INSTANTANEOUS MOBILITIES IN ELECTRIC FIELDS
OF PARTICLES SUSPENDED IN LIQUIDS

Thesis by
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INTRODUCTION

The theory of the motion of particles suspended in liquids in an electric field, first given by Helmholtz and later modified by Smoluchowski and Debye, has had many successes. However, some recent experiments have thrown doubt upon its complete applicability. Among these experiments may be mentioned those of Kruyt[1], of Mooney[2] and of Blüh[3].

Kruyt found that some of his experiments upon the connection between the cataphoretic mobility and the coagulation of colloids did not check with the theory of critical potentials. He asserts that since the critical potential theory is so well established, the electrokinetic potential must not always be proportional to the mobility of the particles as the Helmholtz-Debye theory requires.

Mooney, working with large oil drops in water, found the first proof of a variation of mobility with the size of the drops, while the theory requires complete independence of the mobility with particle size.

Blüh, following the lead of Cotton and Mouton[4] used an A. C. field and observed the lengths of the paths of the oscillating particles in an ultramicroscope. He claimed an accuracy of a few percent, but his published data shows a wide spread in the mobilities of particles of the same sol, some having twice the mobility of others. He made no comment upon this but it certainly is in opposition to the theory requiring all particles of a sol to have the same mobility.

The facts make it desirable to find out more about the true mechanism of the phenomena of cataphoresis. Therefore, it was considered desirable to develop some method of measuring the instantaneous mobilities of individual particles.

Measurements of mobilities are complicated by the fact that whenever an electric field is applied to a suspension, the liquid as well as the particles move, so that the true mobility cannot be directly measured. To overcome this difficulty, Blüh[3] used an A. C. field and a very thin cell to damp out the motion of the liquid. He made tests which showed that the motion of the liquid was definitely reduced by making the cell thinner and thinner, and he thought that it was practically eliminated at a thickness of 0.006 mm.

The A. C. method has the definite advantage that it gives the instantaneous mobility of the particles, whereas all of the other methods can give only an average value, either a statistical average for all of the particles or else a time average for individual particles. However, the A. C. method has not been held in high favor; partly because it has not been suspected that the instantaneous mobility of colloidal particles might be different from the average mobility and partly because of the difficulty of interpretation of the results. The difficulty of interpretation lies in the fact that the Helmholtz-Debye law applies to uniform velocity only, whereas in the A. C. field the velocity must be constantly changing. There is every reason to believe that the Helmholtz "double layer" will be out of phase with the particle and the field, and it is not known what the motion would be under these circumstances.

It occurred to the author that these objections might be overcome if he could cause the particles to move in circles with uniform speeds. The particles would then come to practically the same kind of equilibrium as if they were moving in straight lines, and their instantaneous mobilities would be more easily observed than by the A. C. method. This can be accomplished by using two A. C. fields at right angles to each other which would produce a field constant in magnitude, but whose direction would be rotating at a constant angular velocity. This rotating field should cause each particle to describe a complete circle with every rotation of the field, and the diameters of these circles would be direct measures of their instantaneous velocities.

This circular method was therefore tried out and developed, using a thin cell like Blüh had used to dampen out the motion of the liquid. The method has distinct advantages over the single phase A. C. method in that the instantaneous speed of the particles is much more evident to the eye and in that the individual particles can be brought back into the field of view for observation by applying D. C. momentarily to one or the other of the two phases.

THEORY

Motion of the Particles. This problem will be treated in the simple manner indicated in the Introduction in which a particle moving in its circle is considered equivalent to one moving in a straight line at the same speed. The speed v of the particle will then be given by

$$v = \pi D \nu \qquad (1)$$

where D is the diameter of the orbit of the particle and ν is the frequency of the impressed field. The mobility M will be given by

$$M = \frac{v}{E} = \frac{\pi D \nu}{E} \qquad (2)$$

where E is the constant value of the rotating vector field, or what amounts to the same thing, the maximum value of one of the phases.

In equation (2) the component of the field parallel to the motion of the particle should be used in place of E. A component perpendicular to the motion is necessary to keep the particle in the circle. If we assume that the motion can be treated as the motion of a sphere through a viscous liquid under the action of a force in the direction of and proportional to the electric field, we can show that the perpendicular component of the field is negligible, and that the parallel component, therefore, is practically equal to the field E.

