VARIATIONS IN THE CATAPHORETIC MOBILITIES OF OIL DROPS IN WATER

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Abstract

Cataphoretic mobilities of oil drops in water and weak electrolytes.—The cell used was a thin walled glass tube 20 cm in length and 6 mm in diam., with gold electrodes sealed into the ends, held in a vertical position. By means of a microscope, velocity measurements were made on suspended drops both along the axis and in the stationary layer $R/\sqrt{2}$ from the axis, where R is the inner radius. (1) *Variation with diameter of drop.* For emulsions of ten oils in distilled water, the mobility for a field of 10 volts/cm, was found to increase with the diameter D for the range from .0005 to .04 mm. This is also true for emulsions of Stanolind in weak electrolytes, but for .0008 normal $CuSO_4$ the mobility is constant. In all cases the drops were negatively charged. (2) *Variation with the potential gradient.* For the smaller drops the mobility is constant, but larger drops, above .02 mm, show a slight increase for fields of 10 volts/cm. (3) *Initial time lag.* Observation on a large drop in a capillary tube open at both ends and immersed in a dish filled with .0001 normal NaOH, indicates that the mobility increases with time during the first 5 or 10 sec. after the electric field is applied. (4) *Theory.* It is suggested that the electric double layer around a drop is considerably distorted by an external electric field, so that equilibrium is established rather slowly.

Endosmotic flow of water in a closed cylindrical tube.—(1) *Hydrodynamic theory* gives the velocity as a linear function of the square of the distance from the axis, with a zero value for $r=R/\sqrt{2}$. This was experimentally verified. (2) *Mobility past an oil surface* was measured after coating the inside surface of the cell with oil, and was found approximately equal to the cataphoretic mobility of large drops of oil in water. This is also true for .0004 molar $CuSO_4$ solution.

I. Introduction

Electric endosmose is illustrated in the motion of a liquid through a porous diaphragm which results when a potential difference is maintained between the two sides of the diaphragm. Helmholtz[1] was the first to develop a mathematical theory of the phenomenon, and the formulas which he obtained were found to agree with experimental results. According to Helmholtz's theory, as a result of contact potential there is a very thin double layer of equal and opposite charges of electricity at the boundary between the diaphragm and the liquid within its pores. It is assumed that the layer next to the diaphragm is fixed to the surface but that the layer within the liquid is free to move. Consequently when a potential difference is maintained between the liquid on the two

[1] Helmholtz, Wiedemann's Annalen der Physik, **7**, 333 (1879)

sides of the diaphragm, the mobile part of the electric double layer moves through the pores and carries with it, by viscous drag, the entire liquid content of the pores.

Cataphoresis is the motion, parallel to an external electric field, of a particle suspended in a liquid. This phenomenon, like endosmose, is explained on the assumption that there is an electric double layer at the boundary between the particles and the liquid. Both Lamb[2] and Smoluchowski,[3,4] working independently, have developed theoretical formulas for the cataphoretic velocity of a suspended particle. Lamb's theory is more general than Smoluchowski's in that it takes into account the possibility of a hydrodynamic slip at the surface of the particle; but there are no experimental results to indicate such a slip, and recent work on the orientation of surface molecules seems to indicate that such a slip would not occur. Consequently Smoluchowski's formulas will be used in comparing with theory the experimental results reported in this paper.

Smoluchowski's formula for the cataphoretic mobility of a particle is

$$m_c = u/X = K(\varphi_i - \varphi_a)/4\pi\eta, \tag{1}$$

where u = the velocity of the particle,
X = the external electric field in e.s.u.,
$\varphi_i - \varphi_a$ = the contact potential in e.s.u. between the interior of the liquid and the surface of the particle,
K = the dielectric constant of the liquid,
η = the coefficient of viscosity of the liquid.

Since the dimensions of the particle do not appear in the formula, the velocity of the particle should be independent of its size. This element of the theory has been verified by Burton,[5] working with Bredig solutions of silver, and by Hardy,[6] working with solutions of globulin. But observations have been reported which indicate, though with some uncertainty, that the mobility varies with the size of the particle. Also preliminary experiments with oil drops in water indicated a variation in velocity with the size of the oil drop. Hence the research herewith reported was undertaken for the purpose of studying this variation in velocity, using very dilute emulsions of oil in water.

