Effect of Radio-Frequency Fields on the Electrophoretic Mobility of Some Colloids

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(Received 26 June 1963)

Four sizes of polystyrene latex, starch grains, and gelatin-coated polystyrene showed a voltage-dependent, frequency-specific response to radio-frequency fields as a function of particle size.

This response was a loss of negative surface charge irrespective of whether the initial surface charge was negative or positive.

The charge returned to original values linearly with time over a period of hours, but returned to original values in 1 min if exposed to another frequency.

At high concentrations of colloid (mean interparticle distance greater than 20 diam) no change in surface charge was apparent after exposure to an rf field. But dilution of this concentrated colloid without further exposure to rf reduced the surface charge to the value which it would have had if the diluted material had been exposed to rf.

All these phenomena occurred irrespective of whether the colloids were in distilled water or in $10^{-3} M$ NaCl.

I. INTRODUCTION

IN a previous communication from this laboratory[1] it was shown that the electrophoretic mobility of a polystyrene latex (PSL) could be reduced by exposure to radio-frequency (rf) fields. Further, it was shown that for a particle diameter of 1.305 μ a specific frequency (13.00 Mc/sec) and a voltage of 500 V/cm were required to produce the optimum reduction. In this paper further experimental data are presented on the effects of rf fields upon PSL of different diameters and upon different colloidal materials.

II. METHODS AND MATERIALS

1. Colloids

The PSL of diameters 1.305, 1.17, 0.802, and 0.761 μ were extensively dialyzed against distilled water. Particle concentrations were determined with a Model B Coulter counter.

For some of the experiments PSL was coated with gelatin in the following manner. PSL was suspended in 5% gelatin solution at 45°, cooled, and washed three times by centrifuging in distilled water. Starch grains of *Amaranthus cruentus* were sized in the Coulter counter and found to have a mean diameter of 1.464 μ. The water used throughout these experiments was de-ionized and distilled from Pyrex glass. Conductivity measurements were made in a standard Pyrex conductivity cell with platinum electrodes and a cell constant of 0.17, using a Wayne Kerr B221 Universal bridge. Conductivity of the water was found to be 1.705±0.025 μmho/cm at 25°.

2. Microelectrophoresis

Electrophoretic mobilities were measured in a cylindrical microelectrophoresis cell of the type described by Bangham *et al.*[2] The cell was suspended in a temper-

ature-controlled water bath and all measurements were made at 25°±0.5°. All electrophoretic results are expressed in microns/second/volt/centimeter, and represent the mean of at least 20 determinations. Under the conditions obtaining in these experiments, i.e., low salt concentrations and relatively large particle diameters, the equation of Smoluchowski[3] for conversion of mobility to zeta potential is inadequate. To calculate zeta potentials, it would therefore be necessary to use Overbeek's equation,[4] which takes relaxation and the variation of κa into account. This was unnecessary since absolute values of zeta potential were not required for these experiments.

3. Radio-Frequency Equipment

The rf generator, designed and built to our specifications by the General Telephone and Electronics Corporation, operates over a frequency range of 5–50 Mc/sec with voltage continuously variable from 0–20 000 V peak to peak (ptp)/cm. The output was pulsed so that heating effects were negligible: pulse duration may be varied from 5–100 μsec and pulse repetition frequency (prf) is variable from 4–1000 pulses/sec.

Frequency of the driving oscillator was continuously monitored with a Hewlett–Packard Model 524C digital electronic counter and 525A frequency converter unit. The output voltage, prf, pulse duration, and waveform were measured using Tektronix 545 and 581 oscilloscopes. The oscilloscope voltage measurements were verified using a Jennings vacuum-tube voltmeter, Model J-1003.

The cuvet into which the colloidal solutions were placed for irradiation measured 2×2×4.5 cm. Two opposing sides were of sheet platinum which served as electrodes, the other two sides and bottom were made of 1/8-in. sheet polystyrene. The output from the generator was connected to one electrode and the other

