ELECTROKINETIC PHENOMENA

IV. A Comparison of Electrophoretic and Streaming Potentials

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(Accepted for publication, February 27, 1931)

Theoretical

It has long been known that a simple relationship may exist between the electrical mobility of a particle relative to a liquid in which it is suspended and the electrical potential produced by the liquid streaming past a surface having the same chemical constitution as the surface of the particle.[1] From the electrical mobility, V, of a particle, the electrokinetic potential, ζ_c may be calculated:

$$\zeta_c = C\frac{V\eta}{DX} = 4\pi\frac{V\eta}{DX}, \tag{1}$$

where C = constant, here taken as 4π; η = coefficient of viscosity of the medium; D = dielectric constant of the medium; X = field strength. Similarly, from measurements of streaming potentials the electrokinetic potential, ζ_s, may be calculated:

$$\zeta_s = \frac{KH}{P}\frac{4\pi\eta}{D}, \tag{2}$$

where K = specific conductance of the liquid;* P = hydrostatic pressure difference; H = streaming potential. The units of equations (1) and (2) are c.g.s., electrostatic. Until the appearance of an article by Briggs,[2] no data were available for the direct experimental comparison of ζ_c and ζ_s. Briggs studied the streaming potentials set up by

* Surface conductance is here neglected.

buffer solutions flowing through quartz diaphragms covered with adsorbed crude egg albumin. He employed this system in order to compare his values of ζ_s with values of ζ_e obtained by Abramson[3] and by Freundlich and Abramson.[4] The agreement between ζ_s and ζ_e found by Briggs was indeed quite remarkable, as Gortner[5] points out, and substantiated quite well the underlying soundness of the present theory. This result had been predicted by one of us[6] on the basis of experiments with protein-covered quartz particles. It was shown that, since quartz particles covered with egg albumin had the same mobility regardless of size and shape, if the theory were correct the streaming potentials across diaphragms composed of similar particles should give a ratio of $\frac{\zeta_e}{\zeta_s} = 1.00$, approximately.

Briggs' data on streaming potentials were obtained in 0.0004 M mixtures of HCl-LiCl, while the values of ζ_e had been calculated from data obtained in N/50 acetate buffers. In consequence, a strictly quantitative comparison of ζ_s and ζ_e was hindered by the fact that important differences in ionic strength and ionic species were present in the two series of experiments. It is necessary at this point to stress the significance of data previously obtained[7] which describe the relationship between electrophoretic and electroosmotic mobilities. It has been found that the ratio of ζ_e to ζ_e, the potentials calculated on the basis of electroosmotic experiments for *flat* and for *curved surfaces* respectively, covered with protein, is 1.00, very nearly. This ratio is not dependent upon the bulk constitution of the particle. Since therefore, ζ_e and ζ_s are very intimately connected, on the basis of these experiments it is evident that a similar relationship should exist between ζ_e and ζ_s. Whatever may be the theoretical justification for believing that electrophoresis and electroosmosis differ in some fundamental way, the experiments just cited certainly give excellent evidence that these differences, if they do exist, are probably within the limits of error of the technic employed. Thon,[8] for example, has recently pointed out that the positions of the well known maxima and minima in the ζ-concentration curves differ in electrophoresis and streaming potential measurements on substances having the same bulk constitution. It will be evident from the following discussion that a simple comparison of the sort made by Thon is not a sufficient test of

the theory postulating agreement between the values of ζ_c, ζ_s, and ζ_e; for surfaces can be employed to test the electrokinetic theory under discussion only when *surface properties* of the materials studied are the same. This is discussed in detail in the following paragraphs.

The experimental problem, in reality, may be said to center about this question: What surfaces are most suitable for the determination of the relationships between ζ_c, ζ_s, and ζ_e? The answer to this query must concern itself with the following facts:

1. It is evident from equation (1) that the velocity, V, depends upon the potential, ζ. If we consider the double layer as a rigid system in the Helmholtz sense,

$$\zeta = \frac{4\pi\sigma}{D}\lambda, \tag{3}$$

where λ is the thickness of the double layer, σ being the density of charge. The potential, ζ, and in consequence the velocity, V, can vary with the chemical constitution of the surface, which can determine σ, and with the thickness of the double layer λ. As Müller[9] has emphasized, the theory of Debye and Hückel leads to the relationship,

$$\lambda = \frac{1}{\kappa}\cdot\frac{\kappa R}{1+\kappa R}, \tag{4}$$

where R is the radius of the particle (and here the radius of curvature of all points on the surface), $\mu = \frac{1}{2}\Sigma n_i z_i^2$, one half the sum of the products of the concentrations of all ions of the i^{th} type into the squares of their valences; $\kappa = 0.3\sqrt{\mu}10^8$. The thickness of the double layer is independent of R within the limits of experimental error when $\kappa R \gg 1$. This is evident from (4), for then

$$\lambda = \frac{1}{\kappa}, \text{ very nearly;}$$

and if the chemical make-up of the surface does not appreciably change with change in R, there results the familiar consequence of the Helmholtz theory in equation (1); this, lacking a size term, predicts V to be independent of particle radius.