[2] Lamb, Phil. Mag., (5) **25**, 52 (1888)

[3] Smoluchowski, Bull. Int. Acad. Sci. Cracovie, p. 182 (1903)

[4] Graetz, Handbuch der Elektrizitaet und des Magnetismus, Johann Ambrosius Barth, Leipzig, Vol. II, p. 381

[5] Burton, Physical Properties of Colloidal Solutions, Longmans, Green and Co., p. 144

[6] Hardy, Journal of Physiology, **29**, p. 26, (1903).

II. Apparatus

Attempts were first made to use a rectangular cell modelled after the one used by Ellis,[7] but larger. However, when used in a vertical position, convection currents in the water prevented any determination of cataphoretic velocities. The cell finally adopted is shown in Figure 1. It consists essentially of a straight glass tube *A*, about 6 mm in diameter and 20 cm long, with gold electrodes *E* cemented into the ends of the tube. One of the electrodes has a small hole through its center to allow for expansion of the water in the cell while sealing the electrode in place.

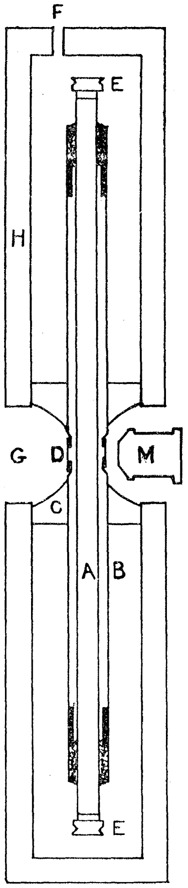

Fig. 1

In order to maintain uniform temperature the glass tube is surrounded by the brass tube *B*, cemented to the glass tube at either end. In the middle of this tube are two openings *D* for the purpose of admitting light and of making observations with the microscope *M*, which are covered by miscroscope cover glasses, cemented to the brass. By using very thin glass tubing, about .2 mm in thickness, and by having water on the outside as well as on the inside of the glass tube, the distortion of the optical image of the drops, resulting from the curvature of the glass tube, is reduced to a minimum. Even so, there is still sufficient distortion to be annoying and to make the measurements of the diameters difficult. Another source of trouble lies in the ease with which the glass tube is broken. Some fifteen or twenty were broken and replaced during the course of the work.

To maintain constant temperature the cell is enclosed in a wooden box *H*, with openings *G*. In order to reduce the temperature effects of outside air currents, a small block of wood *C*, through which the cell passes, is cut to fit snugly into the box. This block and two electrodes and supports for the cell not shown in the figure, are all fastened to the door of the box, which is removable.

In most of the experimental work the cell was in the vertical position and the microscope horizontal. With this arrangement the motion of the

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[7] Ellis, Zeitschrift für physikalische Chemie, **78**, p. 321 (1911)

drops under gravity is parallel to the stream lines due to the electric endosmose and the drops remain in a region where the water has a constant velocity; thus it is easier to control the drop and to make velocity measurements.

The counter electromotive force developed at the electrodes was measured by reducing the external voltage to that necessary to give zero current through the circuit. Temperature readings were made by means of a thermocouple, one junction of which was inserted into the wooden box, at *F*, while the other junction was kept in a mercury bath with a thermometer graduated at 1/5° C.

The microscope consisted of a 2/3-inch objective and a Ramsden eyepiece. Distances perpendicular to the axis of the microscope were measured by means of a glass scale in the eye-piece. The magnification of the objective with respect to this scale was 9.156 diameters. Distances parallel to the axis were measured by means of the graduated scale on the fine movement of the microscope. Time measurements were made with a stop-watch which gave readings to 1/10 sec. Ordinarily the distance on the eye-piece scale used for velocity measurements was chosen such that the time measurements was between 3 and 15 seconds. To absorb the heat rays from the light source a water cell 2 feet long was inserted.

III. Theory of the Closed Cylindrical Cell

Neglecting for the present the velocity of an oil drop due to gravity, the observed velocity due to the electric field is the resultant of the cataphoretic velocity and the velocity of the water in the neighborhood of the drop. Due to electric endosmose the water near the surface of the cell moves parallel to the axis; and since the cell is closed at each end, this motion results in a hydrostatic pressure gradient which causes the water along the axis to flow in the reverse direction. Lamb[8] has shown theoretically that in such a system the flow of the water follows the equation,

$$w=(P/4\eta)(r^2-\tfrac{1}{2}R^2) \tag{2}$$

where w = the velocity of the water; P = the hydrostatic pressure gradient parallel to the axis; η = the coefficient of viscosity of the water; r = the distance from the axis of the cell, and R = the radius of the cell.

