

The Measurement of Potentials at the Interface Between Vitreous Silica and Solutions of Potassium Chloride by the Streaming Potential Method

Grinnell Jones and Lloyd A. Wood

Citation: *J. Chem. Phys.* **13**, 106 (1945); doi: 10.1063/1.1724006

View online: <http://dx.doi.org/10.1063/1.1724006>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v13/i3>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>



Goodfellow

metals • ceramics • polymers
composites • compounds • glasses

Save 5% • Buy online

70,000 products • Fast shipping

www.goodfellowusa.com

and those having observed p values less than 0.78 to be polarized.

ACKNOWLEDGMENTS

The microdensitometer used in the intensity measurements was obtained with a grant made to the author from the Penrose Fund of the American Philosophical Society. The Hilger,

E-518, spectrograph used to obtain the spectrograms was obtained, in part, with a grant made to the author from the Permanent Science Fund of the American Academy of Arts and Sciences. The enlargement of the toluene spectrogram, Fig. 2, was made by Dr. M. Alden Countryman. The author wishes to express his appreciation for this assistance.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 13, NUMBER 3

MARCH, 1945

The Measurement of Potentials at the Interface Between Vitreous Silica and Solutions of Potassium Chloride by the Streaming Potential Method*

GRINNELL JONES¹ AND LLOYD A. WOOD

Department of Chemistry, Harvard University, Cambridge, Massachusetts

(Received December 5, 1944)

Improvements in the technique for the determination of the electric potential at the interface between a non-conducting solid and an aqueous solution of an electrolyte (commonly called the zeta-potential) have been developed and are described in detail. Zeta-potentials of vitreous silica capillaries in contact with three dilute solutions of potassium chloride (10^{-3} , 10^{-4} , $10^{-5}N$) have been determined. These data have been used for the interpretation of the surface tension data of Jones and Ray by using Langmuir's theory for the thickness of wetting films as a function of the zeta-potential.

INTRODUCTION

JONES and Ray² have made measurements of capillary rise of water and of solutions of electrolytes in the same silica tube which showed that the first trace of added salt decreases the capillary rise and the product of the density and capillary rise which is the so-called "capillary constant"; but that with further additions of salt the capillary constant passes through a minimum and then rises (although not an increase in the capillary rise). Their interpretation was that

there is a minimum in the surface tension-concentration curve at about $0.001N$. Thirteen salts of varied valence type give the effect, but sucrose does not. However, Langmuir³ has suggested an alternative interpretation of these observations, that the apparent minimum in the surface tension is not real but is a result of a variation in the thickness of the wetting film which influences the effective diameter of the tube. The theory is developed in a somewhat more rigid mathematical form, and its implications are discussed by Jones and Frizzell.⁴ According to Langmuir's hypothesis, this film with pure water and with extremely dilute solutions is not negligible in comparison with the radius of the capillary, as has been assumed by all experimenters using the capillary rise method, but may be several hundred angstrom units thick. The thickness of the wetting film of solutions of electrolytes, according to Langmuir's theory, is

* Contribution from the Mallinckrodt Chemical Laboratory of Harvard University.

¹ The preliminary work on the development of the apparatus and technique was carried out by Mr. Harvey S. Collins under the supervision of the senior author. Mr. Collins' work made it evident that a potentiometer and detector of very high internal resistance must be used, that silver-silver chloride electrodes are preferable to platinum electrodes used by many other investigators, and that the previous history of the capillaries plays a significant role and must be controlled as fully as is feasible. Mr. Collins found it necessary to terminate his work before the improved technique was developed and publishable results were obtained. We wish to express our appreciation for his contributions to the work described here.

² G. Jones and W. A. Ray, *J. Am. Chem. Soc.* **59**, 187 (1937); **63**, 288 (1941); **63**, 3262 (1941); **64**, 2744 (1942).

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

⁴ G. Jones and L. D. Frizzell, *J. Chem. Phys.* **8**, 986 (1940).

dependent mainly on the potential at the interface between the wall of the capillary and the water or solution, commonly called the zeta-potential, but also on the concentration of the solution, the temperature, and the capillary rise (which in turn depends upon the radius of the capillary and the surface tension of the liquid). The zeta-potential itself may be dependent on the temperature, the chemical nature and concentration of the electrolyte, the chemical nature of the capillary (glass or vitreous silica), and perhaps on its previous history which may influence the amount and nature of adsorbed ions. According to this theory the thickness of the wetting film is greatly influenced by the concentration of electrolyte within the range from 0 to about 0.01*N* (unless there are compensating changes in the zeta-potential). If the wetting film for water is thicker than for 0.001*N* solution by as much as 250 angstrom, the data on capillary rise could be interpreted without inferring that there is a minimum in the surface tension-concentration curves.

In the Langmuir theory the zeta-potential plays a controlling role. In order to make quantitative tests of this theory, it is necessary to have reliable data on the magnitude of these zeta-potentials. Significant improvements in the technique of measuring zeta-potentials are described in this paper.

Moreover, the Langmuir theory assumes that the charge at the air-solution interface is zero, although there are in the literature experimental observations of several kinds which have been interpreted by the experimenters as proof that solutions at an air-solution interface are electrically charged.⁵ A paper developing a modification of the original theory so as to take into account a charge on the solution-air interface is in preparation. However, the quantitative testing of the modified theory will require reliable measurements of the potential at air-solution

interfaces which are not available and which will be extremely difficult to determine experimentally, as well as measurement of potentials at solid-solution interfaces commonly called the zeta-potential.

Dole and Swartout⁶ have developed a twin-ring tensiometer which is capable of high precision and have found a minimum in the surface tension-concentration curve for potassium chloride solutions at 0.001*N*, in agreement with Jones and Ray. On the other hand, Long and Nutting,⁷ using an improved differential bubble pressure method, do not find a minimum in the curve.

MEASUREMENT OF ZETA-POTENTIALS— GENERAL REQUIREMENTS

Zeta-potentials may be computed from four different electrokinetic effects: streaming potentials, electro-osmosis, sedimentation potentials, and electrophoresis—provided that certain other necessary data are available. The method based on streaming potentials lends itself most readily to precision measurement, since all of the quantities involved in the computation are measurable with greater accuracy and less difficulty than the fundamental experimental data for the other three methods.

A streaming potential is the potential difference which develops between the ends of a capillary tube when a solution of an electrolyte (including the purest available water which contains enough ions to produce the effect) is forced through the tube by external pressure or by gravity. If the flow is slow enough to be streamlined, so that Poiseuille's law is applicable, this potential is related to the zeta-potential at the wall of the tube by the equation of Helmholtz:⁸

$$\zeta = 4\pi\eta\kappa E/DP, \quad (1)$$

where η is the viscosity, K is the specific conductance of the liquid in the capillary, E is the streaming potential resulting when the liquid is forced through the capillary under the pressure P , and D is the average dielectric constant of the liquid in the ionic double layer.

⁵ H. A. McTaggart, *Phil. Mag.* [5] **27**, 297 (1914); N. Bach and A. Gilman, *Acta Physicochimica U.R.S.S.* **9**, 1 (1938); P. Lenard, *Ann. d. Physik* [4] **47**, 463 (1915); W. Obolensky, *ibid.* [4] **39**, 961 (1912); W. Busse, *ibid.* [4] **76**, 493 (1925); A. Bühl, *ibid.* [4] **83**, 1207 (1927); *ibid.* [4] **84**, 211 (1928); *ibid.* [4] **87**, 877 (1928); *Kolloid Zeits.* **59**, 346 (1932); F. B. Kenrick, *Zeits. f. physik. Chemie* **19**, 625 (1896); **109**, 34 (1924); **111**, 190 (1924); **116**, 485 (1925); see also H. Freundlich, *Kapillarchemie* (Leipzig, 1930), fourth edition, Vol. 1, pp. 388–399, which gives many additional references.

⁶ M. Dole and J. A. Swartout, *J. Am. Chem. Soc.* **62**, 3039 (1940).

⁷ F. A. Long and G. C. Nutting, *J. Am. Chem. Soc.*, **64**, 2476 (1942).

⁸ H. Helmholtz, *Wied. Ann.* **7**, 337 (1879).

Several experimenters⁹ have measured zeta-potentials by the streaming method, mostly on glass capillaries, but there are also some measurements on vitreous silica capillaries. However, nearly all data on comparable systems are greatly at variance, and it is difficult to evaluate their relative reliability for several reasons. Several different varieties of glass, some entirely unspecified, have been used for these determinations, which therefore could hardly be expected to be in

conductance on streaming potentials has commonly been neglected. It is evident from a survey of the literature that most of the data are unreliable, and it is difficult to determine which, if any, are worthy of confidence. Therefore it was thought advisable to undertake an investigation for the purpose of improving the experimental technique of measuring streaming potentials and the other necessary quantities, and thus obtain some reliable data which can be used to test the Langmuir theory.