2. There are two groups of relevant experimental data[10] available for the testing of theories of electrokinetic phenomena. One group

concerns microscopic particles whose electrical mobilities are independent of size and shape. This group is characterically represented by quartz particles and paraffin oil droplets, each covered with adsorbed protein. The other group comprises mainly emulsions of the type studied by Mooney.[11] This author found, for example, that the droplets of an emulsion prepared by shaking a *mixture* of red oil and benzyl chloride in distilled water, have mobilities which depend upon R. Up to $R = 0.07$ mm., approximately, the mobility increases rapidly with increasing radius. Droplets from 0.07 to 0.22 mm. in radius show no differences in mobility within the limits of experimental error. Mooney's interpretation of his data is slightly different from ours.

3. The group of particles whose mobilities depend upon R is not suitable for the investigation of the relationship between ζ_c, ζ_s, and ζ_e, for then the ratios obtained depend upon R. In remarkable contrast is the behavior of protein-covered particles. These particles are unaffected by slight changes in ionic strength and ionic type (with the exception of the hydrogen ion activity), in the case of ions of low valence. Because in the case of certain microscopic particles, regardless of size, shape, and bulk conductance, all particles have equal mobilities, and because little if any difference is to be found in the mobilities of adsorbed ($R = 10^{-4}$ cm.) and freely-dispersed protein ($R = 10^{-7}$ cm.), it seems logical to assume that a comparison of ζ_c, ζ_s, and ζ_e is most suitably carried out with these systems, which for practical purposes have mobilities independent of R.*

ζ_c has now been reinvestigated in electrophoresis apparatus which has enhanced the accuracy of this method. Solutions of the same ionic strengths and ionic species as those used by Briggs have been employed. The agreement found here for ζ_c and ζ_s is not as satisfactory as that deduced from older experiments. A suitable explanation is proposed.

* Recent preliminary experiments on quartz particles covered with adsorbed crystalline serum albumin have confirmed earlier data.[12] The mobilities of these quartz particles were very close to the mobilities observed under similar conditions by Tiselius.[13] These and related data will be presented in a further communication.

Methods

During the past 3 years modifications of the technic for measuring electrical mobilities have been developed. It is desirable to describe and to reemphasize these at this time.

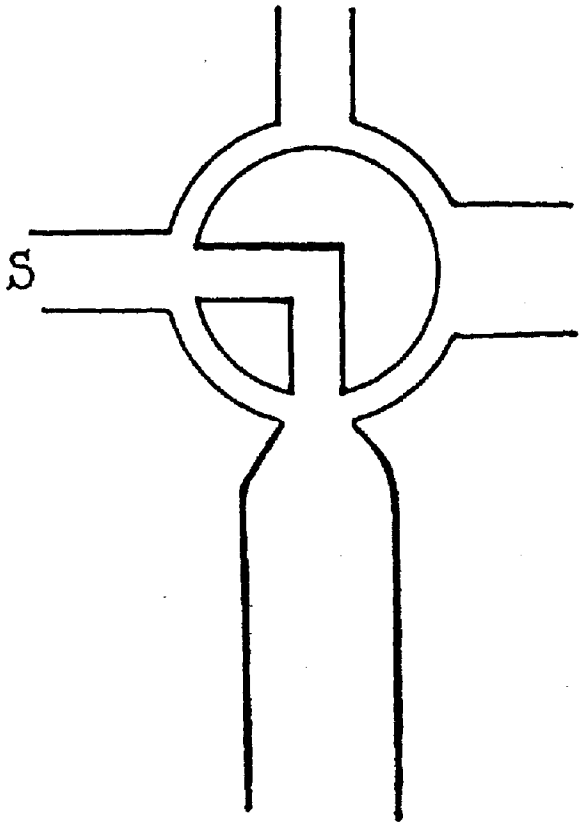

FIG. 1. Tube *S* is used to keep the pressure in the electrode equal to that of the air when the electrophoresis apparatus is not in use. For the complete description of the apparatus, the earlier publications may be consulted.

Electrodes.—We have continued to use Cu-$CuSO_4$ (sat.) reversible electrodes.[14] Agar plugs have been discarded and in their place plaster of paris plugs have been

more useful and are more satisfactory.* The agar plugs deteriorate quickly and must be replaced frequently. Plugs of plaster of paris, on the other hand, although having the undesirable quality of a lower electrical conductance, may be used over periods as long as 6 months without replacement if care is taken to prevent erosion by solutions employed in experimentation. The plugs are made in the fashion described previously.

