ELECTROKINETIC PHENOMENA. II

THE FACTOR OF PROPORTIONALITY FOR CATAPHORETIC AND ELECTROENDOSMOTIC MOBILITIES*

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I

INTRODUCTION

According to the Helmholtz-von Smoluchowski (1) theory of cataphoresis, the equation for V_p, the cataphoretic velocity of a particle relative to a given medium is,

$$V_p = \frac{1}{4\pi} \frac{XD\zeta}{\eta} = \frac{CX}{\eta} \tag{1}$$

(X = field strength; D = dielectric constant of the medium; ζ = electrokinetic potential; η = viscosity of the medium; C = constant; all units c.g.s. electrostatic.)

Equation (1) predicts that (1) cataphoretic mobility should be independent of size and shape of the particle, and (2) for similar surfaces (ion atmospheres), V_E, the electroendosmotic velocity of a liquid past the surfaces should be equal to V_p, the velocity of the particle through the liquid.

Debye and Hückel (2) on the other hand, maintained on theoretical grounds that the constant, $\frac{1}{4\pi}$, in Equation (1) was valid only for the cataphoresis of cylindrical particles. For spherical particles the factor, 1/6, was substituted. We have previously shown by experiment in collaboration with Freundlich, and later with Michaelis (3), that the cataphoretic velocity of microscopic particles having similar

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surfaces is independent of their size and shape. There is, in addition, evidence that as a first approximation this independence of velocity of size may extend to the order of magnitude of the radius of the egg albumin molecule far below the limits of microscopic visibility (4).

While these experiments were performed with rather extreme variations of size and shape, they were not definitely a test of that boundary condition of Debye and Hückel's theory which assumed that the radius of curvature of the cylinder was very large in comparison with the thickness of the ion atmosphere. An experimental investigation including a test of the boundary condition would be the measurement of cataphoretic mobility of particles in a given medium simultaneously with the electroendosmotic mobility of the medium relative to a flat surface[1] having an ion atmosphere identical with that of the particle. Substituting the values of Debye and Hückel for C in Equation (1) and solving for R, the ratio of V_E and V_p, we obtain

$$R = \frac{V_E}{V_p} = 1.5$$

In other words, according to this theory electroendosmotic mobility must be 50 per cent greater than cataphoretic mobility.

II

HISTORICAL

Mooney (5) appears to be the first investigator to attempt to evaluate R. Among Mooney's as yet unexplained findings was the fact previously noted that oil droplets in dilute electrolytes have migration velocities that increase with particle size. Dilute $CuSO_4$ solutions anomalously abolished this effect. In these $CuSO_4$ solutions, therefore, mobility was independent of size. Taking advantage of this fact, Mooney wet the inside of a round capillary tube with a paraffin oil and studied in this system the cataphoretic velocity of the oil droplets and the electroendosmotic velocity of the liquid against a surface presumably covered with oil. In one system V_p was very nearly equal to V_E.

[1] An absolutely flat surface is, of course, not realizable experimentally.

The data of van der Grinten (6), obtained in a flat cataphoresis cell, are in contrast to the finding of Mooney that $R = 1.0$ (approximately) for a round capillary. Van der Grinten studied the cataphoresis in distilled water of small glass particles made of the same glass coverslips from which his flat cataphoresis cell had been assembled. He thus assumed that the surfaces of the particles of glass powder obtained by breaking up his coverslips were the same as that of the flat uninjured coverslip. Van der Grinten interpreted his data to give a mean value of $R = 1.59$, thus apparently confirming fairly well the theory of Debye and Hückel. Abramson (7) powdered pyrex glass and repeated the experiments of van der Grinten with a cell made of the same pyrex glass. This author found that for a given cataphoresis cell, R varied from 1.27 to 3.2 as a function of the nature of the medium. This cell of pyrex glass was not of uniform rectangular cross-section. The values obtained for R were consequently not considered absolute but rather pointing to the fact that a complete reinvestigation of the value of R was necessary under known hydrodynamic conditions and where the flat surface and surface of the particle were chemically identical.

III

The Movement of Liquids in Flat Cataphoresis Cells, Produced by Electroendosmosis

The movement of liquids in flat cataphoresis cells has been previously adequately considered for cells of various types by Ellis (8), von Smoluchowski (1), Svedberg and Andersson (9), Tuorilla (10), Freundlich and Abramson, and Abramson (11). Since the recalculations to be made here of certain data depend upon the movement of liquids in cataphoresis cells, we shall briefly review the facts pertinent to our subsequent recalculations and investigations.