From formula (26) Page 635 of the 4th edition of Lamb's hydrodynamics the equations of motion of the particle are

$$A\frac{d^2x}{dt^2}+B\frac{dx}{dt} = -F\sin\omega t \qquad (3)$$
$$A\frac{d^2y}{dt^2}+B\frac{dy}{dt} = F\cos\omega t$$

where A and B are the coefficients as given by Lamb and F is the maximum value of the effective force produced by either phase of the field on the particle. Solving these two equations and neglecting the constant term and the terms containing $e^{-\frac{Bt}{A}}$ as a factor, we get

$$x = \frac{F\cos\delta}{B\omega}\cos(\omega t-\delta) \qquad (4)$$
$$y = \frac{F\cos\delta}{B\omega}\sin(\omega t-\delta)$$

where $\delta = \tan^{-1}\frac{\omega A}{B}$. The path is obviously a circle of radius $\frac{F\cos\delta}{B\omega}$.

On differentiating equations (4) we find

$$\frac{dx}{dt} = -\frac{F\cos\delta}{B}\sin(\omega t-\delta)$$
$$\frac{dy}{dt} = \frac{F\cos\delta}{B}\cos(\omega t-\delta) \qquad (5)$$

and

$$\frac{d^2x}{dt^2} = -\frac{F\sin\delta}{A}\cos(\omega t-\delta)$$
$$\frac{d^2y}{dt^2} = -\frac{F\sin\delta}{A}\sin(\omega t-\delta) \qquad (6)$$

These equations show that the motion of such a sphere can be represented as shown in the diagram, Fig. 1,

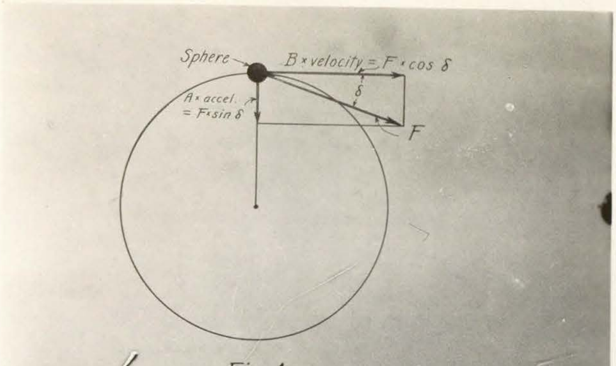

Fig. 1.

where δ is the angle by which the velocity of the sphere lags behind the field. In fact, this diagram could be taken as our original assumption, using the ordinary formulas for the speed and acceleration in uniform circular motion.

Using the values for A and B given in Lamb, formula (26), we find that the angle δ depends upon the radius of the sphere a, the frequency $\nu = \frac{\omega}{2\pi}$, the density of the liquid ρ and the coefficient of viscoscity η. For the values used in this experiment, we can write $B = 6\pi\eta a$ and $A = 3\pi a^2\sqrt{\frac{2\rho\eta}{\omega}}$ to a very close approximation. Hence

$$\tan\delta = \frac{\omega A}{B} = a\sqrt{\frac{\rho\omega}{2\eta}} \qquad (7)$$

Substituting the largest values of a and ω used in this research, namely, 2×10^{-4} cm and 120π respectively, we find that $\tan\delta$ must be less than 0.027. Hence $\cos\delta$ differs from unity by less than 5×10^{-4}, and from (5)

$$B v = F$$

which is the same formula that applies in the case of a sphere moving through a viscous medium under the action of a constant force F. Thus we see that our original equations (1) and (2) are justified by the ordinary laws of hydrodynamics.