From Eq. (1) it is evident the apparatus required for measuring zeta-potentials must include devices for measuring the streaming potential, the pressure producing the liquid flow, and the specific electrical conductivity of the solution used in the capillaries. The viscosity of the solutions used are nearly the same as water, and sufficiently reliable data are available in the literature. The dielectric constant of the solutions is assumed to be the same as that of water.

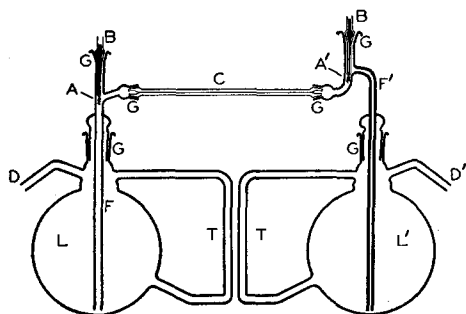


FIG. 1.

agreement. It is most unfortunate that the investigators did not choose silica or some other pure substance rather than a mixture of such indefinite composition as glass as a subject for study. Some experimenters have failed to appreciate the importance of, or to describe adequately, the previous history and treatment of the solid surfaces. Measuring instruments have been used which are unsuitable for measuring such a delicate effect as the streaming potential or have not been described sufficiently to permit a critical appraisal of their suitability. The conductance of solutions used has in some cases not been determined but the values for κ used in the calculations were taken from the literature. However, since the solutions used are commonly quite dilute (less than 0.001*N*) the undetermined and uncertain "water correction" may introduce a substantial error in the assumed value of κ , and hence in ζ . The possible influence of surface

DESIGN OF STREAMING APPARATUS AND DRIVING PRESSURE

The apparatus for developing streaming potentials consisted essentially of two Pyrex reservoirs of 1-liter capacity, *L* and *L'* in Fig. 1, connected by a vitreous silica capillary *C*. Pressure applied from a nitrogen tank through *D* on one side forced the solution through the tube *F*, around the electrode *A*, through the capillary *C*, around the other electrode *A'*, and finally into the opposite reservoir *L'*. The tubes were so designed that pressure in *L* forced all air bubbles out through *L'* which accounts for the lack of symmetry shown in the diagram. The delivery tube *F'* is a capillary of about 1-mm bore which is small enough so that air bubbles will be forced down the tube. After the initial filling the direction of flow may be reversed. The tight fitting ground joints *G* connecting the various parts of the apparatus were sealed with a minimum of paraffin, which was not surface active and was kept on the outward half of the joints as much as possible. The capillary *C* was about 19.1 cm long and 0.032 cm in diameter. A second apparatus, differing slightly in detail, was in use simultaneously with a capillary 19.2 cm long and 0.017 cm in diameter.

⁹ H. R. Kruyt and van der Willigen, *Kolloid Zeits.* **45**, 307 (1928); Furutani, Kurokuchi, and Asoda, *Jap. J. Gastroent.* **2**, 148 (1930); H. Freundlich and G. Ettisch, *Zeits. f. physik. Chemie* **116**, 401 (1925); H. Lachs and J. Biczysk, *Zeits. f. physik. Chemie* **A148**, 441 (1930); R. DuBois and A. H. Roberts, *J. Phys. Chem.* **40**, 543 (1936); A. J. Rutgers, *Trans. Faraday Soc.* **36**, 69 (1940); A. J. Rutgers, Ed. Verlende, and MaMoorkens, *Proc. K. Ned. Akad. Wet. Amst.* **41**, 763 (1938).

For measurements of the pressure difference applied between L and L' , a mercury manometer was satisfactory for the range required, from 15 to 35 cm of mercury. Constancy of pressure was maintained through the use of large ballast reservoirs covered with heat lagging on both the pressure and exhaust sides of the apparatus. The tubes T permitted a measurement of the difference in hydrostatic head between the reservoirs which was applied as a small correction to the measured gas pressure.

The Helmholtz equation for the calculation of zeta-potentials is based on the assumption that the flow in the capillary is stream-lined and obeys Poiseuille's law.

With the larger of our two capillaries (diameter 0.032 cm) and with the highest pressure used (35 cm of Hg) the rate of flow is 0.07 cc/sec., and the Reynolds number is 310. For the smaller of our capillaries and the greatest velocity the rate of flow is 0.0056 cc/sec., and the Reynolds number is 48. These Reynolds numbers are well below the critical value of 2000 for the Reynolds number which indicates danger of turbulence.¹⁰

MEASUREMENT OF STREAMING POTENTIAL AND TEMPERATURE CONTROL

The electrodes A were spirals of No. 28 gauge platinum wire on which a silver-silver chloride mixture was formed by heating a paste of 10 percent silver chlorate-90 percent silver oxide mixture at 500° for 15 minutes.¹¹ The platinum wires supporting the silver-silver chloride electrodes were sealed through glass which permitted them to be connected to the measuring instruments by copper wires dipping into the mercury cups B .

It was necessary to apply rather elaborate

electrical insulation and electrostatic shielding to the capillary apparatus and one of the connecting wires to the potentiometer, owing to the separation of this part of the electrical system from the remainder by the extremely high resistance of the capillary and the still higher resistance of the vacuum tube in the null instrument of the potentiometer. In order to take advantage of air insulation, the apparatus was enclosed in an air thermostat rather than a liquid bath. This thermostat was designed essentially in the manner of one constructed by Mr. E. B. Damon of the Mallinckrodt Chemical Laboratory.¹² An inner chamber entirely shielded with a grounded copper sheet or a 16 mesh wire screen, with a removable glass door in front and an illuminated pane of frosted glass in the rear, contained the two units of capillary apparatus which were essentially duplicates except for the capillaries which differed appreciably in diameter as explained above. The inner chamber was mounted inside an outer larger cabinet with walls of low heat conductivity and also provided with glass windows to permit inspection of the apparatus in the inner chamber. The temperature of the air in the outer chamber was automatically maintained at the desired value by a low lag intermittent electric heater

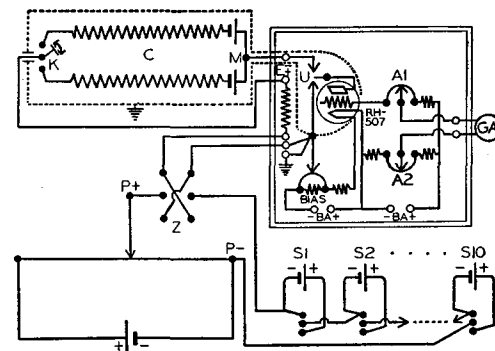


FIG. 2.

controlled by a sensitive metallic spiral. Occasionally when the room temperature was high enough to require it, constant cooling was applied by circulating cold water through some copper coils in the outer chamber. A small fan circulated the air over the heater, regulator, drying agent,

¹⁰ O. Reynolds, *Phil. Trans.* **174**, 935 (1883); **A186**, 123 (1895). See also E. C. Bingham, *Fluidity and Plasticity* (McGraw-Hill Book Company, Inc., New York, 1922), p. 40. It should be noted that in his first paper Reynolds defines his criterion (a dimensionless number) in terms of the radius $Re = r\rho u/\eta$ where r = radius of capillary; u is mean velocity of flow, cm/sec., averaged over the cross section; ρ is the density of the liquid; and η is the viscosity of the liquid. Bingham in his book uses this definition. However, in his second paper Reynolds defines his criterion in terms of the diameter of the tube $Re = D\rho u/\eta$ where $D = 2r$. We have used this definition because it is customarily used in books on chemical engineering and is therefore more familiar.

¹¹ C. K. Rule and Victor K. LaMer, *J. Am. Chem. Soc.*, **58**, 2339 (1936).

¹² Mr. Damon has not published a description of this air thermostat. We wish to express our thanks for permission to use his design and publish this description of it.

and around the inner chamber. Suitable partitions were built into the apparatus to ensure that the air circulated all around the inner chamber and that a small part of the circulating air passed through the inner chamber. The inner chamber also contained open dishes containing a drying agent (calcium chloride) to maintain the humidity at a low value. The temperature in the inner chamber was maintained at $25^{\circ}\text{C} \pm 0.03^{\circ}$. This thermostat has the unavoidable drawback that owing to its low heat capacity a long wait is necessary after opening the chamber to change the solution or for any other purpose, before adequate temperature control is established so that measurements can be made.