[1] J. H. Heller, D. J. Wilkins, and J. F. Freeborn, Nature **197**, 997 (1963).
[2] A. D. Bangham, D. H. Heard, R. Flemens, and G. V. F. Seaman, Nature **182**, 642 (1958).
[3] M. Von Smoluchowski, Physik. Z. **17**, 557–585 (1916).
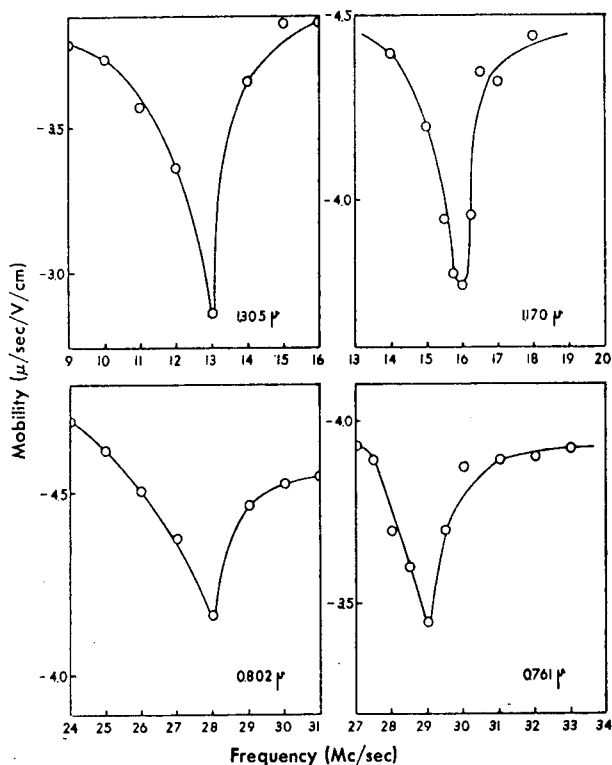[4] J. Th. G. Overbeek, Advan. Colloid. Sci. **3**, 97–135 (1950).

FIG. 1. Electrophoretic mobility in distilled water of PSL of various diameters against frequency. Each point represents a mean of 30 separate determinations. Voltage for 1.305 and 1.170 μ diam is 500 V/cm, for 0.802 μ and 0.761 μ diam 1000 V/cm; pulse duration is 10 μsec; prf 500; time in field 1 min.

electrode was connected directly to ground. In a typical experiment 15 ml of a suitably diluted suspension of PSL or other colloid was introduced into the cuvet and exposed to an rf field. After exposure it was removed and the electrophoretic mobility was measured.

III. RESULTS

1. Effect of Varying Particle Size

Upon exposure of PSL's of various particle diameters, it was found that each size had a specific frequency at which maximum reduction in electrophoretic mobility occurred, (Fig. 1). Figure 2 shows the relationship between the frequency optimum and the particle diameter. 1.305 μ-diam PSL with adsorbed gelatin was suspended in diluted Michaelis buffer (of ionic strength $10^{-3}M$ at pH 3.1 and pH 10.0). In these media the particles were positively and negatively charged, respectively. The maximum change in mobility in both cases occurred after exposure at 13 000 Mc/sec, the positive particles becoming more positive and the negative particles becoming less negative.

The frequency optimum was found not to alter as a function of added salt up to the maximum concentration of $10^{-3}M$ NaCl used in these experiments, although of course the initial mobilities were different.

A suspension of *Amaranthus cruentus* starch grains

was found to have a maximum reduction of mobility at 7.50 Mc/sec.

2. Effect of Voltage

The effect of varying rf voltage upon the decrease in mobility at 16.00 Mc/sec for the 1.170 μ-diam spheres is shown in Fig. 3. It can be seen that there was no further reduction above about 500 V-ptp/cm. The same held true for the 1.305-μ-diam spheres at 13 000 Mc/sec.[1] However, the plateau for the 0.802-μ spheres at their frequency optima was not reached until 1000 V-ptp/cm.

3. Effect of Varying Pulse Duration, Pulse Repetition Frequency, and Total Time of Exposure

The optimum change in mobility in, e.g., the 1.305-μ-diam particles, when exposed at 13.00 Mc/sec and 500 V/cm for 1 min, was obtained using a duty cycle of 0.5%, i.e., a 10-μsec pulse at 500 pulses/sec. If the duty cycle was increased, no further change could be induced. However, if the duty cycle was decreased, and the time of exposure increased by the same factor (e.g., increase of time of exposure to 5 min and decrease of prf to 100) then the same results were obtained. If the duty cycle was increased above 0.5%, at a lower voltage, however, the reduction of mobility was not as great. The above duty cycle corresponded to a total exposure time of 0.3 sec. Upon exposure of PSL for 0.3 sec CW the same reduction in mobility was obtained.