The theories of Ellis and von Smoluchowski (based upon an old observation of Quincke) have made possible the quantitative measurements of cataphoretic mobility. Ellis assumed that for a closed flat cataphoresis cell of depth x, the observed cataphoretic velocity of a particle was, at any level in the cell (for a system with no turbulence),

$$V_{obs.} = V_p + V_w \tag{2}$$

(V_p = absolute mobility relative to the liquid due to the charge, constant at all levels; V_w = the velocity of the liquid.) The velocity of the liquid, as is well known, may vary from level to level so that if the electroendosmosis be in one direction, the return flow in the mid-regions of the closed cell must be in the opposite direction in closed systems like those considered. $V_{\text{obs.}}$ is, therefore, a function of the liquid streaming. The absolute velocity of a particle is, then, the mean velocity, M, of the particle within the cell,

$$M = \frac{1}{x_1}\int_o^{x_1} V_{\text{obs.}}\, dx \tag{3}$$

Substituting (2) in (3)

$$M = \frac{1}{x_1}\int_o^{x_1} (V_p + V_w)\, dx = V_p + \frac{1}{x_1}\int_o^{x_1} V_w\, dx \tag{4}$$

For a closed cell $\frac{1}{x_1}\int_o^{x_1} V_w\, dx = 0$ and since V_p is a constant for a given field strength,

$$M = \frac{1}{x_1}\int_o^{x_1} V_{\text{obs.}}\, dx = V_p \tag{5}$$

By measuring V at various levels, V_p may be calculated from the analytic expression relating $V_{\text{obs.}}$ to x, or V_p is readily obtained by graphical integration.

Von Smoluchowski simplified the method adopted by Ellis by proposing that

$$V_p = \frac{3}{4}V_{\frac{1}{8}} + \frac{1}{4}V_{\frac{7}{8}} = V_{\frac{3}{8}} = V_{\frac{5}{8}} \tag{6}$$

where the small sub-numerals represent level $\left(\text{level} = \frac{\text{Depth}}{\text{Total Depth}}\right)$ in the cataphoresis cell. From the foregoing it can also be readily shown that

$$V_E = 2(V_{\frac{1}{2}} - V_p) \tag{7}$$

The data of Ellis and of Svedberg and Andersson have amply confirmed von Smoluchowski's theory for the simple types of systems used by

Ellis and by Svedberg and Andersson. Their experiments are in accord with Equation (6) in that

$$V_{.2} = V_{.8} = (V_p) = \frac{1}{x_1}\int_0^{x_1} V_{\text{obs.}}\, dx \tag{8}$$

for flat cells from 50μ to about 1.0 mm. This means that *in cataphoresis cells of this type and these depths the mobility is constant at a given level. And conversely, if flat cells of different depths have mobilities in agreement with Equations (6) and (8), then the absolute mobilities of the particles measured are governed by Equations (6) and (8).* This is of the utmost importance in the recalculation of van der Grinten's data.

TABLE I

Recalculation of van der Grinten's Data

V_E is calculated by means of Equation (4)

Curve No.	$V_{\frac{1}{2}}$ μ/sec.	V_E μ/sec.	$V_{(\frac{1}{2}V_{\frac{1}{2}}+\frac{1}{2}V_{\frac{1}{2}})}$ μ/sec.	V_E μ/sec.	$V_{\text{Graphical integration}}$ μ/sec.	V_E μ/sec.	Mean R
1 (Fig. I)	2.7	6.6	2.8	6.6	2.8	6.4	2.4
2 (Fig. I)	2.7	6.2	2.8	6.0	2.9	5.8	2.15
3 (Fig. I)	2.7	7.2	3.0	6.6	2.9	6.8	2.4
Fig. 4, van der Grinten, p. 228	2.5	7.2		2.5	7.4	6.8	2.8

IV

Recalculation of van der Grinten's Data

It has been mentioned that van der Grinten found $R = 1.5$ approximately. The data submitted by van der Grinten is of the type given in Fig. I which is reproduced from the paper of this author. Curves 1, 2, 3, and 4 in Fig. I demonstrate that when van der Grinten's cataphoresis cells were more than 0.52 mm. thick, the cataphoretic velocity of the particle (as well as the endosmotic velocity) remained practically constant for the same level in cells of different thicknesses. This does not mean, as van der Grinten interpreted it, that V_p, the absolute speed of the particle, is that found in the mid-regions of the cells. It is rather, as Table I demonstrates, a further confirmation