From this the velocity at the surface is

$$w_R=PR^2/8\eta,$$

and Eq. (2) may be written,

$$w=w_R(2r^2/R^2-1). \tag{3}$$

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[8] Lamb, 1. c.,[2] p. 58

Now for an oil drop which is small compared with the diameter of the cell we will assume that u, its velocity with respect to the water, is independent of its position in the cell. Then for v, the observed velocity of a given oil drop, we shall have,

$$v = u + w = u - w_R + (2r^2/R^2)w_R. \tag{4}$$

To test this equation experimentally the cell was placed on the microscope table in a horizontal position; and an oil drop of the right size to rise under gravity at a convenient rate was located near the bottom of the cell. Then as the drop slowly rose to the top of the cell it was driven back and forth by reversing the electric field, and its velocity measured. To obtain the displacement of the drop from the axis of the cell, its vertical height was determined from the scale on the fine movement of the microscope when the drop was in focus; and its lateral displacement was measured by the scale in the eye-piece. According to Eq. (4), the velocity of a drop is a linear function of the square of its distance from the axis of the cell.

In Fig. 2 the small dots and circles represent readings made when the drop was respectively below and above the axis. Due to slow convection currents in the water, successive points lie alternately too high and too low. To eliminate the effect of the convection currents, the large dots and circles are located midway between each adjacent pair of experimentally determined points; these are seen to lie approximately on a straight line.

On the basis of these results we can consider that Eqs. (3) and (4) are verified by experiment. It is evident from Eq. (3) that at a distance from the axis equal to $R/\sqrt{2}$ the water is stationary. The cataphoretic velocity can be determined therefore, merely by measuring the velocity of an oil drop in this stationary layer of water. However, the drops would generally be displaced more or less from this position, and the velocity gradient in this region of the cell is rather high. Therefore since the primary purpose of these experiments was to detect differences in mobility rather than to measure the absolute value of the mobility, most of the measurements were made near the axis of the cell, where the velocity gradient of the water was a minimum. For determining the absolute mobility a few measurements in each experiment were made near the stationary layer also.

For drops which were not exactly in the stationary layer or on the axis, the observed velocity required a correction. The required correction formulas can easily be obtained from Eq. (4).

The correction to be applied to v for drops near the axis comes out

$$+2(r^2/R^2)(v_0 - v_s), \tag{5}$$

and the correction for drops near the stationary layer is

$$+2\sqrt{2}\frac{(r-R\sqrt{2})}{R}\,(v_0-v_s)+2\,\frac{(r-R/\sqrt{2})^2}{R^2}(v_0-v_s) \qquad (6)$$

where v_0 and v_s are respecting the velocities of the drop on the axis and in the stationary layer.

The approximate value of (v_0-v_s) is obtained from the uncorrected observed velocities. As a rule the only term in either formula large enough to be of any importance is the first term in Eq. (6).