4. Effect of Temperature

Under the experimental conditions described above, there was no measurable rise in temperature of the colloidal suspension. If the colloid was cooled to 4°
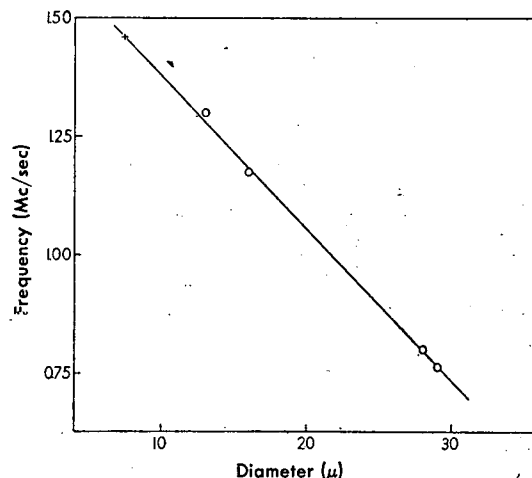

FIG. 2. Diameter of PSL (O) and starch (+) in microns against frequency required to produce maximum reduction in electrophoretic mobility. Voltage for 1.305 and 1.170 μ is 500 V/cm; for 0.802 and 0.761 μ diam 1000 V/cm; pulse duration 10 μsec; prf 500; time in field 1 min.

or heated to 50° before rf exposure, or if heating was induced in the suspension by increasing the rf voltage and/or duty cycle, the same percentage change in mobility was obtained.

5. Recovery of Mobility with Time

After exposure of a colloid under conditions chosen to produce maximum reduction of mobility, the recovery to the initial mobility as a function of time was measured. The mobility was found to recover linearly with time. Table I shows the average time required to recover initial mobilities for the various particle sizes. It can be seen that the time to recover to the initial mobility approximates to a linear function of particle diameter.

It was found that the initial mobility of the colloid could be recovered by exposure for a further minute at a frequency other than that required to produce maximum reduction. Figure 4 shows results obtained by exposing a suspension of 1.170-μ spheres at the frequency and voltage at which maximum reduction in mobility was obtained, i.e., 16.00 Mc/sec and 500 V/cm for 1 min, followed immediately by exposure for an additional minute at another frequency.

6. Effects of Particle Concentration

Under optimum conditions of frequency and voltage for maximum reduction of mobility, the effect of varying the concentration of polystyrene was explored. Figure 5 shows that for 0.802 μ diam with PSL above a concentration of 1.85×10^8 particles/ml (C_{max}), the rf field produced no reduction in mobility. Below a concentration of 2.1×10^7 particles/ml (C_{min}) there was no further reduction in mobility. The same effect was observed for all sizes of PSL, and Table II shows the relevant concentrations for all the samples examined. However, if a suspension of PSL with a particle concentration of 10^8 particles/ml was exposed to the
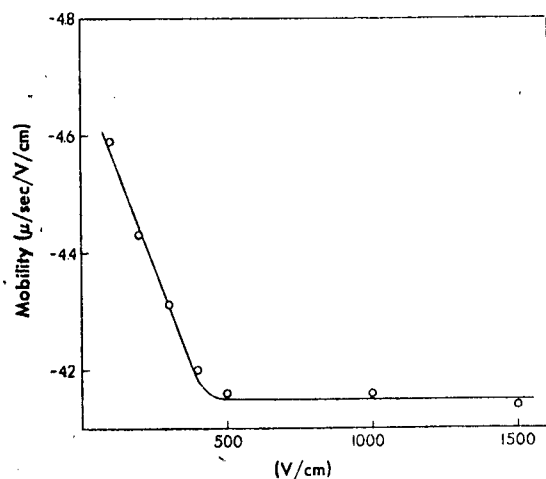
FIG. 3. Electrophoretic mobility in distilled water of 1.170-μ-diam PSL against RF field strength at 16 Mc/sec. Pulse duration 10 μsec; prf 500; time in field 1 min.

TABLE I. Time for recovery to initial mobility of PSL.

Particle diameter (μ)	Concentration (No./ml)	Time (h)
1.305	8.07×10^6	3.9 ± 0.1
1.170	2.12×10^7	3.7 ± 0.1
0.802	3.18×10^7	2.9 ± 0.1
0.761	3.86×10^7	2.7 ± 0.1

rf field under conditions for maximum reduction of mobility and subsequently diluted, it was found that the mobility of the diluted suspension fell at the same place on the curve as it would have, had it been exposed at this dilution in the first place. A typical example can be seen in Fig. 5.

