CCIX.—*The Electroendosmosis of Aqueous Solutions through a Diaphragm of Sintered Glass Powder.*

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GLASS capillaries and diaphragms of powdered glass have been used for many quantitative investigations on electrokinetic phenomena. A review of the earlier work (to the end of 1913) is given by Smoluchowski (Graetz, " Handb. d. Elektrizität u. des Magnetismus," Vol. 2, p. 366). Powis (*Z. physikal. Chem.*, 1915, **89**, 91), Kruyt (*Kolloid Z.*, 1918, **22**, 81), Freundlich and Rona (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397), and Hepburn (*Proc. Physical Soc.*, 1926, **38**, 363 ; 1927, **39**, 99) have also used a glass–water interface for electrokinetic experiments.

The results of Lachs and Kronman (*Bull. International Acad. Polonaise*, 1925, **10**, *A*, 289), however, appear to throw some doubt on the quantitative value of previous work, for they found that the stream potentials through glass and quartz capillaries could be reproduced with an accuracy of only 14% under seemingly identical conditions, and they state that " the streaming potential has no constant value and is varying in time." Hence they argue that all results obtained for flow potentials of aqueous solutions in glass or quartz capillaries must be considered to be merely qualitative (*Rocz. Chem.*, 1926, **6**, 641). Such a conclusion necessarily involves also electroendosmosis of aqueous solutions through glass powder or capillary tubes.

The results now recorded, which were carried out before the work of Lachs and Kronman came to our notice, were the outcome of preliminary experiments with diaphragms of sintered Jena-glass powder, carried out with aqueous solutions prior to the use of such a diaphragm for electroendosmotic investigations in non-aqueous systems.

A diaphragm of sintered glass powder possesses the advantages of rigidity and simplicity, *i.e.*, no foreign material (glass wool, etc.) is required to keep the diaphragm in place, and the apparatus can be made of the same kind of glass holding the diaphragm fused in position.

EXPERIMENTAL.

The apparatus employed was essentially that described by Fairbrother and Mastin (J., 1924, **125**, 2319), the central compartment A (*loc. cit.*) being replaced by a tube carrying the sintered diaphragm fused into its centre, and the capillary tubes, EE, extended to the sides of the diaphragm. The particular glass disc used, of sintered Jena " Geräte " glass, was of the closest grain manufactured (designated as G3/<7), and was approximately 2 cm. in diameter and 3 mm. thick. It was supplied fused in position by the makers, Messrs. Schott u. Gen. of Jena.

The diaphragm was cleaned first in alcohol or acetone to remove grease, and then in concentrated sulphuric acid. Air was removed from the pores by placing the tube carrying the diaphragm in a larger tube, and evacuating by a water pump; a small quantity of air-free water was then admitted to the containing vessel and allowed to boil under reduced pressure for some time, after which air-free water was allowed to fill the vessel. Before each series of estimations, the apparatus was well rinsed with the solution employed, several hundred c.c. being allowed to pass through the diaphragm over-night.

The value of l/q (the ratio of the effective length of the diaphragm to its effective cross section) was measured with several solutions in the manner described by Fairbrother and Mastin (*loc. cit.*). Each estimation was repeated many times with various voltages across the diaphragm. The individual readings showed good agreement. In Table I are the average values of l/q for each solution; they show a small increase with concentration, even in such comparatively well-conducting solutions.

TABLE I.

Solution.	l/q.	Solution.	l/q.
$N/100$-KCl	1·723	$N/100$-HCl	1·758
$N/10$-KCl	1·736	$N/10$-HCl	1·782
$N/5$-KCl	1·751	$N/5$-HCl	1·783
$N/1$-KCl	1·755		

In Table II are the results of electroendosmosis experiments with water and dilute hydrochloric acid. ET (in volt-seconds) is the product of the potential gradient across the diaphragm and the time for the transport of 1 c.c. of solution. ζ, the potential of the double layer as calculated from the Helmholtz–Smoluchowski formula, is also given for comparison; in making this calculation, a value for l/q of 1·77 has been assumed.