Electric Field. As will be described under APPARATUS, the electrodes used for this study consisted of four circular gold disks, placed with their centers at the corners of a square and connected to the outside by thin strips of gold. Fig. 2. It is obvious that if a simple harmonic alternating potential difference be applied between two opposite electrodes (the other two electrodes remaining neutral) then at all points in the liquid a

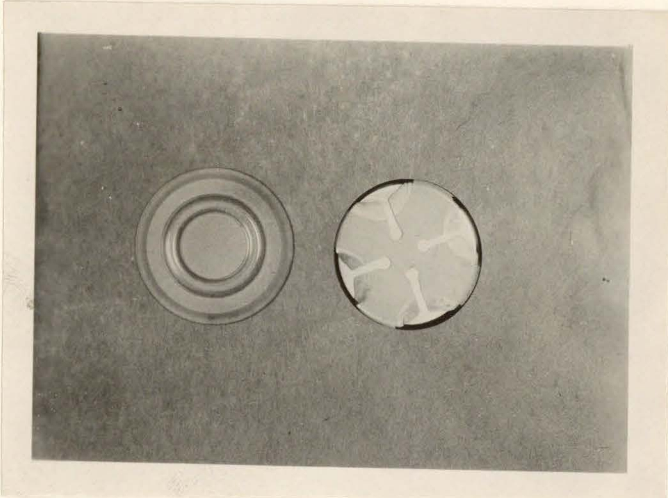

Fig. 2. Quartz Cell with Electrodes on Cover-Glass.

simple harmonic alternating field will be produced, whose maximum value will be proportional to the maximum value of the applied potential.

Over a small area S at the center of the square the field will be quite uniform, since the lines of force must be nearly parallel at this point as can be seen by sketching them in to a figure like Fig. 2.

Now if a second A. C. potential difference is applied to the other two electrodes, the effect will be to superpose the two fields. If the two phases are equal in magnitude but 90 deg. out of step, the resultant field in S will be quite uniform and constant in magnitude and will rotate with a constant angular velocity ω. Using vectors we have from the principle of superposition of fields,

$$\begin{aligned} \bar{E} &= \bar{i}\, E_x + \bar{j}\, E_y \\ &= -\bar{i}\, E_o \sin \omega t + \bar{j}\, E_o \cos \omega t \\ &= E_o\left(-\bar{i} \sin \omega t + \bar{j} \cos \omega t\right) \qquad (8) \end{aligned}$$

The term in the brackets is the equation of a rotating unit vector, so the magnitude of the rotating field is equal to the maximum value E_o of either phase.

To check the order of magnitude of our measured mobilities with those of other experimenters, we have calculated the field E_o at the center S, by considering a two dimensional flat field between two equal but oppositely charged circular disks. Our calculated value will be a trifle larger than the true field, since we have neglected the shielding effect of the other two electrodes. However, it will be sufficiently accurate for most purposes. If greater accuracy were desired, the field could be measured experimentally.

From Jean's Electricity and Magnetism para. 220, the potential difference between the disks will be

$$V = 4e \log \frac{p}{r}$$

and the field at S will be

$$E = \frac{8e}{p} = \frac{2V}{p \log \frac{p}{r}} \qquad (9)$$

where p is the distance between the centers of two opposite disks in Fig. 2 and r is the radius of one of the disks. Therefore, if V_m is the maximum of the potential difference applied to either phase, the value of the electric field at S is constant and equal to

$$E_0 = \frac{2 V_m}{p \log \frac{p}{r}} .$$

APPARATUS

The Quartz Cell. The requirements for this cell are very exacting, and a large number of different kinds of cells were made and tried out before the present kind was perfected. The cell must be thin, as previously mentioned, and the sides must be fairly plane and parallel. The quartz cell (Fig. 2, left) manufactured by Zeiss for use with their Cardiod Ultramicroscope fulfills these requirements and is well suited for the purpose. The electrodes are the greatest problem for they must be smooth edged circular disks of equal diameters and accurately spaced. They must be thin enough that they will not greatly increase the thickness of the cell and yet they must withstand thorough cleaning without injury.

All of the attempts to make these electrodes mechanically failed because the machined surfaces caused bubbles to form in the liquid as soon as the A. C. field was applied. Attempts to make them by cold chemical deposition or by sputtering on of metal films failed because they would not withstand the treatment to which they must be subjected.

The electrodes which have been found to satisfy all of the above requirements are made by painting the proper design (Fig. 2.) on the regular Zeiss quartz cover-glass with the paint used in decorating fine china. For this purpose a mixture of technical "Liquid Bright Gold" and a small quantity of "Roman Gold" was used. When this was heated in a furnace to about 900 deg. C, a fine coat of gold was deposited which adhered so strongly to the quartz that it can be cleaned by dipping it quickly in warm cleaning solution without harm. This is very important for the cell must be absolutely clean to obtain consistent results.