IV. DISCUSSION

The surface of undialyzed PSL consists of an adsorbed layer of emulsifier (in this case, an alkyl aryl sulfonate). This layer may be removed by dialysis, but the residual charge is still high and is thought to be due to carboxyl groups (from the oxidation of vinyl side chains) and sulfate groups (from a polymerization chain-termination step).[5] These groups are linked to the polymer by covalent —C—C— or —C—S— bonds. The reduction in electrophoretic mobility is a reflection of a reduction of the surface charge or zeta potential. This change can be achieved in several ways. For example by a change in the ionic strength of the medium which does not apply in these experiments. Thus the only change of interest in the present context is one of surface-charge density which could conceivably be lowered by:

(a) removal of carboxyl or sulfate groups by fission of —C—C— or —C—S— bonds;

(b) desorption of anions such as OH^-, Cl^-, or strongly bound emulsifier which resists dialysis;

(c) emergence of cationic groups from the polymer or "diffusion" of anionic groups into the polymer;

(d) a change in the dissociation in the anionic groups;

(e) a steric recombination of groups on the surface.

(a) The first possibility is not reasonable, since the energy input is too low by many orders of magnitude. Further, the bonds could not reform and hence recover their initial mobility (see Table I) without further energy input.

(b) Desorption from the surface is unlikely since it should be rapidly reversible. In addition, no change of either pH or conductivity was observed. (However, any changes of pH or conductivity would be extremely small.) Also, if the charge were lost by desorption, it

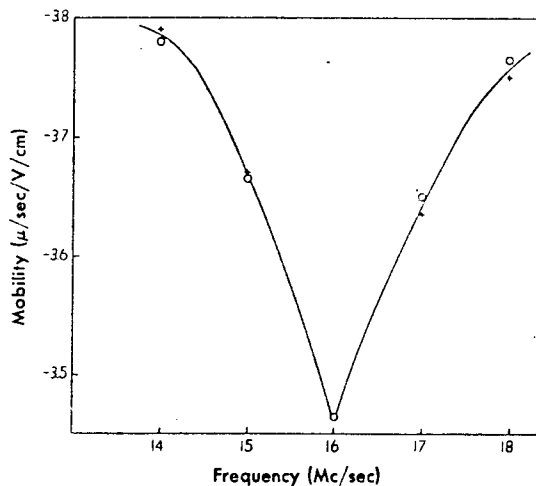[5] R. H. Ottewill (personal communication).

FIG. 4. (O) Electrophoretic mobility in distilled water of 1.170-μ-diam PSL against frequency; (+) Electrophoretic mobility in distilled water of 1.170-μ-diam PSL vs frequency *after* an initial exposure for optimal mobility reduction at 16 Mc/sec. Voltage 500 V/cm; pulse duration 10 μsec, prf 500; time in field 1 min.

would be difficult to explain the long recovery times (see Table I) and the recovery in 1 min at a different frequency.

(c) The likelihood of diffusion into or out of the polymer also seems unlikely, for while one might expect a slow diffusion in such a high viscosity medium, i.e., the polymer, it is difficult to see how this could be accelerated by exposure at another frequency.

(d) A change in the dissociation of carboxyl or sulfate groups seems unlikely since one would expect only a change in the bulk pH to produce this, and no such change was observed.

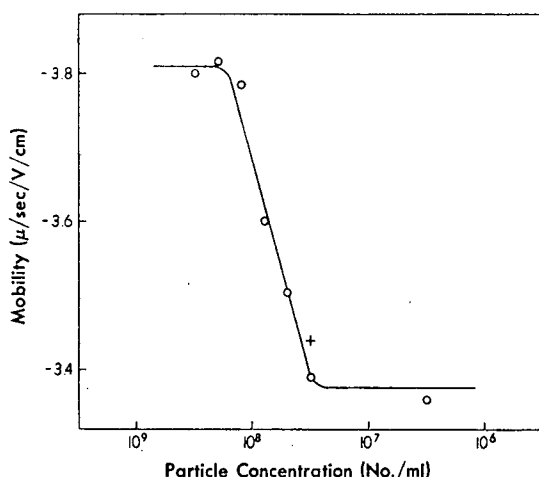(e) According to Sieglaff and Mazur[6] the area

FIG. 5. Electrophoretic mobility in distilled water of 0.802-μ-diam PSL vs particle concentration at 28 Mc/sec. + is the mobility of a suspension of 3×10^8 particles/ml diluted to 3×10^7 particles/ml. Voltage 500 V/cm; pulse duration 10 μsec; prf 500; time in field 1 min.

[6] C. L. Sieglaff and J. Mazur, J. Colloid Sci. **15**, 437 (1960).

occupied per charged group for PSL is approximately 500 Å^2, and assuming an area per molecule for carboxyl and sulfate groups of approximately 25 Å^2, the possibility of steric interference of these anions producing a reduced surface charge density seems unlikely.