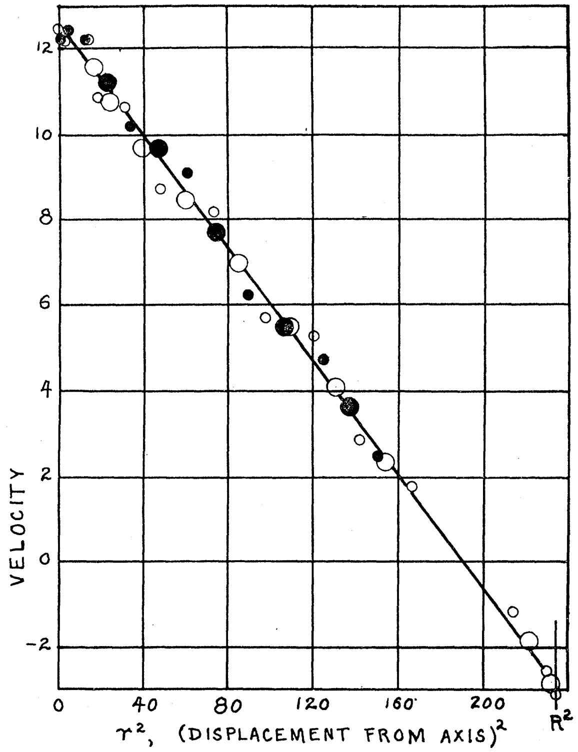

Fig. 2

IV. Experimental Determination of the Mobility-Diameter Curve

The experimental procedure was in general as follows. Two or three drops of the oil were shaken vigorously in a separatory funnel with about 200 cc of distilled water. The emulsion thus formed then stood for about a minute to allow the larger oil drops to settle out. One electrode was sealed in the cell, which had been cleaned with chromic acid and thoroughly washed with distilled water, and the cell was filled with the emulsion from the bottom of the separatory funnel. The other electrode was then sealed in place, the cell and the electrode cooled with tap water, and the small hole in the second electrode sealed up. It was then necessary to wait twenty or thirty minutes for the cell to come to uniform temperature. In order to prevent the oil drops from settling to one side, the cell was kept in a vertical position and frequently inverted during this interval. After a sufficient lapse of time velocity measurements were made on a series of oil drops near the axis of the cell; and next on a series near the stationary layer. Of course, there was constant movement of the drops under gravity; and even when there was no electric field, there were slow currents in the water. It was found, however, that within experimental error the resultant vertical velocity of a drop without the electric field was equal to half the difference between the upward and downward velocities with the electric field. Consequently the velocity due to cataphoresis and endosmose, free from the effects of gravity and of convection currents, is obtained by taking the arithmetic mean between the upward and downward velocities under the electric field. Each velocity was calculated from the average time obtained from two or three measurements. The diameter was measured on the scale in the eye-piece, the drop being held as nearly stationary as possible by applying just sufficient voltage to counterbalance the velocity of the drop under gravity.

A typical graph obtained in this way is shown in Figure 3, in which the velocities corrected according to Eqs. (5) and (6) are plotted against D, the diameter of the drop. Throughout this paper, diameters and velocities will be given in scale divisions, each equal to .001092 cm. The horizontal line gives the velocity of the water on the axis and is obtained from the difference between the upper and lower curves. Except for sign, the line also gives w_R, the velocity of the water at the surface of the tube.

The applied voltage was 199, giving 197.5 as the effective voltage E, after subtracting 1.5 volts for the counter electro-motive force.

The points enclosed in the dotted circle in Fig. 3 were the first three points obtained; and it was often observed that the first few points obtained in a series of measurements were low. The reason for this has not yet been thoroughly investigated; but it seems likely that this effect is due to a change in the conductivity of the water near the electrodes. It is difficult to keep the electrodes clean while sealing them in place; and a very small amount of impurities diffusing away from the electrodes into the pure water would increase the conductivity near the electrodes and hence increase the potential gradient in the middle of the cell.

These results prove that for oil drops of the size investigated ranging in diameter from $.05 \times 10^{-3}$ to 4×10^{-3} cm and for a field of 10 volts per cm the velocity in pure water is not even approximately constant. It was found difficult, if not impossible, to work with drops outside of this range since larger drops move too fast under gravity and smaller drops are difficult to see and to measure accurately with the magnification used. But the results obtained seem to indicate that as the diameter increases the mobility approaches asymtotically an upper limit. Whether the lower limit, as D approaches zero, is zero or finite, is hard to judge from the curves so far obtained.

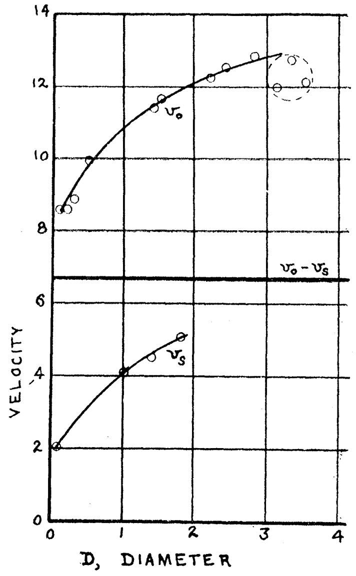

Fig. 3

The oil used in the measurements shown in Fig. 3 was "Nujol," a commercial oil consisting of saturated hydrocarbons of the paraffin series. Quite similar results were obtained with a number of other oils, namely:

Bromoform, $CHBr_3$;
Bromonaphthalene, $C_{10}H_7Br$;
Dimethyl anilin, $C_6H_5N(CH_3)_2$—see Fig. 4, c;
Iodo-benzene, C_6H_5I—see Fig. 4, a;
Phenetol, $C_6H_6OC_2H_5$;
Phenyl mustard oil, C_6H_5NCS;
Tri-brom-hydrine, $CH_2Br \cdot CHBr \cdot CH_2Br$—see Fig. 4, b;
m-Xylene, $C_6H_4(CH_3)_2$;
"Stanolind," a paraffin hydrocarbon much like Nujol.

In all cases the motion was in the direction of the external field, indicating a negative charge on the surface of the drop. In Fig. 4 are shown the mobility-diameter curves for iodo-benzene (a), tri-brom-hydrine (b) and dimethyl anilin (c). The curves (a) and (c) are extreme types, the curves for all the other oils lying between these limits.

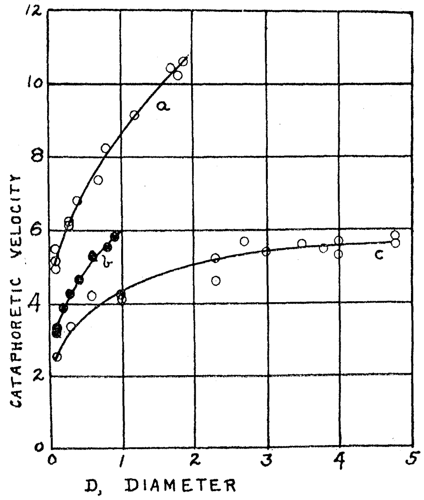

Fig. 4

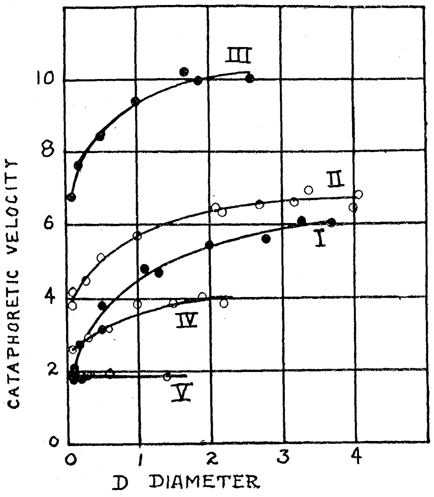

Fig. 5

Curve	Electrolyte	Normality
I	Impurities?	.00002
II	NaOH	.0001
III	NaOH	.001
IV	HCl	.0001
V	$CuSO_4$	.0008

Further experiments were carried out to determine the effects of added electrolytes and of variations in the potential gradient. Some of the results here reported are obviously only preliminary and require further extension and refinement before they can be accepted as final.

V. Effects of Electrolytes on Mobility

The cell used in these experiments was not designed for use with electrolytes, and with only moderate concentrations the electric current is so great that bubble formation at the electrodes makes measurements impossible. However, enough data were obtained with dilute solutions of a few electrolytes to indicate the general effect of added electrolytes on the nature of the mobility diameter curve. "Stanolind" is well suited for this purpose because of its chemical inertness. In Fig. 5 are shown the results obtained with Stanolind with various concentrations of sodium hydroxide, hydrochloric acid and copper sulphate. The concentrations of the electrolytes are given under the figure. The concentration of impurities in the distilled water (Curve I) was estimated from the specific conductivity of the emulsion.

Curve V shows that with an .0008 normal solution of the divalent electrolyte $CuSO_4$ the mobility curve becomes practically a horizontal straight line. The effect of the monovalent electrolytes, though not so marked is similar, as can be seen from a comparison of the different curves.

VI. Effect of Potential Gradient on Mobility

According to Eq. (1) cataphoretic mobility should be independent of the external field. Moreover, according to Smoluchowski's theory the endosmotic mobility[9] is also independent of the potential gradient. This theory was tested rather carefully for pure water and was found to hold within experimental error for endosmotic mobility and for cataphoretic mobility of the small drops; but for the large drops the mobility was found to increase with the potential gradient.

