CATAPHORESIS IN ROTATING ELECTRIC FIELDS*

By E. M. Pugh and C. A. Swartz**
California Institute of Technology

(Received September 17, 1930)

Abstract

A new method of making cataphoresis measurements on colloid particles has been developed and tested. The method makes use of a rotating electric field which causes the particles to move in circles. In this way it is easily possible to test the effect of variable speed of the particle on the distribution of the diffuse electric double layer surrounding it. The results obtained indicate that this effect is negligible. Furthermore, it has been discovered that the mobility of the small particles (below 10^{-4} cm in diameter) fluctuates widely and this is made very evident to the eye by the fluctuations in the circular paths of the particles. The fluctuations are quite violent with particles as small as 10^{-6} cm in diameter. Considerable study of these variations has been made as well as an attempt to explain them qualitatively.

Introduction

THE alternating field method of measuring cataphoresis of colloid particles in the ultramicroscope, first introduced by Cotton and Mouton,[1] has not come into general use for this purpose although it possesses the distinct advantage of measuring instantaneous mobilities of individual particles. This is undoubtedly due to the fact that the interpretations of such measurements have been open to question since the particles cannot have the uniform velocities, always assumed in cataphoretic theories, when in A.C. fields. They must have different velocities in different parts of their paths.

For example, Blüh[2] found that the apparent mobility of silver particles in water increased with the frequency—an unexplainable result.[3] It was a question whether the diffuse double layer could be out of phase with the particle and thus noticeably influence the measurements.

The advantages of the A.C. method can be preserved and most of the objectionable features removed by using a rotating field[4] produced by applying a two phase A.C. source to four electrodes placed at the corners of a square

* This paper contains results obtained in an investigation on "The Fundamentals of the Retention of Oil by Sand" listed as Project No. 36 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

** American Petroleum Institute Research Fellows.

[1] Cotton and Mouton, Compt. Rend. **138,** 1584, 1692 (1904).

[2] Blüh, Ann. d. Physik **78,** 177 (1925).

[3] Blüh, Ann. d Physik **79,** 143 (1926); **80,** 181 (1926).

[4] Cotton and Mouton, in Compt. Rend. **138,** 1584 (1904) suggested the possibility of using colloid particles in a rotating field as a kind of oscilloscope to analyze three-phase potentials.

in a cataphoretic cell. Over a small area in the center of the square, the field thus produced will be practically uniform, constant in magnitude, and rotating with a constant angular velocity. This rotating field will cause each particle in this small area to describe the circumference of a circle with each rotation of the field. The greater the mobility of the particle the larger will be the circle which it will be able to traverse, and its speed will be given simply by the product of the circumference of the orbit by the frequency applied. Particles with constant mobility thus will move at constant speed, and the double layer or ionic cloud generally assumed to surround all colloid particles will reach the same kind of dynamic equilibrium as it would if the particle were moving in a straight line.

In the cell here developed, the electrodes were spaced sufficiently far apart so that the entire field of view in the high power microscope was small enough to fulfill the requirement of being a small area. On looking into the microscope, one finds the entire field of view filled with small circles or toroids of light.

Theory

In the small section of the cell under observation, the electrostatic field will be that due to the superposition of the two fields arising from the alternating potentials applied separately to the two opposite sets of electrodes, and its x and y components given as functions of time will be

$$X = F \cos \omega t$$
$$Y = F \sin \omega t.$$

Here F is the maximum value of the field strength, in the small region under consideration, due to the potential applied across one of the two sets of electrodes. The total resultant field is a uniform electric field of constant strength F rotating with the constant angular velocity ω.