Before painting the cover-glass, its edges had to be ground and polished, for otherwise the gold strips shown in Fig. 1 would not make conducting connections around the edge to the areas of gold on the top surface of the cover-glass. Fig. 2.

This cell was mounted in the bottom section of the cell-mounting supplied by Zeiss. Fig. 3. The rest of the mounting could not be used, but instead the cell was

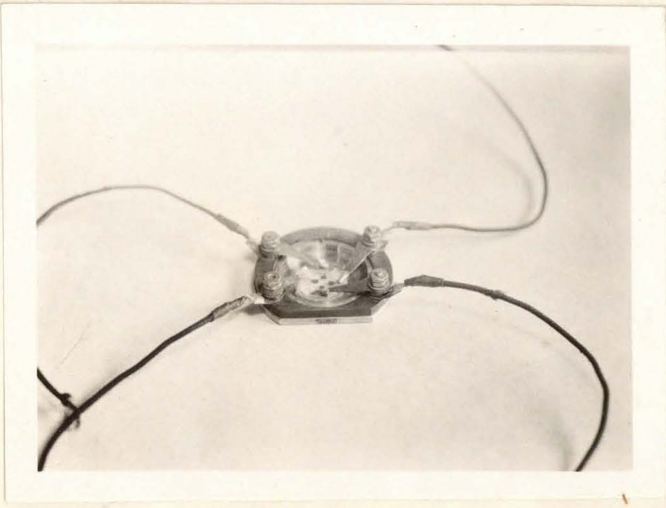

Fig. 3. Quartz Cell in its Mounting.

held in place by means of four spring clips attached to a bakelite ring. These spring clips served to make contact to the electrodes through the areas of gold on the top surface of the cover-glass mentioned in the last paragraph. The whole was then mounted in the usual way on a Cardiod Ultramiscroscope. The objective used for viewing the particles in the cell was a 3 mm homogenous objective, and the illumination was supplied by a Pointelite lamp.

For visual observations a 25-times eyepiece containing a cross-section scale graduated in tenth millimeter squares was used. Photographic measurements were taken with a Leitz Microscope camera arranged so that the field could be viewed at the same time as the plate was being exposed.

Commutator for Supplying Two-phase A. C. Field. In order to investigate the effect of changes in the frequency and in the electric field upon the mobility of colloids, it was desirable to have a source by which the voltage and the frequency could be independently varied. For this purpose, a rather elaborate commutator (Fig. 4) was built of

Fig. 4. Two-phase Commutator with Brush Holder.

72 segments. One of the segments was connected to one slip ring and the segment diametrically opposite was connected to the other slip ring. Fig. 5. These two segments were connected together by a 16000 ohm non-inductive resistance made of advance wire. This resistance was tapped at intervals and connected to the other segments as shown in Fig. 5 in such a way that when a D. C. voltage was applied to the slip rimgs, the potential distribution on the segments varied as a sine function around the periphery. Four gathering brushes were spaced equally on the periphery of the commutator as shown in Figs. 4 and 5. When the commutator was rotated, a two-phase A. C. field was produced whose frequency depended only upon the speed of rotation and whose voltage depended only upon the voltage of the D. C. applied at the slip rings.

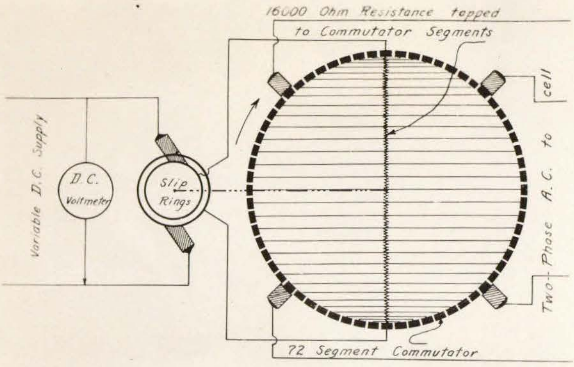

Fig. 5. Two-phase Sine-wave Commutator

A small separately excited D. C. generator was connected on the same shaft as the commutator in order to indicate the speed of the latter. The field excitation was kept constant at 0.8 amps. throughout the entire research so that the voltage it delivered would be a direct measure of its speed. The voltage was measured by an accurate D. C. voltmeter, which was calibrated in terms of revolutions per second by means of a revolution counter and a stop watch.

