3} M$ solutions had been 5 millivolts lower, and the value for the $10^{-3} M$ solution had been 5 millivolts higher than they were, then the points would have described a smooth curve. Therefore, it seems evident that the discrepancy can be attributed entirely to the inability to reproduce the surface, after a long time has elapsed, so that the zeta-potential is reproduced to better than 5 millivolts of its true value. However, in spite of these minor inconsistencies, the measurements represent a substantial improvement in the state of present knowledge of zeta-potentials.

⁹ A. J. Rutgers, Trans. Faraday Soc. **36**, 69 (1940); Rutgers, Verlende, and Moorkens, Proc. Ned. Akad. Wet. Amst. **41**, 763 (1938).