In order to find the motion of a particle suspended in the liquid and acted upon by such a rotating field, some assumptions must be made from both the electrical and the hydrodynamic standpoints in order to make the problem soluble and yet represent the facts fairly accurately. It is, therefore, assumed that the force acting on the particle due to the electric field is directly proportional to the field strength and that the equations of motion of the particle are

$$\begin{aligned} A\frac{d^2x}{dt^2} + B\frac{dx}{dt} &= kX = kF \cos \omega t \\ A\frac{d^2y}{dt^2} + B\frac{dy}{dt} &= kY = kF \sin \omega t \end{aligned} \tag{1}$$

where A and B are constants. A represents the effect of the inertia of the particle and B represents the viscous drag of the liquid surrounding the particle. Solving these equations, neglecting the constant terms, and introducing the initial condition that the velocity is zero when $t = 0$ we get

$$x = R_0 \cos\delta \sin(\omega t - \delta) + R_0 \cos\delta \sin\delta e^{-\omega t/\tan\delta}$$
$$y = -R_0 \cos\delta \cos(\omega t - \delta) - R_0 \sin^2\delta e^{-\omega t/\tan\delta} \quad (2)$$

where $R_0 = kF/B\omega$ and $\delta = \tan^{-1}\omega A/B$.

Omitting the last or transient term in each of these equations, the path of the particle is seen to be a circle of radius $R = R_0 \cos\delta$. The velocity of the particle is

$$R\omega = kF \cos\delta/B$$

whereas, in cataphoretic measurements in a straight line it would be $V = kF/B$ as seen from equations (1) and these two will agree within the limits of accuracy of our experiment if $\cos\delta$ is sufficiently near to unity. Now δ is the angle by which the velocity vector of the particle lags behind

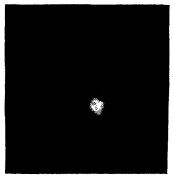

Fig. 1. Initial position and final path of oil particle. Diameter of particle 2×10^{-4} cm, field 225 volts/cm, frequency 21.5 r.p.s.

the electric field vector. One would expect it to be quite small because for colloid particles one would expect A to be very small compared to B. Fortunately, there is a simple experimental method of determining $\cos\delta$ with just

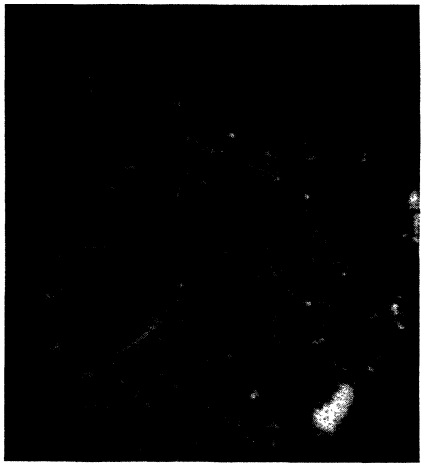

Fig. 2. Arcs of circular paths showing particles all of same sign but varying mobility.

the accuracy required, for on putting $t=0$ in equations (2), it is found that the initial position of the particle is at a distance R_0 from the center of the final circle of radius R. Long exposure microphotographs can then be taken in which the rotating field is not applied until the exposure is partly com-

pleted. The result is that the initial position and the final circle of the particle are recorded upon the plate from which R and R_0 can be measured, whence $\cos \delta = R/R_0$.

Fig. 1 is an example of such a photograph for a particle of mineral oil in water. It is seen that the initial position lies almost exactly in the path of the final circle. From this and several other such photographs, it can be concluded that $\cos \delta = 1$ within the limits of experimental error.

If particles of opposite sign should exist in the same sol, these could be detected by exposing the photograph for only a fraction of a period of revolution. Since particles of opposite sign must rotate in the same direction as the field but 180° apart in phase, they will produce arcs of circles curved in opposite directions. Fig. 2 is a photograph taken in this manner of a mineral oil emulsion with particles ranging in size from 10^{-6} to 10^{-5} cm.

Apparatus

The apparatus consists essentially of three parts, the ultramicroscope and light source, the quartz cell (Fig. 3) containing the sol and electrodes, and the machine for producing the two phase A.C. potential (Fig. 4).