The capillary apparatus was mounted on glass plates without metal supports, and the connecting wires from the electrodes to M and K (Fig. 2) were air insulated. The wire from M to the E -terminal of the amplifier passing through the walls of the thermostat was a length of coaxial cable with polystyrene beads for insulation and a grounded metallic braided shield. The knife switch K , with contacts mounted in a block of paraffin, was controlled from the outside of the thermostat by a Bakelite rod and made possible alternate measurements with either set of capillary apparatus. The reason for the paraffin insulation is made apparent by recalling that the positive terminals of both capillaries were connected to the terminals of this switch. Since the resistance of ordinary porcelain switches when open is in some instances low compared with that of the capillary the effect would be that of a closed circuit through both capillaries. It is believed that these insulation precautions have ensured that the resistance of all electrical paths between the electrodes other than through the capillary was greater than 10^{13} ohms.

The potential difference between the electrodes was measured with a Wolff potentiometer having a resistance of 19,000 ohms. The proper choice of the null instrument is important because Eq. (1) assumes that the electrical current which escapes through the measuring instrument or by other leakage owing to inadequate insulation is negligible, i.e., is so small that it does not permit the discharge of the electrodes to a significant extent. Many previous investigators have used galvanometers or capillary electrometers which did not

satisfy this requirement. In practice this requirement may be met by ensuring that the losses will be negligible in comparison with the magnitude of E/R , where E is the streaming potential and R the resistance of the capillary. The resistance may be as high as 10^{10} ohms and the streaming potential as low as 100 millivolts in extreme circumstances, giving a minimum value of E/R of 10^{-11} ampere. In this work a Leeds and Northrup thermionic amplifier (Cat. No. 7673) was used as a null instrument, which permits a leak of not more than 10^{-13} ampere, and gives streaming potential measurements which are sensitive to better than 0.5 percent in the most difficult cases and to 0.1 percent or better in the more favorable cases.

The potentiometer circuit is shown diagrammatically in Fig. 2, including the thermionic amplifier. A brief explanation of this instrument will be helpful, and further information is available elsewhere.¹³ The vacuum tube of the amplifier (R.H.-507, Westinghouse electrometer tube) is so designed that with correct adjustment of the bias voltage less than 10^{-13} ampere of electron current flows from filament to plate which is in series with the capillary. The filament-to-grid flow is incorporated in one arm of the bridge which is a part of the electrical system of the instrument and which can be balanced by adjusting the resistors $A1$ and $A2$, so that a galvanometer across the midpoints will give a null reading for some definite value of the filament-to-grid potential difference. Since this difference depends upon the potential of the plate, the galvanometer is really actuated by the potential difference between filament and plate.

In the diagram (Fig. 2) it is assumed that the direction of flow in the capillary is such that the end marked M is positive. In measuring the streaming potential, the switch U was first depressed, which connected the plate to ground and to the positive side of the potentiometer ($P+$), the switch Z being in such position that the positive side of the potentiometer is grounded. The resistors $A1$ and $A2$ were then adjusted so that when the plate was at ground potential, the

¹³ *Directions for No. 7673 Thermionic Amplifier* (Leeds and Northrup Company, Philadelphia, Pennsylvania); R. H. Cherry, *Trans. Am. Electrochem. Soc.* **78**, 11 (1940); Müller, Gorman, and Droz, *Experimental Electronics* (Prentice-Hall, Inc., New York, 1942), p. 168.

filament-to-grid potential difference was such that the galvanometer was not deflected. Then switch U was released, and the plate assumed the potential of the positive electrode of the capillary (represented diagrammatically in Fig. 2 by C). The negative end of the capillary was connected through the knife switch K to $E+$, which in turn connected through a low resistance to $P-$, the negative side of the potentiometer. By adjusting the potentiometer until its potential was equal and opposite to the streaming potential, the potential of the plate was returned to ground potential. This state of affairs was indicated by the return of the galvanometer to null reading. Thus the streaming potential is obtained.

When the direction of liquid flow was reversed, the polarity of the electrodes was also reversed, and it was necessary to have switch Z changed so that the negative side of the potentiometer was connected to ground. When the streaming potentials exceed the 1.9-volt range of the potentiometer, the Weston standard cells $S1$ to $S10$ were placed in series with the potentiometer to extend the range to 12 volts. The e.m.f.'s of these cells were checked individually with the potentiometer through another circuit not shown.

SPECIFIC CONDUCTIVITY OF SOLUTIONS USED

Most investigators have assumed the electrical resistance of the capillary to be determined by the geometry of the capillary and by the bulk conductance of the system. McBain and co-workers¹⁴ have published evidence indicating that the specific conductance of the layer near the surface of the glass interface is greater than the specific conductance of the portion of solution at a greater distance from the interface. The excess of the actual conductance over the bulk conductance is called the surface conductance. If this is correct the value of the specific conductance determined in tubes of comparatively large diameter, such as the conventional conductivity cells, would be lower than the effective specific conductance in a narrow capillary tube. The error introduced in this way would be a function of the concentration of the solution—

decreasing with increase in concentration. However, White, Urban, and co-workers¹⁵ have obtained contradictory results. Rutgers, Verlende, and Moorkens¹⁶ believing that surface conductance is appreciable, have measured streaming potentials with glass capillaries of different sizes and have calculated zeta-potentials and surface conductances from these, on the assumption that the zeta-potentials of the different capillaries are identical. However, since zeta-potentials are hard to reproduce and are apparently influenced by the previous history of the tube, this assumption is somewhat uncertain. Their results are in good agreement with McBain's. In view of this uncertainty existing as to the effect of surface conductivity, it was believed desirable to measure the conductance of the solution in the capillary at the time of each streaming potential measurement. Furthermore, since a trace of impurities produces a relatively large effect on the electrolyte concentration of extremely dilute solutions, this measurement also could give warning of the accumulation of impurities, mainly carbon dioxide. If the surface conductance plays a significant role in these measurements then the actual conductance of the capillary ($1/R$) will be given by the equations

$$\frac{1}{R} = \frac{\pi r^2}{l} \kappa_B + \frac{2\pi r}{l} \kappa_s, \quad (2)$$

$$\frac{l}{\pi r^2 R} = \kappa_B + \frac{2\kappa_s}{r} = \kappa_B \left(1 + \frac{2\kappa_s}{\kappa_B r} \right) = \kappa, \quad (3)$$

where κ_B is the bulk specific conductivity and κ_s is the surface specific conductivity and κ is the total effective specific conductivity which is needed for insertion in Eq. (1). Therefore, if the cell constant, $l/\pi r^2$, can be determined with sufficient precision in a manner which avoids errors owing to surface conductance, then the effective specific conductivity, κ , can be computed from the measurements of the actual resistance (R) in the capillaries.

¹⁴ McBain, Peaker, and King, *J. Am. Chem. Soc.* **51**, 3294 (1929); J. W. McBain and C. R. Peaker, *J. Phys. Chem.* **34**, 1033 (1930); J. W. McBain and J. F. Foster, *J. Phys. Chem.* **39**, 331 (1935).

¹⁵ White, Urban, and Krick, *J. Phys. Chem.* **36**, 120 (1932); White, Urban, and van Atta, *J. Phys. Chem.* **36**, 3152 (1932); White, Urban, and Monaghan, *J. Phys. Chem.* **45**, 560 (1941).

¹⁶ A. J. Rutgers, *Trans. Faraday Soc.* **36**, 69 (1940); Rutgers, Verlende, and Moorkens, *Proc. K. Ned. Akad. Wet. Amst.* **41**, 763 (1938).

According to McBain, Peaker, and King,¹⁴ the ratio κ_s/κ_B decreases rapidly with increasing concentration. It is also clear that the difference $\kappa - \kappa_B = 2\kappa_s/r$ decreases with increasing diameter of the cell and is generally assumed to be negligible for cells of the conventional non-capillary design. The procedure for the determination of the cell constant and the estimation of the influence of the surface conductance was as follows: An approximately 0.1*N* KCl solu-

TABLE I. Data on capillaries used.