For some time no great difficulty was experienced in obtaining concordant and reproducible results, which are given as Series I.

TABLE II.

	Series I.		Series II.	
Solution.	*ET*.	ζ (volt).	*ET*.	ζ (volt).
Water	4,520	−0·0557	14,880	−0·0169
N/5000-HCl	4,880	−0·0516	26,700	−0·0094
N/1250-HCl	5,668	−0·0444	43,500	−0·0058
N/400-HCl	6,546	−0·0394	?	0·00
N/100-HCl	10,200	−0·0247	17,970	+0·0140

At this time, the glass was still negatively charged in *N*/40-hydrochloric acid. During experiments with this solution, however, effects similar to those found by Lachs and Kronman were first observed, *i.e.*, ζ became less negative with time. Repetition of the estimations in the solutions previously used gave the results of Series II, the diaphragm having in the meantime been carefully cleaned. The results obtained in this series were also quite concordant among themselves, but ζ was throughout less negative than in the same solution in Series I. The glass surface appears to have undergone some change which has the effect of rendering it more positive. Experiments with dilute solutions of lanthanum nitrate gave further indications that ζ was decreasing with increase of time; and at the conclusion of these experiments, ζ in distilled water was found to have undergone a further decrease.

Some time previous to the foregoing experiments, the permeability of this particular diaphragm had been measured for the purpose of proving that Poiseuille's law held good, and that the resistance of the bubble and connecting tubes to the flow of water was negligible compared with that of the diaphragm—necessary conditions for accurate work by our method. It was found that the diaphragm had a " specific permeability " at 20° of $2{\cdot}10 \times 10^{-4}$: by this term is meant the number of c.c. of water passing through per second under a head of 1 cm. of water. After the foregoing experiments, the permeability was redetermined, and was found to have fallen to $2{\cdot}43 \times 10^{-5}$, or about one-ninth of its former value.

The permeability estimations were carried out by allowing boiled distilled water, under a head of about 80 cm. (measured by a cathetometer), to flow through the diaphragm and escape by a small tube into a tared weighing bottle. The estimations were performed in a room the temperature of which remained practically constant during an estimation. The temperature of the water was further observed in the proximity of the diaphragm, and the permeability corrected for changes in viscosity and density to 20°. Great care was taken to ensure the absence of grease or suspended impurities in the water.

Continued passage of water through the diaphragm brought about a still further decrease of permeability. After the diaphragm had been soaked over-night in pure concentrated nitric acid, the permeability rose to $2{\cdot}038 \times 10^{-4}$, which is approximately the same as that found originally. Subsequent passage of water again effected a decrease in the permeability, rapidly at first, and then more slowly.

It was observed that the permeability decreased at a greater rate if the water were passed through than if it were allowed merely to remain in the diaphragm. A determination of the electroendosmosis in distilled water, immediately after the diaphragm had been treated with nitric acid, gave $\zeta = -0{\cdot}0557$ volt, which is the same as that initially found. This, however, was only a temporary value, and subsequent estimations in dilute hydrochloric acid agreed more nearly with Series II.

The decrease in permeability on passage of water was confirmed with other diaphragms. In one case, where the porous plug was of the same kind as that used above, but 5 mm. instead of 3 mm. thick, even consecutive estimations showed a decrease, and in 4—5 hours the permeability fell from $1{\cdot}746 \times 10^{-5}$ to $0{\cdot}574 \times 10^{-5}$. Another plug of the same porosity, 3 cm. diam. and 3 mm. thick, was attached directly to the receiver of a conductivity-water still: passage of about 3 litres of water, over a period of a week, reduced the permeability to half its initial value.

In these latter cases the change appears to have taken place much more quickly than with the apparently similar filter disc used in the first set of experiments. This may be partly accounted for by the fact that the first disc had been heated and annealed more than the others, during the process of forming ground joints on the tube which contained it. In the case of this diaphragm also, it would almost appear that there was an initial period during which no appreciable change took place.

Discussion.