A D. C. voltmeter was connected across the slip rings of the commutator. Since its reading was equal to the maximum value of the potential difference of either A. C. phase, its reading was substituted directly into formula (9) to obtain the value of the field in the center of the cell.

The wave form of this machine was a very good sine wave in 72 discrete steps as was found by direct test with a Braun tube oscillograph.

Variations in speed of the commutator were obtained by connecting it directly to a D. C. motor, whose field current and armature voltage were separately variable. All speeds between 4 and 70 revolutions per second were obtainable, giving frequencies of 4 to 70 cycles for the field.

Control of Particles. It was desired to study individual particles for a considerable length of time, which would ordinarily be impossible since they usually drift out of the small field of view rather quickly. Four 45 volt B-batteries were connected as shown in Fig. 6 so that a D. C. field of either sign could be applied to either of the phases. The four keys shown in Fig. 6 were conveniently placed for the observer so that he could control the particles at will. This arrangement also served to test the sign of the charge on the particles. In practise, it was found best to operate the control only when the rotating field was not on. It was also found best to apply the rotating field only while taking readings.

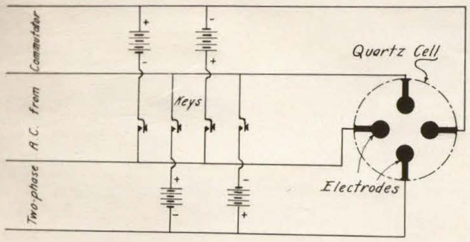

Fig.6. Control of Particles in Cell.

METHOD

Most of the readings upon the diameters of the orbits of the particles were taken visually, but the recent acquisition of a good microscope camera and improvements in the lighting have made it possible to get some photographically. It is necessary to be able to watch the field at the same time as the exposure is being made in order to catch the desired orbit when it is practically stationary.

A sample photograph of the orbit of a bubble of olive oil in distilled water is shown in Fig. 7. The