Capillary	Resistance megohms	Cell constant	Length cm	Radius cm
I	1.826±0.001	23365	19.1	0.01613
II	6.792±0.005	86920	19.2	0.00837

tion, whose specific conductivity at 25°C, $\kappa_B = 0.012798$, was known by comparison with the Jones and Bradshaw¹⁷ standards, was placed in the capillary cells and the resistance measured with direct current on the special bridge described below. The resistances in these capillaries are so great that errors owing to capacitive by-paths make the usual procedure using alternating current inapplicable and errors due to polarization with direct current are minimized. Then assuming as a first approximation that for this comparatively high concentration $2\kappa_s/\kappa_B r$ is negligible in comparison with unity, the cell constants, $l/\pi r^2 = \kappa R$, are computed. The length of the capillary l can be measured within about 0.1 cm (the uncertainty is owing to the somewhat flaring or trumpet shaped ends) and hence the radius of the capillary can be computed (assuming that the capillaries have a circular cross section and are uniform in radius throughout their length). The results are shown in Table I. Then solutions of 10^{-3} , 10^{-4} , and 10^{-5} *N* KCl were prepared and placed in the capillaries for the zeta-potential measurements and the resistance (R) measured while the fluid flow was in progress as described below, and the effective specific conductance, κ , including the surface conductance computed by the equation $\kappa = l/\pi r^2 R$. Then, in order to determine whether or not the surface conductance made a significant contribution to the conductance, the bulk conductance

κ_B of the same solution was determined in a conventional non-capillary cell by the use of alternating current on a Jones bridge and the apparent surface conductivity computed

$$\kappa_s = [(\kappa - \kappa_B)/2]r. \quad (4)$$

The results are shown in Table II.

The values of the apparent specific surface conductivity are so small and erratic as to be within the limit of error of these measurements and indicate that (except possibly for the 10^{-5} *N* solution) the influence of surface conductance on our measurements of zeta-potential is negligible. In this respect our results are in agreement with White, Urban, and associates. However, our method of measuring the specific conductivity with a direct current bridge in the capillary itself during the flow of the liquid includes the effect of surface conductance, if any, on the zeta-potential measurements. Since the value of κ_s/κ_B decreases with increasing concentration, our original assumption that the influence of surface conductivity can be neglected when working with 0.1*N* KCl is justified.

Although the indicated surface conductivity in our measurements are much below the values obtained by McBain, Peaker, and King, we do not regard our results as necessarily inconsistent

TABLE II. Data on surface conductivity.

Concen- tration	Cap- illary	κ_B $\times 10^6$	R meg- ohms	κ $= l/\pi r^2 R$ $\times 10^6$	$\kappa - \kappa_B$ $\times 10^6$	κ_s $= [(\kappa - \kappa_B)/2]r$ $\times 10^6$
10^{-3}	I	151.4	154.9	150.8	-0.6	-0.0048
	I	147.6	159.1	146.9	-0.7	-0.0056
	II	151.4	574.4	151.3	-0.1	-0.0004
	II	148.3	585.8	148.4	+0.1	+0.0004
10^{-4}	I	15.66	1488	15.70	+0.04	+0.00032
	II	15.08	5618	15.47	+0.39	+0.0017
10^{-5}	I	2.243	9765	2.393	+0.15	+0.0012
	II	2.851	29500	2.946	+0.10	+0.0004

or contradictory with theirs because the experimental conditions are different in several respects. In our experiments the solutions were flowing at a rate of 32 to 85 cm per second averaged over the cross section of the capillary for the larger tube, depending upon the pressure used, and from 10 to 25 cm per second for the smaller tube. Although Reynolds' criterion indicates that the flow is straight-lined instead of turbulent in the sense that these terms are used in discussions of fluid

¹⁷ Grinnell Jones and B. C. Bradshaw, J. Am. Chem. Soc. 55, 1780 (1933).

flow, nevertheless there may be sufficient disturbance of the ionic distribution to reduce the surface conductance in comparison with stationary conditions which prevailed in McBain's experiments. Moreover, we used direct current instead of alternating current, and our capillaries were vitreous silica whereas theirs were made of glass which may be expected to differ from silica in its tendency to emit ions into the surface layer of the solution.

To make possible such measurements, a direct current bridge was built capable of measuring resistances in the range 10^5 to 10^{11} ohms with a precision of 0.5 percent, or better, under optimum conditions. The wiring diagram of this bridge is shown in Fig. 3. The Wolff potentiometer without working battery was used as the variable resistor R_3 , adjustable in steps of 0.1 ohm, with the range 0.1 to 19,000 ohms (although the range below 100 ohms was not used). The resistance coils of the potentiometer were calibrated against Bureau of Standards calibrated resistors with a Mueller bridge and found to be close enough to their nominal values to make corrections unnecessary. The resistance R_4 was a Type W W2 precision wire-wound resistor of 1 megohm resistance (± 0.1 percent) manufactured by the International Resistance Corporation of Philadelphia. The resistance R_1 of 10^7 ohms consisted of ten of these megohm resistors connected in series. Both R_1 and R_4 were calibrated at 25°C against the variable resistor and the two Bureau of Standards calibrated resistors of 100 and 10,000 ohms, and were close enough to their nominal values to make a correction unnecessary. It, therefore, seems probable that the errors in these resistors could not be responsible for an error of more than 0.1 percent of the true value of the capillary resistance when calculated from $R_2 = R_1 R_4 / R_3$.

With the resistors constituting the bridge, unknown resistances in the range 5×10^8 to 10^{11} ohms could be measured to 0.1 percent insofar as the limitations imposed by the resistors are concerned. By substituting a 10,000-ohm resistor for the megohm at R_4 , the range between 5×10^6 and 10^9 ohms could be measured, and if a 1000-ohm resistor is used at R_4 the range is dropped to 5×10^5 to 10^8 ohms. As a null instrument, the thermionic amplifier was connected across the midpoints of the bridge, with the $P+$ and $P-$

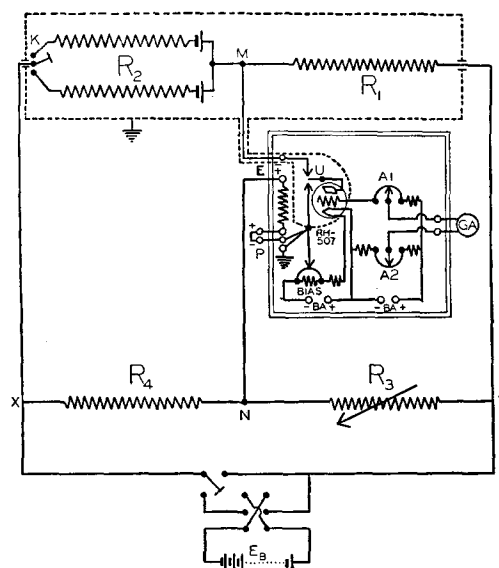


FIG. 3.

terminals short-circuited. It was well suited for this purpose because a bridge in which the resistances were so large and with great inequalities of the arms requires that the null instrument have an extremely high internal resistance.

The same shielding and insulation precautions as described above were observed on the high resistance side, the arms R_1 , R_2 , and R_4 being inside the air thermostat where the air was maintained at low humidity to avoid surface leakage. The bridge current was supplied by B batteries at E_B , and because of the inequality of the bridge arms, potentials as high as 250 volts were used to obtain the necessary sensitivity. With no solution flowing through the capillary the streaming potential is zero, and except for a possible disturbance due to the small difference between the two silver-silver chloride electrodes, the bridge functions in the normal manner as a direct current bridge with resistance of the cell R_2 computed from the usual condition of balance $R_2 = R_1 R_4 / R_3$. Since the battery voltage is of the order of 250 volts the slight voltage, if any, in arm R_2 , owing to asymmetry of the electrodes or polarization is negligible. Since the resistance of the capillary in the work reported here is within the range 2×10^6 to 4×10^{10} ohms and is in series with 10^7 ohms in R_1 , direct current may be used without serious trouble from polarization.

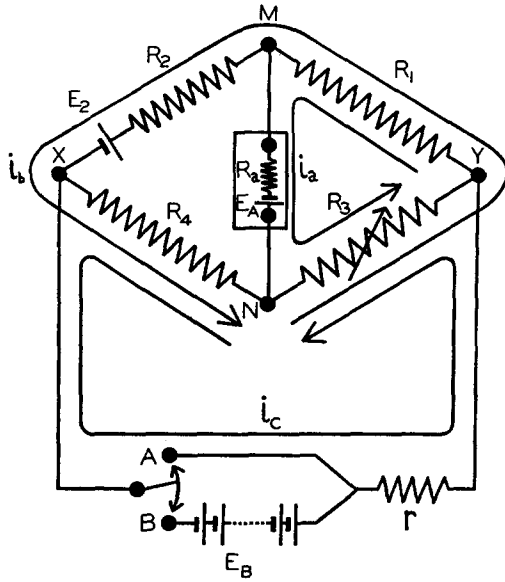


FIG. 4.

This bridge was also used to measure the resistance of the capillary R_2 with the solution flowing through under pressure and hence with a streaming potential E_2 on the electrodes. To do this an experimental procedure was devised which enabled us to adjust R_3 so that the condition $R_2R_3 = R_1R_4$ was satisfied, and to have a suitable criterion that this condition is fulfilled.