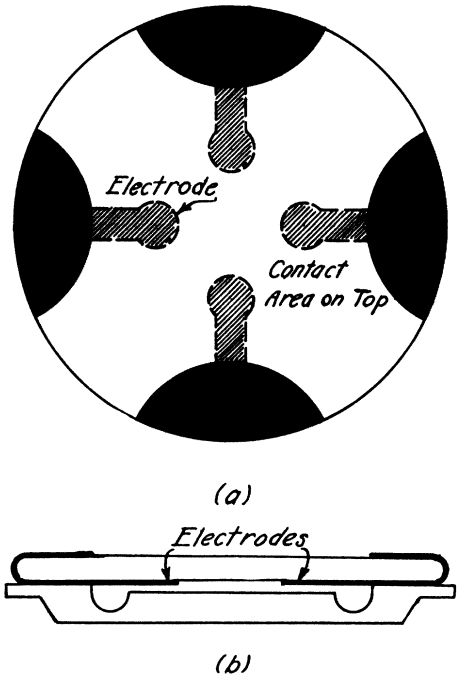

Fig. 3 a. Quartz cover glass with gold electrodes to produce rotating field.
Fig. 3 b. Cross-section of cataphoretic cell with cover glass.

The quartz cell, with its mounting and the high power oil-immersion objective are the special equipment made by Zeiss for colloidal work, and were adapted with slight modification for this purpose. The light source,

used in connection with a cardioid condenser, consists of a pointolite lamp for visual observation and a carbon arc passing from 15 to 75 amperes for photographic work.

The electrodes in the cell were formed by painting the proper design (Fig. 3a) on the under side of the cover glass with the gold paint used for decorating china and then heating in a furnace to 750°C. The cover glass with electrodes made in this way may be cleaned in hot cleaning solution without injury. Connection to the electrodes was made by strips of the gold paint which extend around the edge of the cover glass and connect to other painted areas on top. It was found necessary to grind the edges of the cover glass round and polish them in order to insure electrical connection. To these painted sections on top, connection is made directly by four spring clips which also serve to hold the cover glass firmly in place against the lower half of the cell.

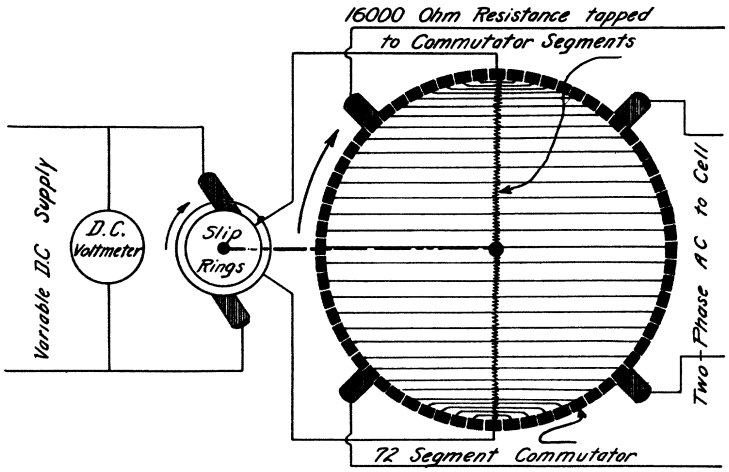

Fig. 4. Two-Phase A.C. potential generator allowing independent variation of voltage and frequency.

In this cell, it is found that the size of circles described by the colloids, and therefore the velocity of the particles, is not a function of the depth of the particle in the cell as is usually found in thin cells. This is due to the fact that the edges are free (Fig. 3b) and the endosmose can, therefore, move the entire layer of liquid in the center as a whole without causing pressures which will give rise to reverse currents. Blüh[2] made tests which seemed to show that endosmose could be entirely damped out by using a cell as thin as ours. Our results, however, indicate that the endosmose is only reduced and not entirely eliminated. In use, the cell thickness was about 10μ.