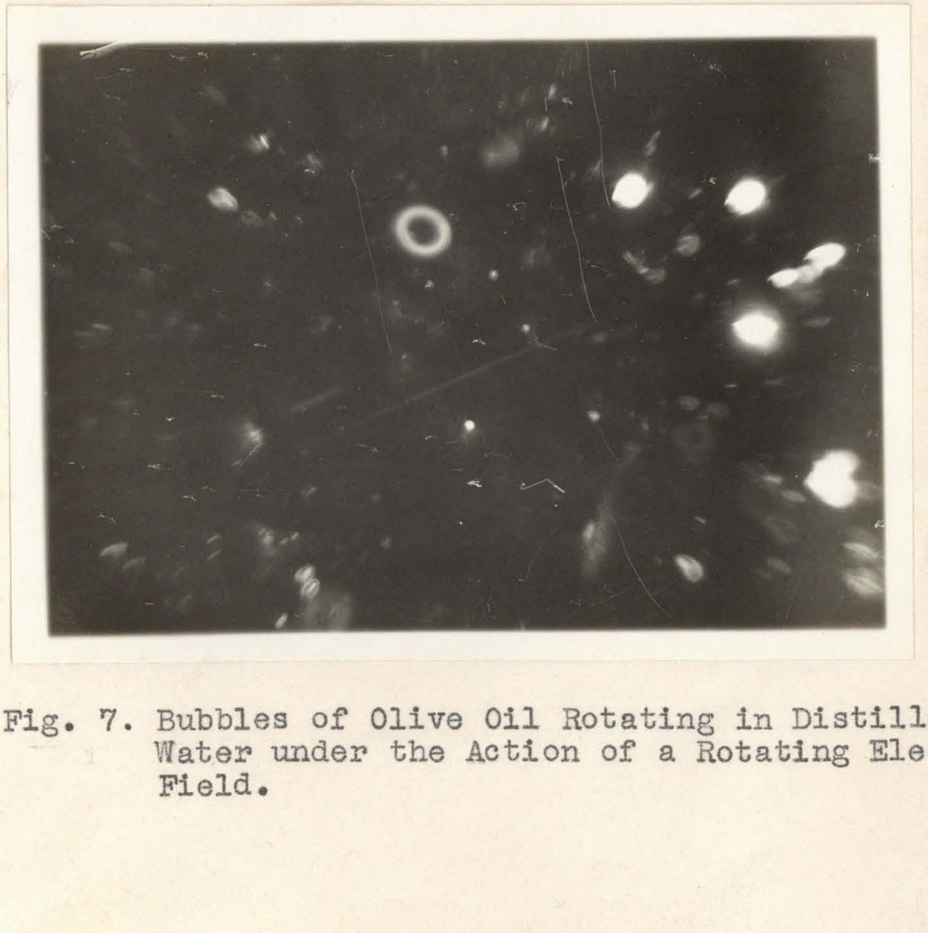

Fig. 7. Bubbles of Olive Oil Rotating in Distilled Water under the Action of a Rotating Electric Field.

bubble is 2×10^{-4} cm in diameter, the orbit is 12×10^{-4} cm in diameter, the electric field is 93 volts/cm and the frequency is 11.4 cycles per sec. This gives a mobility of $4.6 \times 10^{-4} \frac{cm^2}{volt\text{-}sec}$. Two other orbits can be seen faintly in the lower right hand corner of the picture. These orbits are not quite circular because the microscope was not focused exactly in the center of the cell.

RESULTS AND DISCUSSION

Magnitudes of Mobilities. A silver hydrosol made by the Bredig method was tried first. The mobility of these particles varied under different conditions from 2×10^{-4} to $4 \times 10^{-4} \frac{cm^2}{volt-sec}$. This is practically the same range of mobility as is given in Bancroft's Colloid Chemistry for silver in distilled water, which furnishes experimental justification for the method.

Rotating Field vs A. C. Field. A number of readings were taken on individual particles, first, with the two phase field and second, with one phase removed. Single particles were thus measured in both a rotating field and a straight alternating field. It was arranged so that this change could be made rapidly, and in every case, the diameter of the circle orbit with the two-phase field was just equal to the length of the oscillating path with the single-phase field, within the limits of error of the experiment. This was tried with both olive oil and mineral oil emulsions in water and with copper and silver hydrosols made by the Bredig method. The same result was obtained in every case, but it should be pointed out that the fluctuations of the small particles of the metal sols made the tests much less conclusive than in the case of the emulsions where relatively large bubbles could be observed. It is planned to make a more accurate study of this point photographically.

The result is just what we should expect if we can assume for both types of motion that the "effective" force (See THEORY, Para. 3) upon the particle is always proportional to the electric field, and that the ordinary laws of hydrodynamics can be applied. However, according to the Helmholtz-Debye law the "effective" force on a particle should be a function of the distribution of its double layer. If the double-layer is distorted when the particle is in motion, its distribution with respect to the particle should be different at different points along the path of the particle in an A. C. field, but not in a rotating field. Therefore, if the double-layer is distorted with the particle in motion, we should expect a difference between the length of the oscillating path in a single-phase field and the diameter of the circle in a rotating field. Since we find no such difference, we must conclude that if the distortion exists it has less effect upon the "effective" force than we might expect, and that the A. C. method of measuring mobilities will give correct results.

<u>Variations in Mobilities with Frequency</u>. Working with a silver hydrosol in an A. C. field, Blüh found a small increase in the measured mobility when the frequency was increased. This increase in the measured mobility he was unable to explain. We have repeated his experiment with

the same results as he obtained, but when a copper hydrosol was used instead of the silver hydrosol, the measured mobility decreased rather than increased with increasing frequency. Table I gives the ratios of the measured mobilities at 27 cycles to the measured mobilities at 40 cycles. Each number represents the average of several taken on a single particle. Each particle whose ratio is recorded here was taken at 40 cycles, then at 27 cycles and back again at least six times.

Table I

Ratio of Mobility at 40 Cycles to that at 27 Cycles.

Silver	Copper
1.03	0.76
1.10	0.86
1.02	0.86
1.04	0.87
1.05	

Since copper and silver colloids have opposite signs in water, it would seem reasonable to suppose that the water would always move in the opposite direction to the silver particles and tend to decrease their measured mobility, while it would move in the same direction as the copper particles and tend to increase their measured mobility. As the frequency increased, the motion of the relatively large body of liquid would decrease and the measured mobility would approach more and more nearly to the true mobility. This would produce the result observed, and it seems to be the most logical explanation of the results reported by Blüh. The results given in Table I were obtained from observations of the "preferred" orbits of the particles. The term "preferred" orbit is explained in 3 of the following paragraph.