In presenting the solution to this problem, it should first be noted that the amplifier, when adjusted properly, creates a counter electromotive force which is equal and opposite to the potential difference across the detector arm, and which reduces the current i_a in this arm to zero within the limit of sensitivity of the instrument. The maker of the instrument states that a current of 10^{-13} ampere is detectable. When the amplifier is developing the counter electromotive force to oppose the potential difference between M and N (see Fig. 4), a certain response of the sensitive galvanometer attached to the instrument is observed. If this response is identical both without and with the battery potential E_B imposed on the bridge, then the condition $R_2R_3 = R_1R_4$ is fulfilled.

To establish this, consider the bridge (Fig. 4) with E_B imposed, with the switch AB in position B . The resistance between X and Y in the battery line is designated as r . Let the current flowing in the various arms of the bridge be considered to be

composed of the current components i_a, i_b, i_c , as indicated in Fig. 4. Thus, for example the current flowing through R_3 from N to Y is equal to $(i_a + i_b - i_c)$. The following equations describe the system:

$$i_a(R_1 + R_2 + R_3) + i_b(R_1 + R_3) + i_c(-R_3) = E_A, \quad (5)$$

$$i_a(R_2) + i_b(-R_4 - R_2) + i_c(R_4) = E_A - E_2, \quad (6)$$

$$i_a(R_1) + i_b(R_1 + R_2) + i_c(r) = E_2 + E_B. \quad (7)$$

Solving for i_a

$$i_a = \frac{\begin{vmatrix} (E_A) & (R_1 + R_3) & (-R_3) \\ (E_A - E_2) & (-R_4 - R_2) & (R_4) \\ (E_2 + E_B) & (R_1 + R_2) & (r) \end{vmatrix}}{\begin{vmatrix} (R_1 + R_2 + R_3) & (R_1 + R_3) & (-R_3) \\ (R_2) & (-R_4 - R_2) & (R_4) \\ (R_1) & (R_1 + R_2) & (r) \end{vmatrix}}. \quad (8)$$

However, since no current flows through the amplifier, $i_a = 0$, and therefore the determinant in the numerator is equal to 0.

$$\begin{vmatrix} (E_A) & (R_1 + R_3) & (-R_3) \\ (E_A - E_2) & (-R_4 - R_2) & (R_4) \\ (E_2 + E_B) & (R_1 + R_2) & (r) \end{vmatrix} = 0. \quad (9)$$

Then solving for E_A ,

$$E_A = \frac{[R_1(R_3 + R_4) + r(R_1 + R_3)]E_2 + (R_1R_4 - R_2R_3)E_B}{(R_1 + R_2)(R_3 + R_4) + r(R_1 + R_2 + R_3 + R_4)}. \quad (10)$$

It is evident from Eq. (10) that if the resistance of R_3 is adjusted so that $R_1R_4 - R_2R_3 = 0$, then the value of E_A is independent of E_B . That means that E_B could have its usually high value, or be short-circuited or reversed without any effect on E_A . This gives a criterion to determine the proper bridge balance. In practice R_3 must be adjusted until the value of E_A becomes independent of E_B . It is also possible to show that if $R_1R_4 - R_2R_3 = 0$, then Eq. (10) can be simplified by the rigid algebraic transformation into

$$E_A = \frac{(R_1 + R_3)E_2}{R_1 + R_2 + R_3 + R_4} = \frac{R_1E_2}{R_1 + R_2}. \quad (11)$$

Here r has been eliminated, which means that the change in the resistance in the battery line between X and Y when the battery is short-circuited does not influence the ratio between E_A and E_2 . It also means that the switch AB need not even be closed to short-circuit X and Y , but need only be opened from position B , to give an open circuit which is equivalent to path XY with very great r . Furthermore, it is apparent from Eq. (10) that when the battery circuit is opened, $E_B = 0$, the value of E_A is extremely insensitive to variations in R_3 because R_3 appears only as part of a sum containing much larger quantities. Experimentally this means that the first step is to open AB and then adjust the thermionic amplifier until the galvanometer gives zero deflection for the particular value of E_A , which is equal and opposite to the potential difference between M and N . Then the battery E_B is applied and R_3 adjusted to give the same value of E_A , as shown by zero galvanometer deflection without change in the amplifier adjustment. If E_B is made large enough (4–250 volts depending upon the concentration of solution used) the E_A becomes sufficiently sensitive to variations in R_3 to give the desired precision in the setting and hence in the computed value of R_2 . In the general case, the adjustment of the variable resistance R_3 so as to make $R_1R_4 = R_2R_3$, is necessary to make the galvanometer read zero both when E_B is imposed and when the battery circuit is open, but in practice with the bridge described, E_A was essentially independent of the value of R_3 , since $R_3 \ll R_4$, so that adjustment of R_3 was necessary only when E_B was imposed, facilitating rapid balancing of the bridge.

CLEANING OF CAPILLARIES

To obtain definite and characteristic zeta-potentials, dependent solely on the nature and concentration of the solution under investigation and on the nature of the solid phase, and independent of the previous history of the tube, it is necessary to have the capillary surface free from all adsorbed impurities remaining from previous use of the tube, particularly from multivalent ions, which may greatly modify the surface electrical properties. This is difficult to accomplish, as multivalent ions are probably more strongly adsorbed than univalent ions. With the

improved technique of measurement described above the reproducibility of the capillary surface is the greatest source of uncertainty in the zeta-potential measurements. Numerous authors have recognized this difficulty, and have recommended various procedures for cleaning the surfaces. Freundlich and Ettisch¹⁸ have stated that treatment with nitric acid and subsequent rinsing with water is sufficient to remove thorium ions, which are among the most strongly adsorbed, and Kruyt and van der Willigen,¹⁹ and Elissasoff²⁰ found that chromic acid apparently had the same result. White, Urban, and Krick¹⁵ reported that chromic acid generally caused a 20 percent lowering in the streaming potential values, and found that washing with hot water and steam, and then heating their capillaries to dull redness was superior to other methods. They were not successful in obtaining reproducible streaming potential values, however. There seems to be little agreement among these and other authors, and no decisive results are in the literature, regarding methods of cleaning the capillary surfaces.

A vigorous but completely volatile cleansing agent was used preceding each series of measurements on a solution to be studied. The volatility of the cleaning solution was important, as it permitted a strong presumption that any traces left after rinsing with conductivity water can be removed by heating to a dull redness. Then by preventing contamination by a non-volatile substance except the potassium chloride being measured, it was hoped that a clean surface could be maintained until these measurements were completed. These data would afterwards be available as a norm for comparison with results of future studies involving methods of freeing the surface from undesired adsorbed ions.

Therefore, preceding a series of measurements, boiling aqua regia, made from c.p. nitric and hydrochloric acids, was drawn through the capillaries for a period of hours, followed by hot conductivity water for an equal period. The capillaries were heated to near redness before installing in place with a stream of steam passing

¹⁸ H. Freundlich and G. Ettisch, *Zeits. f. physik. Chemie* **116**, 401 (1925).

¹⁹ H. R. Kruyt and P. C. van der Willigen, *Kolloid Zeits.* **45**, 307 (1928).

²⁰ G. V. Elissasoff, *Zeits. f. physik. Chemie* **79**, 385–420 (1912).

TABLE III. Measurements on 10^{-3} *N* KCl solutions.

Flow	P cm of Hg	E Milli- volts	R $\times 10^{-3}$	κ $\times 10^6$	$E\kappa/P$ $\times 10^5$	ξ Milli- volts
$L \rightarrow L'$	31.79	250.7	0.5879	147.85	11.659	-112.6
$L \rightarrow L'$	31.69	250.1	0.5882	147.76	11.661	-112.7
$L \leftarrow L'$	31.32	246.4	0.5879	147.85	11.631	-112.4
$L \leftarrow L'$	31.26	246.0	0.5879	147.85	11.634	-112.4
$L \rightarrow L'$	23.14	182.5	0.5879	147.85	11.661	-112.7
$L \rightarrow L'$	23.06	181.8	0.5879	147.85	11.656	-112.6
$L \leftarrow L'$	23.03	180.7	0.5879	147.85	11.600	-112.1
$L \leftarrow L'$	22.95	180.5	0.5879	147.85	11.628	-112.3
				Av.	11.641	-112.5

through them. As will be seen later, however, this procedure was not wholly successful in solving the problem of reproducibility of the surfaces, even though they were presumably free from impurities at the start. The other parts of the apparatus were thoroughly cleaned with hot nitric acid, except for the electrodes, and leached with hot conductivity water. The electrodes were cleaned with nitric acid before forming the silver-silver chloride mixture on the platinum wire, and afterward were leached in conductivity water for several days before use. Care was taken to keep all sections free from impurities at all times.