The foregoing results suggest strongly that the glass surface has undergone a swelling process. Haber and Klemensiewicz (*Z. physikal. Chem.*, 1909, **67**, 385) postulate the existence of a swollen layer on the surface of the glass in explaining their observations with the glass electrode, and Lachs and Kronman (*loc. cit.*) suggest that their results are probably due to a swelling process which advances with time.

A simple decrease in the effective size of the pores of the diaphragm, although explaining a decrease in the amount of electroendosmosis, and hence in the (negative) value of the interfacial potential (when this is calculated on the assumption of a too small value of l/q), would not in itself bring about a reversal in the direction of electroendosmosis. We must therefore conclude, either that the swelling of the surface layer is accompanied by a change which has the effect of imparting a positive charge to the diaphragm, or that the distribution of potential within the swollen layer is such as to cause a reversal of sign in certain solutions, *e.g.*, $N/100$-hydrochloric acid. Lachs and Kronman attribute the decrease of ζ, due to the thickening of the wall layer by swelling, to a shifting of the line along which displacement occurs (Fig. 1, A and B).

If, however, the course of the potential should be as in Fig. 2, as suggested by Freundlich ("Kapillarchemie," 1922, p. 342) in order to explain the difference in sign between thermodynamic and electrokinetic potentials, then we might obtain a reversal of direction of electroendosmosis by a thickening of the wall layer.

FIG. 1.

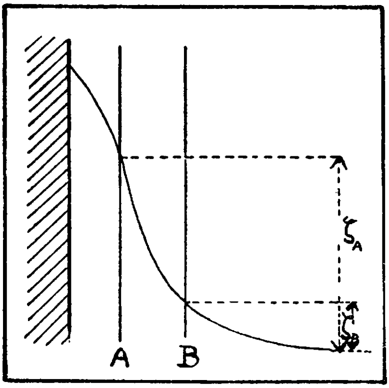
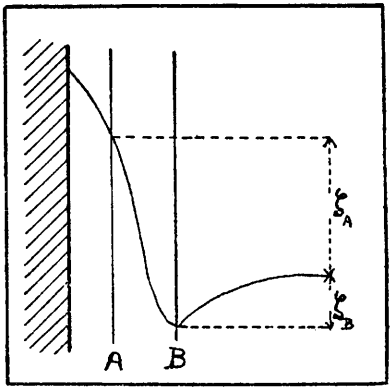


FIG. 2.



The present work therefore supports the conclusion of Lachs and Kronman, that the interfacial equilibrium between glass and aqueous solutions is not a true one, but one which changes with time. Since, however, the change in the surface may, with suitable material, take place relatively slowly, this change does not necessarily invalidate experiments carried out on the effects of ions of different kinds on the interfacial potential. It is to be expected, for example, that the change will occur more slowly with the Jena "Geräte" glass used in the present work than with the ordinary Thuringian glass used by Lachs and Kronman.

We also passed considerable quantities of alcohol and of benzene through the dried diaphragm, without observing any change in the permeability to these liquids. Such a diaphragm, therefore, can probably be used successfully for quantitative experiments in non-aqueous liquids.

Summary.

(1) Electroendosmosis experiments have been carried out with a diaphragm of sintered Jena " Geräte " glass powder in water and in dilute hydrochloric acid.

(2) The amount of electroendosmosis decreased after a time, and in $N/100$-hydrochloric acid it became reversed in direction.

(3) Experiments were also carried out on the permeability of the diaphragm to water. This also decreased with the time during which water was passed through the diaphragm.

(4) It is suggested that these results indicate that the glass surface undergoes a swelling process, and, further, that the distribution of potential within the swollen layer may account for the reversal of direction.

In conclusion, we should like to thank Mr. C. E. Marshall, who carried out a number of preliminary measurements, and to acknowledge our indebtedness to the Chemical Society Research Fund and the Brunner–Mond Research Grant to this Department, which have partly defrayed the cost of this work. One of us (H. V.) also desires to thank the Department of Scientific and Industrial Research for a maintenance grant during its prosecution.

THE UNIVERSITY, MANCHESTER. [*Received, May 5th,* 1927.]