Table I

Values of v/E

	(I)	(II)	(III)	(IV)	(V)
r:	$R/\sqrt{2}$	0	0	0	0
D:	.1	.1	.2	2.0	2.1
20 volts	....	....	53.5 51.7	96.2	97.6
50 volts	68.5 62.2 69.1	49.3 50.0	50.4 51.5	94.0	100.5
100 volts	....	....	51.8 52.1	99.1	101.4
200 volts	65.5 65.4 65.4	49.6 49.6	52.3 52.4	100.2	107.0

In Table I are given some of the results obtained in the experiment. The figures represent in arbitrary units the values of v/E, where v is the mean of several corrected velocities and E is the effective voltage; that is, the applied potential after being corrected for the counter e.m.f. The results in Column I, obtained with a small drop near the stationary layer, show that the cataphoretic mobility of small drops is independent of the potential gradient within experimental error for the range 50 to 200 volts. This being established, the results in Column II, obtained

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[9] Endosmotic mobility is here used to mean the velocity per volt per cm. of a liquid moving past a fixed surface under the influence of an electric field parallel to the surface. It is understood, of course, that the liquid considered is sufficiently far from the surface not to include any of the electric double layer.

with a small drop on the axis, show that the endosmotic mobility also is independent of the voltage over the same range. It is difficult to obtain consistent results in the stationary layer with voltages much less than 50; but measurements on the axis with voltages from 20 to 200 gave the results in Column III. This shows that the sum of cataphoretic and endosmotic mobilities is constant in this range of voltage; and it seems most probable, therefore, that each mobility is constant. Columns IV and V show the results obtained with larger drops on the axis. If we subtract from the observed velocity the component due to the motion of the water along the axis, we find that the difference in cataphoretic mobility for the large drops at 200 volts and at 50 volts is about 15 percent of the mobility at 200.

Attempts to extend these measurements with small drops to voltages lower than 20 led to inconsistent results, which seemed furthermore improbable, for they indicated a large increase in mobility at low voltages. Attempts were made to obtain the effective voltage within the cell from Ohm's Law by making simultaneous measurements of the current through the cell at different voltages while velocity measurements were being made; but the results were still inconsistent. It was therefore decided to try a different cell, much longer and of smaller diameter, thereby reducing both the convection currents in the water and the relative importance of the counter e.m.f. A glass tube was drawn out into a thin-walled capillary about 120 cm long and 1 mm in diameter. It was then bent so as to fit into a shallow glass dish, 10×23 cm, which could be held on the microscope stage. The cell was filled with an emulsion of Stanolind in .0001 normal NaOH, electrodes were sealed into the ends, and the cell was immersed in water in the glass dish. For this work a higher powered objective was used in the microscope, giving a magnification of 45 diameters with respect to the scale in the eye-piece. Measurements were attempted only along the axis of the cell. The results are tabulated in Table II, the data being arranged in columns in the order in which the measurements were made. The potential gradient in this case is about 1/5 of what it is for corresponding voltages in Table I. The limit of error at such low potential gradients is rather high, but within that limit the mobilities are constant.

TABLE II

$D=.2$ $r=0$

Volts:	200	50	200	20	200	50	200
v/E:	19.2	20.9	23.1	24.7	24.2	22.2	24.7
	19.7	24.1	24.7	26.5		22.2	24.6

In concluding this report of the experiments on mobilities, one very interesting observation will be described in detail, for it seems to give some new information as to the mechanism of the phenomenon of cataphoresis. The glass dish used in the last described experiment was filled with .0001 normal NaOH; and a straight capillary tube, open at both ends and about 19 cm long, was filled with an emulsion of Stanolind in .0001 normal NaOH and immersed in the water in the dish in a horizontal position. Electrodes of platinum wire dipped into the water near the ends of the tube. With this arrangement the water in the tube moves through it under the influence of endosmose without any reverse flow along the axis; and the velocity gradient in the tube is practically zero. The observations were made on a rather large drop ($D=1.6$) at the upper surface of the tube. It should be mentioned, however, that many results previously obtained indicate that the proximity of the surface of the tube would have little effect on the velocity of the drop. For example, in the experiments of the kind first described, in which the velocity of the drop is measured in different parts of the cell, there is no large deviation from the straight line shown in Fig. 2 when the drop reaches the surface.