MEASUREMENTS ON SOLUTIONS OF POTASSIUM CHLORIDE

Since Langmuir's argument applies to solutions between the range of pure water and $0.001N$, the zeta-potentials created by solutions of concentrations 10^{-3} , 10^{-4} , $10^{-5}N$ KCl were measured. Solutions were made up gravimetrically from recrystallized KCl and conductivity water of specific conductance less than 0.6×10^{-6} mho cm^{-1} when freed from CO_2 . They were made and stored in non-sol glass bottles which had been steamed with nitric acid and conductivity water, and leached with the latter for days prior to use. Reservoir L was filled directly from the storage flask, and the various sections of the apparatus joined together. Filtered carbon dioxide-free air, saturated with water vapor, was then passed into L' under a slight pressure, and bubbled slowly through the solution for twelve hours or longer to remove carbon dioxide from the solution. Then pressure from the nitrogen tank was used to force half the solution into L' to equalize the levels. All measurements were made at $25^\circ \pm 0.03^\circ$.

In measuring the zeta-potential, the usual procedure was to apply a pressure difference between the reservoirs L and L' , then (1) to measure the electrical resistance R_2 of the solution while flowing in the capillary, according to the method developed above; (2) to measure the streaming potential E and the pressure P producing it; (3) repeat (2); and (4) repeat (1). Then the direction of flow was reversed under approximately the same pressure difference, and the four steps above repeated. This procedure was then repeated at different pressures, yielding several sets of data at different values of the streaming potential. By reversing the direction of flow at each pressure, any asymmetry of the electrodes, which may have developed during the course of the measurements, was immediately evident, as it would cause a deviation of the ratio E/P from the average which depended on the direction of flow. This was owing to the fact that such a potential would be algebraically additive to the streaming potential, causing E/P with flow in one direction to be higher than it would be with flow in the opposite direction.

Experience soon showed that with $10^{-3}N$ and with $10^{-4}N$ solutions, it was unnecessary to measure the conductance at each pressure, as it was essentially constant over the period during which the set of measurements were obtained, and measurement before and after the set were

TABLE IV. Measurements on $10^{-4}N$ KCl solutions.

Flow	P cm of Hg	E Millivolts	$E\kappa/P$ $\times 10^{-4}$	ξ Millivolts
$L \rightarrow L'$	31.52	2829.0	13.83	-133.6
$L \rightarrow L'$	31.49	2829.0	13.84	-133.8
$L \rightarrow L'$	31.49	2829.0	13.84	-133.8
$L \leftarrow L'$	31.47	2829.0	13.85	-133.8
$L \leftarrow L'$	31.52	2829.0	13.83	-133.6
$L \leftarrow L'$	31.58	2829.0	13.80	-133.4
$L \rightarrow L'$	25.49	2289.0	13.84	-133.8
$L \rightarrow L'$	25.49	2289.0	13.84	-133.8
$L \rightarrow L'$	25.49	2289.0	13.84	-133.8
$L \leftarrow L'$	25.48	2289.0	13.84	-133.8
$L \leftarrow L'$	25.50	2289.0	13.83	-133.6
$L \leftarrow L'$	25.55	2289.0	13.81	-133.4
$L \rightarrow L'$	20.37	1830.0	13.84	-133.8
$L \rightarrow L'$	20.38	1830.0	13.84	-133.8
$L \rightarrow L'$	20.38	1830.0	13.84	-133.8
$L \leftarrow L'$	20.34	1830.0	13.86	-134.0
$L \leftarrow L'$	20.39	1830.0	13.83	-133.6
$L \leftarrow L'$	20.41	1830.0	13.82	-133.5
			Average	-133.6
			Average deviation	0.08%

sufficient. With 10^{-5} *N* solutions, however, the more elaborate procedure was necessary, as a certain amount of random variation in the conductance was observed. The cause of this remained unknown, and no amount of mixing would eliminate the effect, so it could probably not be attributed to inhomogeneity of the solutions.

More than fourteen hundred measurements of zeta-potentials have been made, not counting numerous preliminary measurements made during the period when the apparatus and experimental procedures were being developed and tested. The most feasible way to present this mass of data seems to be to give first the details of a typical series of measurements on each of the three concentrations used, namely 10^{-3} , 10^{-4} , and 10^{-5} *N* KCl. These examples will indicate the precision attained in the actual measurements of *E*, *P*, κ , and the zeta-potentials computed from these data for a series of measurements made in rapid succession on a particular solution and capillary. Then we will give a summary of the results of many such series showing the variability of the zeta-potentials for a period of several weeks and the reproducibility of the zeta-potentials on different capillaries and the influence of the previous history of the capillary and of the methods of cleaning used.

A series of results on a 10^{-3} *N* KCl solution in the smaller capillaries is given in Table III, giving a value of $\zeta = -112.5$ millivolts and a

TABLE V. Measurements on 10^{-5} *N* KCl solutions.

Flow	P cm of Hg	E Milli- volts	R $\times 10^{-9}$	$\kappa \times 10^6$ (mhos/cm)	$E\kappa/P$ $\times 10^6$	ζ
$L \rightarrow L'$	11.49	7461	10.57	2.210	14.35	-138.6
$L \rightarrow L'$	11.42	7411	10.56	2.213	14.36	-138.7
$L \leftarrow L'$	10.76	7231	10.53	2.220	14.92	-144.2
$L \leftarrow L'$	10.76	7231	10.53	2.220	14.92	-144.2
$L \leftarrow L'$	18.16	11992	10.46	2.234	14.73	-142.3
$L \leftarrow L'$	18.24	12062	10.46	2.234	14.77	-142.7
$L \rightarrow L'$	18.10	11832	10.34	2.259	14.77	-142.7
$L \rightarrow L'$	17.90	11512	10.35	2.257	14.51	-140.2
$L \leftarrow L'$	15.47	10354	10.52	2.222	14.87	-143.7
$L \leftarrow L'$	15.46	10344	10.52	2.222	14.87	-143.7
$L \rightarrow L'$	15.43	10244	10.36	2.255	14.97	-144.6
$L \rightarrow L'$	15.28	9914	10.36	2.255	14.63	-141.4
Average						-142
Average deviation						1.2%

TABLE VI. Zeta-potentials (millivolts) with 1.000×10^{-3} *N* KCl.

Series	Capillary	Time	No. of determinations	$\kappa (\times 10^6)$	E/P (Av.)	ζ	Av. deviation
A	II	6 days	4	1.5098	7.432	-108.4	0.2%
	II	8	8	1.5063	7.513	-109.4	0.2
	II	10	8	1.5098	7.520	-109.7	0.3
B	I	1	7	1.5052	6.987	-101.6	0.3
	I	4	6	1.5084	7.681	-112.0	0.4
	I	5	8	1.5082	7.728	-112.7	0.3
	I	5	8	1.5082	7.755	-113.0	0.2
	I	6	8	1.5094	7.766	-113.2	0.3
	I	6	6	1.4848	7.717	-110.7	0.3
	I	8	8	1.4848	7.755	-111.2	0.1
	I	11	12	1.5059	7.762	-112.9	0.2
C	I	1	7	1.5077	7.318	-106.6	0.3
	I	1	4	1.5089	7.387	-107.7	0.1
	I	2	8	1.5108	8.145	-118.9	0.1
	I	3	21	1.5080	8.278	-120.6	0.3
	I	5	20	1.5084	8.317	-121.3	0.2
	I	6	12	1.5091	8.382	-122.2	0.2
D	II	0	32	1.5107	8.28 to 8.75	-120.9 to -127.7	
	II	0.5	12	1.5107	8.823	-128.8	0.1
	II	1	12	1.5159	8.804	-129.0	0.2
	II	1	13	1.5133	8.881	-129.9	0.2
	II	2	12	1.5133	8.915	-130.3	0.03
	II	2	17	1.5159	8.888	-130.1	0.2
	II	6	11	1.5124	8.887	-129.9	0.03
E	I	0	26	1.5162	8.310	-121.7	0.3
	I	1	13	1.5171	8.308	-121.7	0.1
	I	7	17	1.5164	8.231	-120.6	0.1

"probable error" of 0.05 millivolt. However, a critical examination of these results shows that the four measurements with flow from left to right give -112.65 ± 0.02 , and the four with flow in the opposite direction give -112.30 ± 0.05 . This indicates an asymmetry, presumably owing to a slight difference in the potentials of the two electrodes used. This asymmetry is eliminated by averaging the results. The four results using a pressure of 31+cm give -112.52 , whereas the four using a pressure of 23+cm give -112.42 . The value of *R* remained essentially constant during this series. The resistance was 587.9 megohms.