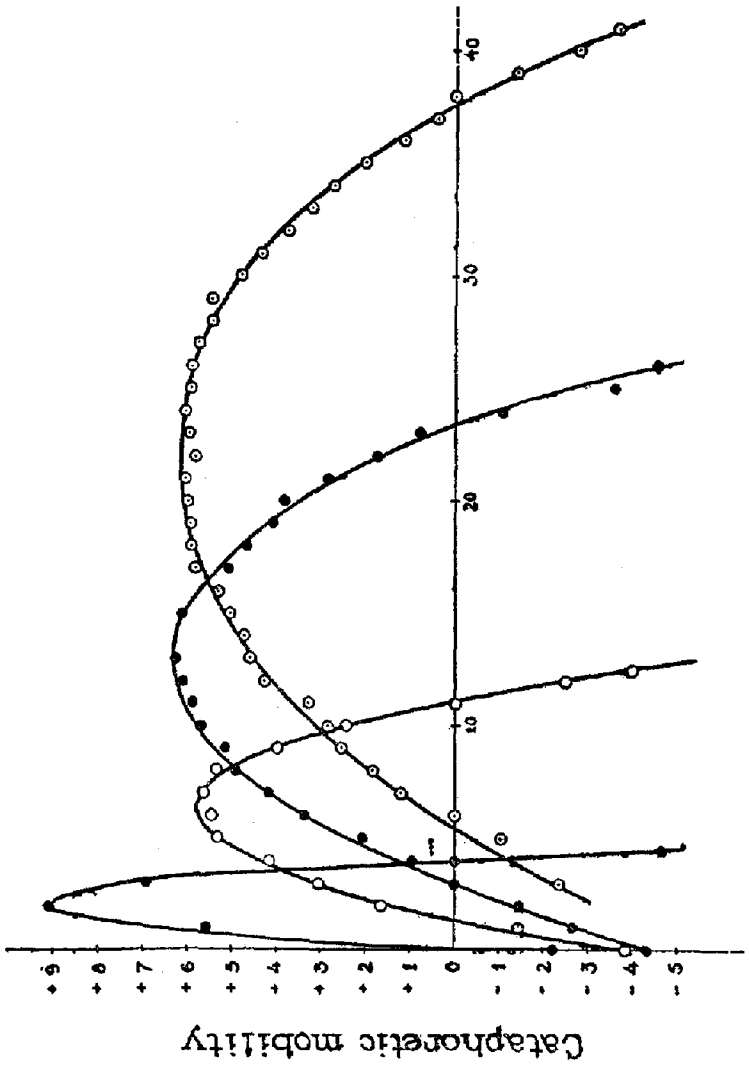

FIG. I. Curves from van der Grinten (6). Electric mobility is plotted against *thickness* of cell for four different cells varying in thickness as indicated. It can be readily calculated from the three curves on the right that the velocity in each case, is, however, practically constant for a given *level* in each cell—confirming, therefore, the theory of von Smoluchowski which may be used to calculate the absolute values of V_p and V_E. Table I and the text indicate the significance of these recalculations.

of the theory of von Smoluchowski. The table gives the values of V_p and V_E calculated from the curves of Fig. I and another curve of van der Grinten's not reproduced here by Equations (6), (7), and (8). It is evident that R is much greater than 1.5 in these systems and varies between 2.15 and 2.8. These data so calculated are in agreement with the author's previous experiments where similar high values of R for glass particle-glass surface systems similar to those of van der Grinten's were obtained. If one considers the data submitted by Lachs and Kronman (12) one can postulate *a priori* that to determine R by means of a flat glass surface and glass particles will be impossible. Lachs and Kronman concluded, after a series of careful streaming potential measurements on glass and quartz surfaces that no true electrokinetic equilibrium was reached. Further, consideration of the well known sensitiveness to stresses of metal surfaces as determined by measurements of thermodynamic potentials makes it not unlikely that localized changes in surface energy due to pulverization of the glass lead to the high value of R. To determine R, a stable system was here sought where R would be independent of the electrolyte content of the medium, and where, with a reasonable degree of certainty the particle surface and the flat surface were the same.