A specially constructed machine was used for producing the A.C. potential its principle being illustrated in Fig. 4. Thirty-six coils, each of proper resistance, were wound non-inductively on an old D.C. generator armature shaft from which the iron core and windings had been removed. The coils

were connected as shown to the seventy-two segments of the commutator so that, as one proceeds from segment to segment around the periphery, the resistance between the two diametrically opposite segments is a sine function of the angle. The coils were of No. 30 "advance" wire and in series they totaled 16000 ohms. When a D.C. potential supply is connected in series with them by means of slip rings and when the shaft is rotated at uniform speed, any number of sine function potentials may be obtained in any desired phase relation to each other by the use of sets of brushes properly spaced about the comutator. Two sets were placed 90° apart for the two phase. The advantage of this construction is that both the voltage and frequency of the A.C. potentials produced are variable over wide ranges and entirely independently of each other.

Results and Discussion

If we calculate the mobility of particles as explained above, we get results in agreement with other observers. For instance, using a silver sol made by the Bredig method we find the mobility to vary between 2×10^{-4} and 4×10^{-4} cm^2/volt · sec. which is practically the same range of mobility as given in Bancroft's "Applied Colloid Chemistry" for silver particles in water.[5]

In order to test the effect of a variable speed on the diffuse electric double layer assumed to surround the particle, several photographs of the same particle have been taken on the same plate, first with the rotating field, then with a straight alternating field obtained by disconnecting one of the phases composing the circular field. In the first case, the path is circular and the *speed* of the particle is constant; in the second case, the path is a straight line vibration and the *speed* varies over wide limits. All photographs thus taken show that the amplitude of the straight line vibration is just equal to the diameter of the corresponding circle. This indicates that the distorting effect of the variation in speed on the distribution of the diffuse double layer and the consequent variation of the effective force on the particle due to the field is very small if it exists at all. A sample of such a photograph is reproduced in Fig. 5. Furthermore, when several photographs are taken on the same plate of the same particle moving in circles with constant frequency but with different field strengths and consequently with different speeds, the diameters of the orbits are in the same ratio as the applied voltages, showing again that the variation in speed has no effect on the double layer, at least for the frequencies and voltages used.

According to the tests described in this paper, the rotating field method must give correct values for the mobilities of the colloid particles. The single phase A.C. method, should also give correct values, since it agrees with that of the rotating field. Why, then, did Blüh[2] using the A.C. method find an increase in his measured mobilities with increasing frequencies. Using the same sol,—Bredig silver in distilled water,—as he used, we repeated and checked his results. However, the test which he made to show that endos-

[5] Bancroft, Applied Colloid Chemistry, p. 258.

mose was entirely eliminated did not seem conclusive. His peculiar results can be easily explained if we assume that there was some endosmose in his cell and that this motion was opposite in direction to the cataphoretic motion of his particles. Since the inertia of the liquid is relatively large, its oscillatory motion, due to endosmose which tends to reduce the motion of the silver particles, would become less and less noticeable as the frequency increased. Consequently, at low frequencies the measured mobility would be too low, but it would approach the true mobility as the frequency increased. Thus, the measured mobility would increase with frequency. If this explanation be correct, then similar experiments using a colloid of sign opposite to that of silver should give a decrease rather than an increase in measured mobility with increasing frequency. This was tried out with a sol of Bredig copper in distilled water, and the result was a definite decrease in mobility with increasing frequency as was expected. Thus Blüh's increase in mobility with frequency can be explained if the endosmose was not entirely eliminated from his cell as he assumed.

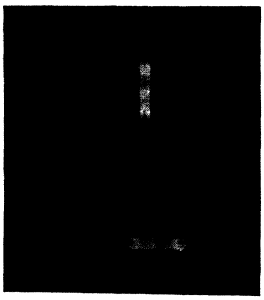

Fig. 5. Paths of an oil particle in the rotating field and in each of the component A.C. fields. (Four exposures)

Probably the most important result of this research is the observation that the mobility of individual particles as measured by the diameter of their orbits is not constant with time but fluctuates considerably. These fluctuations take place so rapidly that it is impossible to make quantitative visual measurements upon them. However, many hours of observation of the phenomena have yielded the following facts:

1. Each particle has one definite size of orbit or speed in which it is most frequently observed. This orbit will be called the preferred orbit. It is the same order of magnitude for all particles from the smallest to the largest found in a mechanically stirred oil emulsion, though it is slightly larger for the larger particles in agreement with Mooney's[6] results.