In Table IV we give a series of results obtained on a 10^{-4} *N* KCl solution in the smaller capillary. These data, which were obtained near the end of the work, are exceptionally good but are selected to show the precision attainable after the apparatus and technique had been perfected. Here

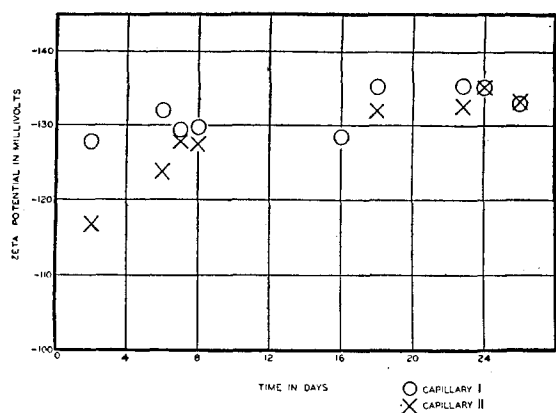


FIG. 5.

there is no difference between the results with variation in the pressure from 20.4 cm of Hg to 31.5 cm of Hg. The average zeta-potential when the flow was from left to right is -133.8 millivolts; and when the flow was in the opposite direction, the result was -133.6 millivolts. The resistance varies from 5646 megohms to 5637 megohms, giving a specific resistance of $\kappa = 15.41 \times 10^{-6}$.

Table V gives a similar series of measurements on a $10^{-5} N$ KCl solution. These data were obtained with the larger capillary. For this dilute solute the streaming potential was about 12 volts with a driving pressure of 18 cm of mercury. The resistance was more than 10^{10} ohms. The results are more erratic than for the more concentrated solutions used. There is no systematic variation in potential with variation in pressure and the asymmetry amounts to about 1.5 percent.

These three tables were selected as examples of the sort of experimental results obtained. They show that the technique for the actual zeta-potential measurements was apparently reliable to a few tenths of a millivolt. However, it soon became evident that constancy and reproducibility of the zeta-potentials was much less satisfactory. In the following tables the results of more than 1400 individual measurements are summarized. We give the average values of each series of measurements made in rapid succession, together with the number of separate measurements and the average deviation from this average. The Roman numeral I indicates that the set of measurements so designated was obtained with the capillary of 0.032-cm diameter, and cell

constant $l/a = 23,365$; and II refers to measurements obtained with the capillary of 0.017-cm diameter, and cell constant $l/a = 86,920$. These data are given in the chronological order in which they were obtained. The "Time" indicates the number of days elapsed since the solution and capillary first came in contact after assembly of the apparatus.

The first zeta-potentials obtained with 0.001,000N KCl solution after the experimental technique had been developed are shown in Table VI, series A, B, and C.

Between each series of measurements the apparatus was dismantled, the capillary cleaned as described above and refilled. It was observed that the zeta-potential of the freshly cleaned capillary surface increased (in absolute value) over a period of many days, presumably approaching an equilibrium value. Earlier preliminary measurements gave much similar experience. This increase was usually irregular and appeared to be a function of time and of amount of previous flow of the solutions through the capillary. It could sometimes be hastened by warming the capillary gently. It was thought that the slow rise was due to a gradual approach of the silica-solution interface to equilibrium with the solution, due possibly to slow adsorption of ions or hydration

TABLE VII. Zeta-potentials (millivolts) with $1.000 \times 10^{-4} N$ KCl.

Time (days)	Number of measurements	$\kappa (\times 10^5)$	E/P (av.)	ζ	Average deviation
<i>Capillary I</i>					
2	8	1.5708	84.21	-127.8	0.5%
6	7	1.5645	87.30	-132.0	0.3
7	15	1.5645	85.62	-129.5	0.1
8	12	1.5643	85.88	-129.8	0.2
16	17	1.5771	84.34	-128.5	0.5
18	9	1.5685	89.26	-135.3	0.4
23	18	1.5709	89.21	-135.4	0.5
24	20	1.5722	88.95	-135.1	0.6
26	16	1.5709	87.63	-133.0	0.5
<i>Capillary II</i>					
2	5	1.6089	75.16	-116.8	0.3%
6	8	1.5941	76.31	-117.5	0.2
7	17	1.5811	81.03	-123.8	0.3
8	12	1.5863	83.47	-127.9	0.4
18	14	1.5793	83.59	-127.5	1.0
23	9	1.5837	86.29	-132.1	0.7
24	18	1.5407	89.78	-133.6	0.1
26	17	1.5576	89.77	-135.1	0.2
26	20	1.5454	89.18	-133.1	0.3

of the surface layer of silica molecules. If this were so, there ought to have been some effect on the initial and none, we hoped, on the final value of the zeta-potential, if the interface were thoroughly saturated with KCl in $N/10$ solution before the measurements were made with $10^{-3} N$ solution. This would have meant that initially the interface, instead of being in an equilibrium condition for pure water as with the thoroughly steamed capillary, was in equilibrium condition with $N/10$ KCl and might reach equilibrium with the $10^{-3} N$ solution more rapidly from the opposite direction. Accordingly capillary II was exposed to $N/10$ KCl, and then, when installed in the apparatus, yielded the data summarized in Table VI, series D. The value of ζ increased rapidly from -120.8 to -127.8 as shown in the first 32 measurements made immediately after installation. After several days some degree of equilibrium seemed finally to have been attained.

This procedure was repeated for capillary I, as summarized in Table VI, series E, and it was found that the zeta-potentials were not in agreement with Table VI, series D. It was found evident that this had not solved the problem of

reproducibility of the equilibrium potentials. This was later confirmed by additional similar experiments.

The data in Table VI demonstrate the variability of the capillary surface conditions, which constitute the major source of uncertainty in the measurements reported here.

We then turned our attention to more dilute solutions. Since control of the condition of the surface was obviously not fully achieved by the technique of previous treatment outlined above,

TABLE IX. Zeta-potentials (millivolts) with $1.000 \times 10^{-3} N$ KCl.

Time (days)	Number of measurements	$\kappa (\times 10^6)$	E/P (av.)	ζ	Average deviation
<i>Capillary I</i>					
11	8	1.4681	7.818	-110.9^*	0.6%
12	12	1.4674	7.847	-111.2^*	0.9
13	8	1.4666	7.937	-112.5^*	0.7
<i>Capillary II</i>					
11	8	1.4785	7.784	-111.2^*	0.4%
12	12	1.4792	7.867	-112.5^*	0.3
13	8	1.4784	7.875	-112.5^*	0.2

* In obtaining these values, κ and E/P were measured at the same time and the ζ 's were computed for each measurement, and then averaged. All earlier ζ values above were determined by measuring κ before and after a series, and taking the average κ , which was then multiplied by the average E/P and the proper factor to give an average ζ . The later method has the advantage of detecting variations in the conductivity which may and do occur, in the extremely dilute solutions, during a series of measurements.

TABLE VIII. Zeta-potentials (millivolts) with $1.00 \times 10^{-5} N$ KCl.

Time (days)	Number of measurements	$\kappa (\times 10^6)$	E/P (av.)	ζ	Average deviation
<i>Capillary I</i>					
3	8	2.005	618.9	-119.8	0.5%
4	10	2.047	582.8	-115.3	0.8
5	8	2.063	592.3	-118.1	0.7
8	4	2.175	646.6	-135.8	1.0
	8	2.304	592.8	-132.0	1.6
15	8	2.195	684.7	-145.2^*	1.5
	8	2.186	684.0	-144.4^*	1.3
16	12	2.233	659.2	-142.2^*	1.2
<i>Capillary II</i>					
3	8	2.547	606.4	-149.3	2.5%
4	10	2.599	577.1	-144.9	0.4
5	8	2.599	579.8	-145.6	0.6
8	10	2.721	535.7	-140.9	1.2
	6	2.860	536.8	-148.3	0.8
15	8	2.916	534.7	-150.6^*	1.0
	8	2.882	541.0	-150.6^*	0.4
16	12	3.048	509.6	-150.1^*	0.7

* In obtaining these values, κ and E/P were measured at the same time and the ζ 's were computed for each measurement, and then averaged. All earlier ζ values above were determined by measuring κ before and after a series, and taking the average κ , which was then multiplied by the average E/P and the proper factor to give an average ζ . The later method has the advantage of detecting variations in the conductivity which may and do occur, in the extremely dilute solutions, during a series of measurements.

or by any other procedure that was later tried, it was believed that a good value for the zeta-potential could only be obtained by allowing time for the two capillaries simultaneously to approach the same value. When this occurred, it could be presumed that equilibrium had been reached. Therefore, the second apparatus already mentioned was built, and both were operated at the same time. The changes in the zeta-potential were studied, and when the two reached identical values, this was taken as the most probable value for the equilibrium potential. This method was applied to the measurements made using $1.000 \times 10^{-4} N$ KCl solution, which are given in Table VII and Fig. 5. These data illustrate very well the change with time of the zeta-potential, with the capillary II displaying a regular increase, and the larger capillary I an irregular one. Each figure represents the average of a set of

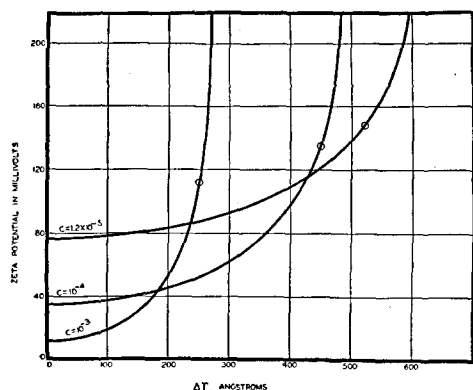


FIG. 6.

measurements made on the stated day after the assembly of the apparatus.