V

The Determination of $\frac{V_E}{Vp}$ *for Flat Surfaces*

It has been shown by Davis (13), Abramson (14), (4), Freundlich and Abramson (4) that surfaces of quartz and glass are practically completely coated with certain proteins when in contact with dilute solutions of these proteins on both sides of the isoelectric point—the particles then acting very much like the native protein in cataphoresis experiments. The most varied substances in addition to quartz and glass coat themselves with gelatin and egg albumin. Thus cystine crystals, menthol, camphor, oil droplets, agar, charcoal, zinc oxide powder and air bubbles behave in this fashion. Briggs (15) has also found that glass capillaries coat themselves with proteins. (His data will be considered in the section on round cataphoresis cells.) By suspending glass, quartz and other particles in a protein solution both particles and flat surface of the cataphoresis cell can, therefore, be

coated with the same substance fulfilling the condition of chemical similarity of glass and particle surface.

TABLE II

Experiments to Determine $\frac{V_E}{V_p}$

G = fused glass cell. C = cemented cell. V_p was taken as $\frac{V_{0.2} + V_{0.8}}{2}$.

Exper. No.	Cell	Nature of system	For a given value of		$R = \frac{V_E}{V_p}$
			V_p μ/sec.	V_E μ/sec.	
1	G	Glass of cell, powdered. pH = 3.6. N/50 Acetate buffer + 0.1 per cent gelatin	11.1	11.8	1.08
2	C	0.004 N HCl + quartz powder + 0.1 per cent gelatin	6.4	6.2	0.97
3	G	0.004 N HCl + quartz powder + 0.1 per cent gelatin	8.7	8.3	0.95
4	G	Benzyl alcohol + 0.2 per cent gelatin	6.0	5.4	0.90
5	G	"	data misplaced		0.97
6	G	Powdered glass in distilled water*	7.3	20.4	3.3
7	G	Quartz in M/150 pH 7.4 phosphate buffer + ⅓ per cent gelatin	1.23	1.28	1.12
8	C	"	8.61	7.8	0.91
9	C	"	9.6	9.1	1.06
10	C	As above but in dilute acetic acid	10.0	7.8	0.78
11	C	"	10.0	9.6	0.96
12	C	"	10.5	11.4	1.08
13	G	0.1 per cent egg albumin + quartz in M/50 acetic acid	3.2	3.3	1.06
14	G	"	10.3	11.8	1.14
15	G	As above but in phosphate buffer	9.75	11.1	1.14
16	G	⅓ per cent gelatin + N/200 H_2SO_4	6.15	5.9	0.96
17	G	"	12.0	13.9	1.16

For protein coated surfaces Mn. $R = 1.01 \pm 0.088$ (except No. 10). Probable error, ±0.02.

* Just one of this type of experiment is indicated here. The results were always similar.

In the experiments to be reported, R was determined in two different flat cataphoresis cells of uniform cross-section. One of the cells was a cemented cell, similar in arrangement to that described by Northrop

(16) and constructed in the fashion previously described. The approximate dimensions of this cell were: length 7.0 cm.; thickness 0.1 cm.; width 1.0 cm. The second cell, of fused glass, was the modification of the Northrup-Kunitz cell described by Abramson (11). The approximate dimensions of this cell[2] were: length 3.5 cm.; thickness 0.08 cm.; width 0.9 cm.

It has been demonstrated for this type of flat cataphoresis cell that "the movements of the water and particle within the cell follow the theory of von Smoluchowski. . . . . When the curve of particle velocity at different levels is parabolic, the curve of velocity as plotted against level is the same near the fused ends of the cell itself as in the middle. The stream lines of the liquid throughout the cell are therefore uniform." The value of R may, therefore, be readily calculated by means of Equations (6), (7), and (8).

Table II gives the values of R for 16 experiments performed with various protein covered particles and the flat glass surfaces of the cataphoresis cells covered with the same proteins. These experiments were performed with two kinds of proteins on both sides of the isoelectric points of the proteins and in the presence of different cations and anions. The field strengths were also varied. The values of R for 15 of these experiments varied between 0.90 and 1.16. The sixteenth value was 0.78. The mean excluding the value 0.78 was equal to 1.01 ± 0.088 with the probable error of the mean equal to ± 0.02. These data point clearly to the conclusion that, under the given conditions, the ratio of cataphoretic to electroendosmotic velocity is very close to 1.00; and that the factor C, in Equation (1) is the same for V_p and V_E.[3]

[2] The diameter of the side tubes connecting cataphoresis cells and stopcocks were large in comparison with the thickness of the cells themselves.

[3] An experimental value of this factor is unknown.