The peculiarity in the behavior of this drop was that, with an applied potential of 200 volts, the drop gradually changed the direction of its motion a few seconds after the switch was thrown on. Since the velocity of the drop with respect to the water is in the opposite direction to the velocity of the water itself, this means that shortly after the current is applied, either the velocity of the water decreases or the velocity of the drop with respect to the water increases. Results already reported indicate that it would be the velocity of the drop that changes; and this is also indicated by the fact that the smaller drops in the capillary seemed to have constant velocities.

It was furthermore noticed that the behavior of the drop depended on its previous treatment. If the electric field was left on for some time and then suddenly reversed, the drop traveled the maximum distance, about .008 mm, and the maximum time, about 6 seconds, before reversing the direction of its motion. If the electric field, instead of being reversed, was merely interrupted for about a fifth of a second, the motion of the drop continued immediately in the same direction without reversal. The effect of previous treatment on the behavior of the drop was still noticeable if 5 or 10 seconds were allowed to intervene from the time the switch was taken off to the time the field was reversed; but the longer the time interval which intervened, the less the time and the shorter the distance the drop traveled before reversing its direction of motion.

The only interpretation of these observations which occurs to the author is that the effect of the external field is to displace with respect to the drop the positive ions constituting the mobile part of the electric double layer; that the final distribution of the charge in the neighborhood of the drop is established only after an interval of several seconds, being opposed by the negative charge on the surface of the drop and by the conductivity of the water near the drop; but that the drop moves faster with this final distribution than it does with the symmetrical distribution that obtains when there is no external field. If this explanation is correct, it seems furthermore probable that the distortion of the charge distribution is considerable. Some of the positive charge may even be drawn completely away, leaving the drop and the surrounding water with a net negative charge.

This theory would readily explain the increase in mobility of the large drops with potential gradient, for the distortion of the charge distribution would no doubt increase with the potential gradient.

The question naturally arises whether the increase in mobility with diameter at 200 volts is due entirely to the increase in the mobility of the large drops with potential gradient; that is, whether the limiting value of the mobility of all drops would be the same as the voltage approaches zero. When it was found that the large drop in the horizontal capillary tube failed to stick to the surface, it was decided to measure its velocity at low voltages. The results obtained are shown in Fig. 6, where v/E is plotted against the applied voltage V. In this case, of course, the observed v is the difference between the final cataphoretic velocity of the drop and the endosmotic velocity of the water. The points represented by dots are the values of v/E at 200 volts for some small drops for which $D=.25$. The velocity of one of these small drops was measured at different voltages from 5 to 200, and it was found that for it v/E was constant and equal to about -6. It is evident, therefore, that the mobility of a large drop even at very low voltage is higher than the mobility of the small drops. If we take into account the velocity of the water through the tube and use previously measured values of endosmotic mobility for .0001 normal NaOH, we can calculate approximately the relative difference in cataphoretic mobilities at 5 volts between the large and the small drops and the relative difference in mobility for the large drops between 5 and 200 volts. We thus get 8 percent for the former and 20 percent for the latter.

For the small drops, also, by qualitative observations, it was possible to detect at 5 volts a variation in mobility with size of the drop. Two drops are chosen, say with diameters .05 and .2, which are very close together. Drops as small as this rise very slowly under gravity, and with an applied potential of 5 volts, both drops will remain in the field long enough for a difference in their relative positions to be easily detected.