For this concentration, the value of -135 on the twenty-fourth day was chosen as the best value instead of the value of -133 on the twenty-sixth day. It was thought that, other considerations being equal, for KCl solutions the higher value was more probably the correct one. Impurities such as multivalent positive ions or carbon dioxide were found to decrease the magnitude of the zeta-potentials for KCl solutions. Consequently, since the value on the twenty-fourth day was the highest attained simultaneously by both capillaries, it was considered the most probable value of the true equilibrium potential.

The zeta-potentials of the silica in contact with $1.00 \times 10^{-5} N$ KCl solution were next determined. Table VIII gives the information obtained. The potentials of the two capillaries did not reach identical values, so it was necessary to take the average of the pair nearest each other for the most probable value. These values were -145.2 mv, from capillary I, and -150.6 mv from capillary II, which gave -148 as the average.

Following this, the solution of $10^{-3} N$ KCl was again put in the apparatus and the zeta-potentials redetermined. The values on the 11th, 12th, and 13th days are given in Table IX. The best value was taken as -112.5 millivolts, which agrees with series A and B, (Table VI), but not with series C, D, and E, (Table VI), the last two having been given a different previous treatment. The results of this last determination were considered to be more reliable than the 5 earlier series.

APPLICATION OF THE LANGMUIR THEORY

The results on zeta-potential measurements recorded above have been used to compute the thickness of the wetting film in accordance with the Langmuir theory. These calculations have been carried out with the rigid forms of the equations given in the paper of Jones and Frizzell.⁴ For the sake of abbreviation the development of these equations and the explanation of the symbols are not repeated here. The parameters used in these calculations are taken from a compilation by Birge.²¹ The results are shown in Table X. The curve giving the thickness of the wetting film (Δr) as a function of the potential for several concentrations of electrolytes is shown in Fig. 6.

The most dilute solution for which we have as yet succeeded in obtaining zeta-potential measurements is a $0.000,01N$ KCl solution for which we find $\zeta = -148$ millivolts. Using $c = 0.000,01$ and $\zeta = -0.148$ gives the thickness of the wetting film $\Delta r = 516$ angstroms. Or if we make allowance for the ions derived from water of $c = 0.000,002N$ ($c\Lambda = 1000\kappa$; $\kappa = 0.8 \times 10^{-6}$, $\Lambda = 400$, $c = 0.000,002$) giving a total of $c = 0.000,012$ the result is $\Delta r = 521$ angstroms.

The correcting factor to be applied to the "apparent relative surface tensions" previously reported would then be $r - \Delta r_c / r - \Delta r_0$.

The radius of the capillary in the instrument used by Jones and Ray was $r = 0.0136$ cm. Since we do not have zeta-potential measurements for pure water we will tentatively assume that the surface tension for a $0.000,01N$ KCl solution is the same as that of water and estimate the Langmuir correction for $0.0001N$ and for $0.001N$ KCl solutions by reference to $0.000,01N$ KCl in-

TABLE X. Calculation of thickness of wetting films.

c	0.000,01	0.000,012	0.000,1	0.001
ψ_m volts	3.150,48	2.984,40	1.356,20	0.458,48
$K = e^{-\psi_m}$	0.080,94	0.076,77	0.034,84	0.011,78
$\sin^{-1} K$	0.042,831	0.050,570	0.025,764	0.032,25
$F\left(\frac{\pi}{2}, \sin^{-1} K\right)$	2.454,8°	2.898,7°	14.929,9°	39.215,9°
ζ (volts)	0.148	0.148	0.135	0.112
ϕ	15.808,5°	14.484,4°	8.201,9°	8.187,5°
$F(\phi, \sin^{-1} K)$	0.275,9	0.252,8	0.143,2	0.143,1
$\frac{1}{\kappa}$	961.85 $\times 10^{-8}$	878.04 $\times 10^{-8}$	304.16 $\times 10^{-8}$	96.185 $\times 10^{-8}$
Δr (Å)	516	521	449	250

²¹ R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

stead of to water. Putting $\Delta r_0 = 521 \times 10^{-8}$ and for Δr_c the values given in Table X give for 0.0001*N* KCl solution

$$\frac{r - \Delta r_c}{r - \Delta r_0} = \frac{0.0136 - 0.000,004,40}{0.0136 - 0.000,005,21} = 1.000,05,$$

and for 0.001*N* KCl

$$\frac{r - \Delta r_c}{r - \Delta r_0} = \frac{0.0136 - 0.000,002,50}{0.0136 - 0.000,005,21} = 1.000,20.$$

Applying these corrections to the relative surface tension given by Jones and Ray gives for 0.000,1*N* KCl

$$\frac{\sigma_c}{\sigma_0} = 0.999,97 \times 1.000,05 = 1.000,02,$$

and for 0.001*N* KCl

$$\frac{\sigma_c}{\sigma_0} = 0.999,82 \times 1.000,20 = 1.000,02.$$

These results therefore support Langmuir's suggestion that there is no minimum in the surface tension-concentration curve.

However, before reaching a definite conclusion as to the general validity of the Langmuir theory, it seems desirable to secure more zeta-potential measurements for many of the other salts for which we have surface tension measurements, and also to explore the effect of the charge at the air-solution interface, which is ignored in the theory as proposed by Langmuir and used in the above calculations.

The Fluorescence of Diethyl Pseudo-Isocyanine Chloride in Solution

E. HIRSCHLAFF HUTTEN AND PETER PRINGSHEIM

Department of Physics and Department of Chemistry, University of Chicago, Chicago, Illinois

(Received July 27, 1944)

The fluorescence and absorption spectra of the dye diethyl pseudo-isocyanine chloride in various solid solutions and at several concentrations and temperatures have been obtained by means of a spectrograph of high dispersion. It has been shown that the dye is fluorescent not only in the polymerized state but also when it is embedded in a "rigid" medium.

I.

IF dyes of the type of pseudo-isocyanine chloride are dissolved in water and if the concentration exceeds 5×10^{-3} molar, the dye begins to polymerize: the viscosity of the solution increases greatly, so that the liquid is transformed into a gel. Simultaneously, a new narrow band appears in the absorption spectrum in the neighborhood of $\lambda 5730\text{\AA}$, while the broad molecular bands in the green and blue-green region ($\lambda 5435\text{\AA}$ and $\lambda 5040\text{\AA}$) become weaker.¹ The absorption spectrum of the dye 1,1'-diethyl-2,2'-cyanine chloride, which has been used in our experiments, has been discussed in detail elsewhere.² For the

sake of brevity the dye will be called " ψ " in the following paragraphs and $\psi (10^{-3})$, for instance, is used to denote a solution of the dye at a concentration of 10^{-3} molar.

Regarding the emission spectrum of the dye the following facts are known. The ordinary solu-

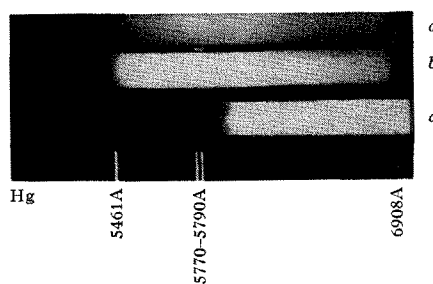


FIG. 1. Fluorescence at -190°C . (a) $\psi (10^{-3})$ in water + 2 g gelatine. (b) $\psi (10^{-3})$ in pentane. (c) Crystalline dye.

¹ E. E. Jelley, *Nature* **138**, 1009 (1936); G. Scheibe, *Zeits. f. angew. Chemie* **50**, 51 (1937).

² R. W. Mattoon, *J. Chem. Phys.* **19**, 268 (1944). For a complete bibliography on the subject we refer to this paper.