Avoidance of Turbulent Streaming.—A further slight modification of the apparatus described previously is successful in almost completely abolishing serious

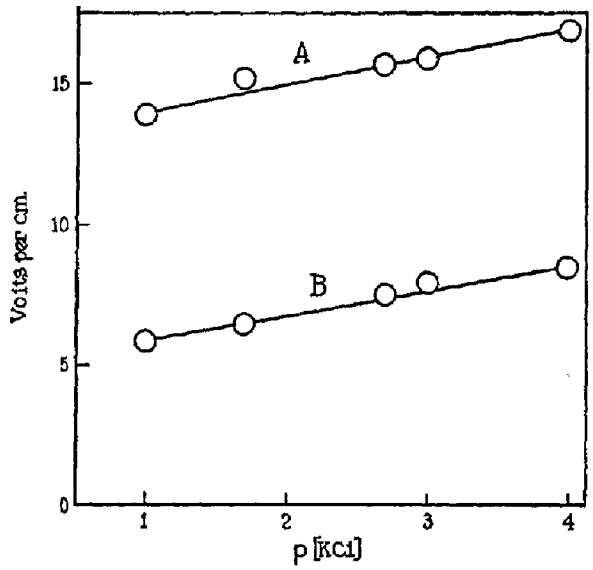

FIG. 2. The gradient of potential (with the total P.D. = 120 volts) in the cells *A* and *B* is plotted against the negative logarithm of the concentration of KCl solution filling the apparatus. The explanation for the rise in gradient of potential with dilution of salt is given in the text. See Table I.

streaming due to unequal pressures in the electrode vessels. Tube *S* in Fig. 1 is merely a short, small glass tube which serves to connect the electrode with the air when the apparatus is not in use. It is employed on both sides of the cell.

* A permanent connecting plug of a porous type of Portland Cement supplied by the Aerocrete Company has been used for 1 year without solution or even erosion. This material is suitable only if very small currents need to be passed through the apparatus. If currents of the usual order of magnitude are employed polarization at the boundaries of these plugs may occur.

Since variation in room temperature causes expansion and contraction of the liquid within the electrode vessels, turbulent streaming is frequently encountered after the cell has not been in use during the night. We had previously left one electrode open through the opposite stop-cock to the outside, after filling the apparatus with saturated $CuSO_4$ or Na_2SO_4 solution. Before the apparatus could be used, however, the other electrode pressure had to be equilibrated Tubes S dispense with the necessity for this procedure of pressure equilibration since the liquids in the electrode vessels are permanently maintained at atmospheric pressure when the apparatus is not in use.

The Drop in Potential in the Cell.—For the past 5 years the number of volts per cm. in the cell has been calculated by means of Ohm's law.[14] This method has

TABLE I

The dimensions of two microelectrophoresis cells suitable for most purposes. These cells are recommended since the differences in dimensions give a considerable difference in working range with possibility of cross-checking.

Approximate dimensions of	Cell A	Cell B	Remarks
	cm.	*cm.*	
Bore of stop-cock	0.3	0.3	It can be shown graphically that no considerable error is introduced by calculating q, the cross-section, from a mean value of the thickness obtained from about ten points across the width of the cell. The cell is not exactly uniform in cross-section. Cells A and B, in addition to the differences noted, had electrode vessels of different sizes and shapes. The type recommended is indicated in Fig. 1.
Length of side-arm	6.5	8.1	
Internal diameter of side-arm	0.9	0.6	
Length of cell	3.5	4.0	
Thickness of cell (mean)	0.081	0.085	
Width of cell	0.99	1.15	

given complete satisfaction at all times throughout this period. Cataphoresis cells varying considerably in dimensions have been used; voltages giving potential drops from 1 to 20 volts per cm. have been employed. At no time has there been any evidence that this manner of determining the potential drop within the cell is incorrect. This method is here again recommended as the most accurate and the simplest method of determining the potential gradient within the cell, since it involves only the measurement of the specific resistance of the suspension, and of the cross-section of the cell, which is made with facility on the square movable microscope stage with verniers. Fig. 2 gives an idea of the relationship between this potential gradient and the concentration of KCl solution contained in two different cells, A and B, during measurements. It is evident that the drop in potential in cell A is considerably greater than that in cell B for a given voltage. The di-

mensions of these two cells are given in Table I. Note in Fig. 2 that the drop in potential in the cell increases with the specific resistance of the liquid and within the limits of experimental error reaches a limiting value. This is easily understood on the basis of the following reasoning. The current flowing in the system is, for a given applied electromotive force, evidently determined by r, the total resistance of the apparatus,

$$r = r_1 + r_2 + r_3$$

where r_1 = resistance of both electrodes
r_2 = resistance of both stop-cocks and of both side-arms
r_3 = resistance in the cell itself.