2. Particles are very rarely found in orbits larger than their preferred orbits—almost all of the fluctuations take place between the preferred orbit and zero. The fluctuations are apparently quite random.

3. The amount and rapidity of these fluctuations depends upon the size

[6] Mooney, Phys. Rev. **23**, 396 (1924).

of the particles in much the same way as the Brownian motion depends upon the size. They are hardly perceptible in particles larger than 10^{-4} cm diameter while the finest particles observable in the ultramicroscope fluctuate so violently that they seldom stay in any circle for one revolution.

4. The same type of fluctuation is found in all sols observed. Emulsions of mineral oil, olive oil and turpentine in distilled water; Bredig sols of copper and silver in distilled water; and Zigmondy's nuclear gold sol[7] have been tried.

Why does the mobility fluctuate? Fluctuations in the charge on the particle seems the most reasonable explanation but how can a particle suddenly lose such a large charge. Calculations show that the change in charge necessary to produce some of the fluctuations observed must be at the very least several hundred electrons. It may be that the charge on all colloid particles is always fluctuating, or it may be that the strong electric field with the aid of an occasional heavy impact due to Brownian motion carries away some of the adsorbed layer of ions causing fluctuations in charge only while the colloid mobility is being observed. At present we cannot answer this question.

The authors wish to thank Dr. R. A. Millikan under whose direction it has been a pleasure to do this work and also the American Petroleum Institute for a grant which defrayed the expenses. During the latter part of the research one of the authors (E. M. P.) has been working as a National Research Fellow and wishes to express his gratitude to the National Research Council.

[7] Rinde, Diss. Upsala, p. 25 (1928)

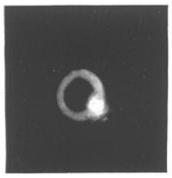

Fig. 1. Initial position and final path of oil particle. Diameter of particle 2×10^{-4} cm, field 225 volts/cm, frequency 21.5 r.p.s.

Fig. 2. Arcs of circular paths showing particles all of same sign but varying mobility.

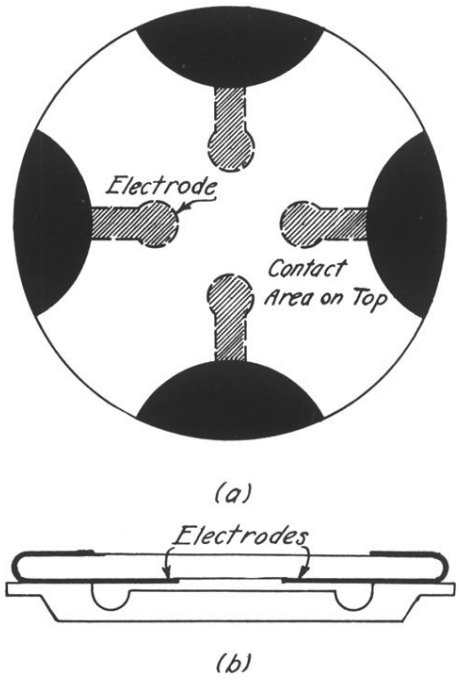

Fig. 3 a. Quartz cover glass with gold electrodes to produce rotating field.
Fig. 3 b. Cross-section of cataphoretic cell with cover glass.

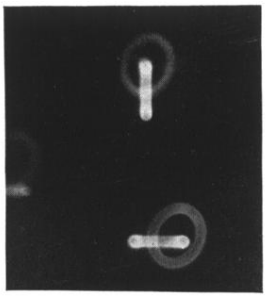

Fig. 5. Paths of an oil particle in the rotating field and in each of the component A.C. fields. (Four exposures)