Thus none of these mechanisms are adequate to account for the change in surface charge.

However, irrespective of the nature of the change on the surface, there is the further problem of the mechanism of "coupling" rf with these particles. It is difficult to understand how radiation of these wavelengths interacts with such particles at all let alone in such a specific manner with particle diameter.

One of the possibilities to consider is a dielectric dispersion phenomenon. First, the sharp frequency response is in contrast with the normal dielectric dispersion curve. Second, dielectric changes as a function of frequency have short relaxation times in contrast to the results discussed here (see Table I).

TABLE II. Concentrations of PSL above which no change in mobility occurred (C_{max}) and below which (C_{min}) no further change occurred.

Diameter (μ)	(No./ml) C_{max}	(No./ml) C_{min}
1.305	8.1×10^7	4.6×10^6
1.170	9.5×10^7	3.4×10^7
0.802	1.85×10^8	2.1×10^7
0.761	3.8×10^7	1.2×10^7

Recently, Schwann et al.[7] have measured the dielectric properties of PSL of various diameters at frequencies from 10 cps to 200 kc/sec, in an attempt to account for the high values of dielectric constant exhibited by colloidal suspensions. These workers find maxima for the loss curves in the kilocycle range, which they explain in terms of a surface conductance and capacitance. Classically, the approach of Wagner[8] is used to explain the dielectric properties of inhomogeneous systems with an interfacial polarization. However, calculations based upon Wagner's equations[7] yield relaxation times of the order of 10^{-6} sec and characteristic frequencies in the kilocycle range.

Further, Wagner's approach does not take the particle diameter specifically into account but includes it as a volume concentration term. Hence, the characteristic frequency should change as a function of particle concentration which is not consistent with the data discussed here. Therefore, the Maxwell-Wagner treatment is not applicable in the present case.

In Fig. 4 it can be seen that above a certain particle concentration the rf field produced no effect on the

[7] H. P. Schwann, G. Schwarz, J. Maczuk, and H. Pauly, J. Phys. Chem. **66**, 2626 (1962).
[8] K. W. Wagner, Arch. Electrotech. **3**, 83 (1914).

mobility; while below a certain concentration, no further change was produced. In this system, the ionic strength (determined by conductivity measurements) corresponded to approximately $1.7 \times 10^{-5} M$ NaCl. Hence, $1/\kappa$, the thickness of the double layer, was approximately 1000 Å. This is quite large compared to the particle diameter, and hence the possibility that double layer interactions could be inhibiting the change at higher concentrations was considered. However, in the concentration concerned, the interparticle distance is approximately 23 μ and it is difficult to envision any interaction over such a distance. The increasing change, with further dilution, again makes particle interactions an unlikely explanation.

It is interesting to note that, having reduced the mobility of PSL maximally, no further reduction could be produced by changing the frequency or increasing voltage, prf, pulse duration, or time in the field. Hence, it would appear that only 10%–15% of the surface is capable of being changed, and therefore the surface may be inhomogeneous. Until more is known of the intimate structure of the surface, it is difficult to suggest what this inhomogeneity could be. Titration of the surface might lead to further information on this point.

As mentioned in an earlier paper,[1] for the 1.305-μ-diam PSL, the frequency at which there is maximum drop in electrophoretic mobility also corresponds to the frequency at which pearl-chain formation is most readily apparent. Pearl-chain formation occurs over a range of frequencies but at the critical frequency the chains form more rapidly and better alignment is observed. It is difficult to derive quantitative data from such an observation, however, and no attempt has been made to correlate these effects with PSL of other sizes. It is not suggested that pearl-chain formation is caused by the reduction in zeta potential[9]

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[9] A. A. Teixeira-Pinto, L. L. Nejelski, Jr., J. L. Cutler, and J. H. Heller, Exptl. Cell Res. **20**, 548–564 (1960).

since: (1) the effect is observed over a range of frequencies and (2) upon removal of the rf-field pearl chains disintegrate and completely randomize in times of the order of seconds. This is in contrast to the zeta potential change which recovers in times of the order of hours (see Table I). However, since the zeta potential is reduced, and hence the repulsion between the particles reduced, it is reasonable that pearl-chain formation should occur more rapidly at the frequency maximum and that the particles are able to approach one another more closely.

In conclusion, the possibility must, therefore, be considered that the data presented represent a new phenomenon, since all the theoretical approaches so far made lead to negative conclusions.

Further experiments are being conducted to try to elucidate the nature of these phenomena.