VI

The Determination of $\frac{V_E}{V_p}$ *for a Round Surface*[4]

By proceeding as in Part I, $\frac{V_E}{V_p}$ was determined in a round microcataphoresis cell by coating particle and glass surface with a protein, here gelatin. The curve drawn through the points in Fig. II is typical of the data of four similar experiments. The absolute mobility of the protein covered particle, V_p, is near the level 0.15. The curve passes through the origin. This is only possible when

$$V_E = V_p \text{ or } \frac{V_E}{V_p} = 1.00$$

The dotted line in Fig. II follows the course of the curve calculated on the assumption that $\frac{V_E}{V_p} = 1.5$. That this ratio does not obtain under these conditions is obvious, confirming, therefore, the data for flat cells.

The data presented in the previous sections fit in with the interpretation of the evidence submitted previously (3) that

$$V_p = \frac{C}{\pi} \frac{DX\zeta}{\eta}$$

where C is a constant independent of the size and shape of the particle. The experimental investigations submitted here and previously have demonstrated that within experimental error

$$V_p = V_E$$

where the radius of the particle varies from about 0.5μ to 100μ, possibly as low as 0.010μ for certain proteins.

[4] Briggs has found that streaming potentials obtained with protein coated quartz surfaces agree with mobilities obtained by the method of cataphoresis. This is evidence that $\frac{V_E}{V_p}$ would be 1.00 for round surfaces, but since different electrolyte concentrations were used this conclusion cannot be made before conditions are made more nearly alike.

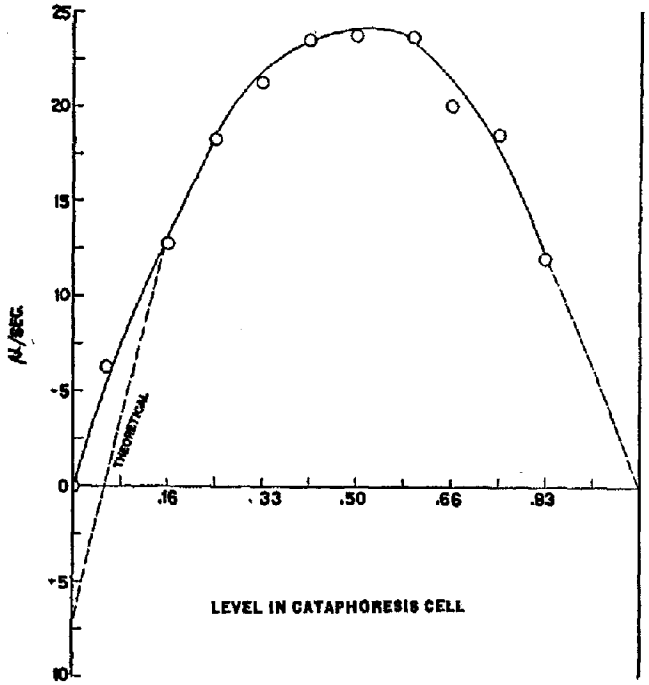

FIG. II. The smooth curve extrapolated to $x = 1.0$ has been drawn through points of cataphoretic mobility of protein covered oil droplets. The curve passes through the origin. Since the origin ($x = 0$ or 1.0) is the wall of the cell, it follows that $V_E = V_p$ or $\frac{V_E}{V_p} = 1.00$, approximately. The arrow points to the value of V_p obtained as described in the text. The dotted line is the course of the curve predicted by the theory of Debye and Hückel for a *flat* surface. This curve has been obtained with a round cell.

SUMMARY

Two theories which predict different values for the ratio of V_E, the electroendosmotic velocity of a liquid past a surface, to V_p, the electric mobility of a particle of the same surface through the same liquid are discussed. The theory demanding that $\frac{V_E}{V_p} = 1.5$ was supported by certain data of van der Grinten for a glass surface. Recalculation of van der Grinten's data reveals that the ratio varies

between 2.1 and 2.8. These results are in accord with previous data of Abramson. It is pointed out that glass is unsuitable for the investigation.

The ratio $\frac{V_E}{V_p}$ is here determined for a flat surface and particles when both are covered by the same proteins. Under these conditions $\frac{V_E}{V_p} = 1.01 \pm 0.02$. The theory is similarly tested for a round surface using a micro-cataphoresis cell. It is shown that $\frac{V_E}{V_p}$ for a round surface is approximately 1.00. These findings are confirmatory of previous data supporting the view that cataphoretic mobility is independent of the size and shape of the particles when all particles compared have similar surface constitutions.

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