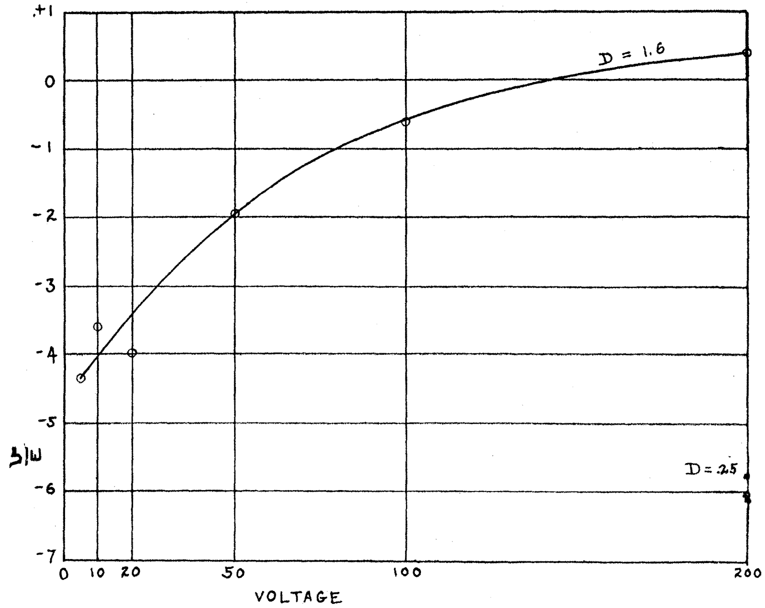

Fig. 6

A number of such comparisons were made and in all cases it was found that the mobility of the larger drop was the greater.

VII. Ratio of Cataphoretic to Endosmotic Mobility

Smoluchowski[3] has developed a theoretical formula for endosmotic mobility which, except for sign, is exactly similar to Eq. (1); so according to this theory the cataphoretic mobility of a sphere moving through a liquid is numerically equal to the endosmotic mobility of the same liquid moving past a surface of the same material as the sphere. So far as the author knows no experimental test of this relationship has ever been published.

If we had a cataphoretic cell whose walls were made of the same material as the particles suspended in the emulsion and if the cataphoretic and endosmotic mobilities were numerically equal, we would have, in our previous notation,

$$w_R = -v_s \tag{7}$$

hence

$$v_s = v_0 - v_s \tag{8}$$

$$v_0 = 2(v_0 - v_s). \tag{9}$$

These equations were tested by wetting the inside of the cataphoresis cell with oil before filling it with the emulsion. One experiment was performed with Stanolind in distilled water and another in .0004 molar $CuSO_4$. In the latter case the gold electrodes of the cell were replaced by copper electrodes. The results of the two experiments are shown in Fig. 7 and 8, respectively. The circles in the upper set of points indicate measurements made before those in the lower set and the dots indicate measurements made after those in the lower set. The reason for the difference in height between the dots and circles in Fig. 8 is most probably that the oil on the surface of the tube was spreading over the electrodes and increasing the electrical resistance. This is indicated by the appearance of the electrodes after the experiment and by the fact that during the progress of the experiment the current through the cell fell off by several percent.

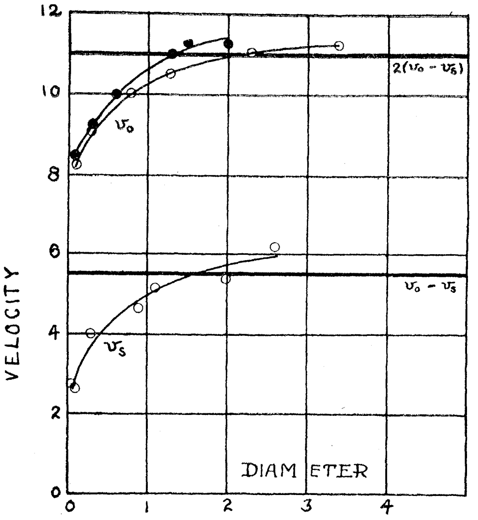

Fig. 7

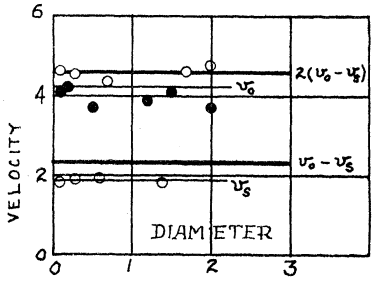

Fig. 8

The results in Fig. 7 show that for the smaller drops in pure water the cataphoretic mobility at 10 volts per cm is less than the endosmotic mobility. In view of the variation with potential gradient in the mobility of the large drops, it appears that at low voltages their cataphoretic mobility would also not be greater than the endosmotic mobility and might even be less. The results in Fig. 8 show that in .0004 molar $CuSO_4$ the cataphoretic mobilities of both large and small drops are equal and approximately the same as endosmotic mobility. Here also there is some indication that the cataphoretic mobility may be a few percent less than endosmotic mobility; but in view of the conditions of the experiment, that conclusion cannot be drawn with certainty.

This experimental work was begun under the direction of Dr. R. A. Millikan while he was still at the University of Chicago; and the author takes pleasure in acknowledging his great indebtedness to him for suggesting such a fruitful field of research.

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