Neglecting diffusion at the stop-cock-plug junction, and assuming $r_1 < r_2 + r_3$, a condition found under ordinary experimental conditions, and considering that, with the increase of specific resistance of the suspension, $\frac{r_2 + \Delta r_2}{r_3 + \Delta r_3} = \frac{r_2}{r_3}$, we have then the conditions which account for the curves in Fig. 2, or

$$\frac{r_3 + \Delta r_3}{r_1 + (r_2 + \Delta r_2) + (r_3 + \Delta r_3)} > \frac{r_3}{r_1 + r_2 + r_3}$$

Only when r_1 is so small that it can be neglected will the drop in potential within the cell be proportional to the applied electromotive force.

EXPERIMENTAL

The two cataphoresis cells just described were used in the investigation of the cataphoresis of protein-covered quartz particles. The suspensions were made up as previously described and the ionic strengths and ionic species were made identical with those in Briggs' experiments. Our data are given in Table II. There is excellent agreement between Cell *A* and Cell *B* in Experiments 6, 7, and 8. Experiment 9B was the last experiment to be performed, late at night, and since it varies appreciably from the other data it is not plotted in Fig. 3. The agreement between the results with the two cells indicates that the precision obtained with the microscopic method of measuring electrical mobilities is approximately as good as that obtained by Gortner and his coworkers with the method of streaming potentials.

To compare our present data with those of Briggs[2] we have plotted in Fig. 3 both sets of data, calculated by means of equations (1) and (2). Our values are consistently higher than those of Briggs. The differences are about twice the extreme limits of the error inherent in

TABLE II

Electrical mobility and ζ-potentials of protein-covered quartz particles suspended in 0.0004 M LiCl-HCl solutions. See text.

Cell	pH	V μ/sec/volt/cm.	volts (E.S.U. $\times$ 3 $\times$ 10^{8})
1 *A*	4.35	−0.81	11.4
2 *A*	4.47	−0.61	8.6
3 *A*	4.05	−1.67	23.6
4 *A*	3.69	−2.16	30.5
5 *A*	4.08	−1.72	24.3
6 *A*	3.95	−1.97	27.8
B		−1.84	26.0
7 *A*	3.76	−2.16	30.6
B		−2.30	32.5
8 *A*	4.74	<0.1	<1.4
B		<0.1	<1.4
9 *A*	4.03	−1.77	25.0
B		−2.18	30.8

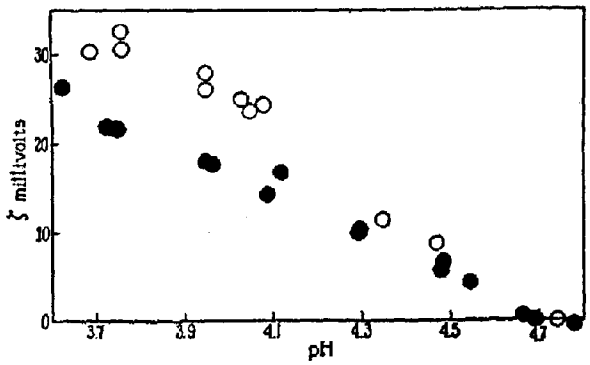

FIG. 3. ● Streaming potential (Briggs) (ζ_s)
○ Electrophoresis (ζ_e)

The difference between ζ_e and ζ_s cannot be taken as real, under the experimental conditions. The data indicate rather a qualitative agreement upon which further experimentation can be planned.

the method of electrophoresis. Since it was impossible to use the *same* suspension of protein-covered quartz particles which Briggs employed, it is difficult to state that an actual difference as large as this exists between ζ_e and ζ_s, calculated as indicated. It seems likely that differences in the two samples of protein used may be responsible for the variation observed. The data at present available for protein-covered quartz surfaces have all been obtained in electrolyte solutions having too high a conductance to be used in streaming potential experiments. In the near future data suitable for comparison will be published. Meanwhile, experimentally, there is the qualitative agreement upon which more precise experimentation may be based.

SUMMARY

1. The conditions are described which are necessary for the comparison of certain types of electrokinetic potentials. An experimental comparison is made of (a) electrophoresis of quartz particles covered with egg albumin; and (b) similar experiments by Briggs on streaming potentials. A slight, consistent, difference is found between the electrophoretic potential and the streaming potential. This difference is probably due to the difference in the protein preparations used rather than to real difference in the electrophoretic and streaming potentials.

2. Data are given which facilitate the measurements and enhance the precision of the estimation of electrical mobilities of microscopic particles.

The authors are indebted to Professor W. J. Crozier for his careful revision of certain parts of this manuscript.

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