Fluctuating Mobilities of Colloidal Particles. Probably the most important result of this research is the observation that the mobility of individual particles, as measured by the diameters of their orbits, is not constant with time but fluctuates considerably. Many attempts were made to make quantitative measurements upon these fluctuations, but the particles changed from one orbit to another too rapidly for one to observe any orbit long enough to determine its size. It is hoped that it may be possible to obtain some such results photographically.

The following qualitative results have always been observed with particles of colloidal size.

1. The mobilities of the larger particles fluctuate less than the mobilities of the smaller ones. Fluctuations disappear for particles above 2×10^{-4} cm diameter. This observation was made best upon the oil emulsions since bubbles of all diameters can be observed at once.

2. The fluctuations occur and are of the same type in all of the kinds of suspensions we have tried. Suspensions of olive oil, mineral oil, turpentine, silver and copper all in distilled water have been tried.

3. Particles have "preferred" orbits in which they remain longest. Particles 10^{-5} cm in diameter frequently remain in this orbit several seconds. They frequently remain in practically zero orbits for a second or more.

4. The fluctuations usually take place between the "preferred" orbit of the particle and a zero orbit. Occasionally particles take orbits larger than the "preferred" orbit.

5. The "preferred" orbit is nearly the same size for all sizes of particles in the same suspension. The large oil drops which show no fluctuations have constant orbits of about the same size as the "preferred" orbits.

What is the cause of these fluctuations? Two possible explanations present themselves. Either the distribution of the double-layer or ionic cloud of the particle fluctuates or else the total charge on the particle fluctuates.

If the phenomena is due to fluctuations in the double layer, its thickness must sometimes be very small indeed to account for the frequent cases of practically zero mobility.

If the fluctuations are due to changes in the total charge on the particle, one would expect that the total number of electrons on each particle must be rather small. However, the usual estimates of the charge on colloidal particles is equivalent to a large number of electrons. These estimates are based upon the Helmholtz-Debye formula for mobility combined with some assumed thickness of the double layer. The larger the thickness of the double layer assumed, the smaller will be the estimate of the charge. We should obtain a minimum value for the charge if we assume that the thickness of the double layer is infinite.

If the double layer is infinite, we merely have a charged particle in a dielectric fluid and its potential ζ will be

$$\zeta = \frac{q}{\epsilon a}$$

where ϵ is the dielectric constant of the fluid and q is the charge on the particle. If we substitute this in the Helmholtz-Debye formula

$$\zeta = \frac{6\pi\eta}{\epsilon E} v$$

we obtain

$$E q = 6\pi\eta a v \qquad (10)$$

which is, as we should expect, Stokes' law for a sphere moving in a viscous fluid under the action of a constant force Eq.

If we substitute in (10) values for the largest particles on which our fluctuating mobilities have been observed, we get

$$q = \frac{6\pi\eta a v}{E} = \frac{6\pi\,(0.01)(0.5\times10^{-4})(35\times10^{-3})}{90/300}$$

$$q = 11\times10^{-7} \text{ e.s.u.}$$

or more than 2000 electrons to make this particle move in its "preferred" orbit. It is difficult to understand how the charge on this particle could be any smaller than that given by the above calculation. It is also difficult to see why we should get noticeable fluctuations with so many electrons present. Further work should be done along this line.

SUMMARY

1. A method has been developed for directly observing and measuring instantaneous values of mobility of individual particles suspended in liquids, the endosmotic motion of the liquid being reduced to a minimum by using a very thin cell and a rotating electric field.

2. It has been found that within the limits of error of the experiment, measurements of the mobility of individual particles by the single-phase A. C. method give the same result as by the rotating electric field method.

3. An explanation has been found for the results of Blüh, where he found an apparent increase in the mobility of his colloid particles in an A. C. field with increasing frequency.

4. It has been found that the mobility of individual particles suspended in distilled water fluctuate with time. These fluctuations are most pronounced for the smallest particles and disappear entirely for particles larger than 2×10^{-4} cm diameter.

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