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The Influence of Electrolytes on the Cataphoretic Charge of Colloidal Particles and the Stability of Their Suspensions

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THE INFLUENCE OF ELECTROLYTES ON THE CATAPH-ORETIC CHARGE OF COLLOIDAL PARTICLES AND THE STABILITY OF THEIR SUSPENSIONS.

I. EXPERIMENTS WITH COLLODION PARTICLES.

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I.

INTRODUCTION.

The work of McTaggart[1] on the electrification of water-gas sur-faces is of fundamental importance for the question concerning the origin of the potential differences responsible for the cataphoresis of solid particles in aqueous solutions. McTaggart found that the P.D. between gas bubbles and water is about 55 millivolts, the water assuming a positive and the bubble a negative charge. The nature of the gas had apparently no influence on the P.D. and even particles of ice moving in water had the same P.D. From this he concludes that these cataphoretic P.D. are determined exclusively by the water. When the bubble moves, one surface of the double layer is fixed to the gas bubble and "preserves its identity more or less as it moves through the liquid." This layer must have an excess of OH ions when the bubble assumes its usual negative charge. He also points out that "the fact that so many substances in contact with water are negatively charged indicates that water by itself produces an elec-trification upon which is superposed an electrification due to the substance in contact with it."

On the basis of experiments on waterfall electricity Lenard[2] also arrived at the conclusion that the cause for the formation of an

[1] McTaggart, H. A., *Phil. Mag.*, 1914, xxvii, 297; xxviii, 367.

[2] Lenard, P., *Ann. Physik*, 1915, xlvii, 463.

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electrical double layer at water surfaces must be in the water itself, and that both strata of the double layer between a colloidal particle and water must lie entirely in the water.   Waterfall electricity is due to the mechanical tearing off of very minute particles of water from the surface.   Lenard observed that when the particles torn off were very minute they were negatively charged, while when they were larger they were electrically neutral.   According to McTaggart it is, however, not entirely certain that the double layer which surrounds a bubble of air in water and is active in a cataphoresis experiment is the same as that which is responsible for waterfall electricity.

The question arises: What causes this ionic stratification near the surface of the liquid?   Since salts raise the surface tension of water, they must be contained in the surface in lower concentration than in the body of liquid.   This was already emphasized by McTaggart. Should it be possible that the OH and H ions have a different effect on the surface tension, the H ions causing a greater rise of the surface tension of water than the OH ions?   In that case the concentration of the OH ions should be higher in the outermost, *i.e.*, most superficial, stratum of the surface of the water than the concentration of the H ions, while the concentration of H ions should be greater in the layer of water underneath.   This would explain why water generally assumes a positive charge in contact with colloidal particles, provided that the most superficial layer of water adheres to the particle moving in the electric field.   It is, however, not necessary to make any definite assumption in regard to the nature of the forces responsible for the ionic stratification beyond stating that they must be "molecular forces" *inherent in the water itself*.

There are, however, cases where the cataphoretic p.d. seems to have a different origin from that of air bubbles moving in an electric field. This is apparently true for protein particles where the charge is obviously connected with the ionization of the particles.   Thus it is well known through the experiments of Hardy, Michaelis,[3] and others that such particles do not migrate in an electric field at the hydrogen ion concentration of their isoelectric point, while they migrate towards the cathode when the hydrogen ion concentration is higher and

[3] Michaelis, L., Die Wasserstoffionenkonzentration, 2nd edition, Berlin, 1922.

towards the anode when the hydrogen ion concentration is lower than that of the isoelectric point of the protein. It is obvious that the ionization of these particles controls their cataphoretic P.D.

It seemed of interest to compare the influence of neutral salts on these two types of cataphoretic potentials. A convenient material was obtained in the form of fine collodion particles which were found to behave cataphoretically very much like air bubbles. When such collodion particles were coated with a protein, *e.g.*, gelatin, they could be used for the study of the cataphoretic potentials of the protein with which the particles were coated. In this paper we shall report only on the experiments with pure collodion particles *free from contamination with protein*.

The method of the evaluation of the cataphoretic P.D. between small particles and aqueous solutions was based on mobility measurements of individual particles by cataphoresis under the microscope, in which the apparatus with non-polarizable electrodes decribed by Northrop[4] was used. The apparent depth of the cell for the mobility measurements was 0.6 mm. and the time required for a particle to travel a distance of 45μ or when necessary 90μ was measured for four depths; namely, 0, 0.1, 0.2, and 0.3 mm., to eliminate the influence of the cataphoresis of the water itself. These measurements were averaged and the mobility in centimeters per second per volt per centimeter $\times$ 10^{-4} was calculated. By multiplying this mobility by the factor 14, the P.D. between the particles and the medium was obtained in millivolts (for a temperature of 24°C.). The details for this calculation may be gathered from Burton[5] and Ellis.[6] The strength of the electric field in our experiments was 4.5 volts per centimeter.

II.

Experiments on the Cataphoretic P.D. of Collodion Particles.

The collodion particles were prepared in the following way. Merck's solution of non-flexible collodion in alcohol and ether was

[4] Northrop, J. H., *J. Gen. Physiol.*, 1921–22, iv, 629.

[5] Burton, E. F., The physical properties of colloidal solutions, 2nd edition, London, New York, Bombay, Calcutta, and Madras, 1921.

[6] Ellis, R., *Z. physik. Chem.*, 1911–12, lxxviii, 321; 1912, lxxx, 597.

poured into H_2O and stirred with a glass rod. A spongy mass of solid collodion accumulated around the rod. The solid collodion was washed a few times with H_2O and dried with filter paper. A strong solution of this collodion was then made up in chemically pure acetone (about 10 gm. in 100 cc.) and enough H_2O was added until a light cloudiness was formed. The acetone was then removed from the solution by distillation under reduced pressure, and the remaining milky fluid was centrifuged. The sediment, when stirred up with H_2O, gives a concentrated suspension of collodion particles. The suspension was centrifuged and the larger particles in the sediment were used. These particles were very convenient for the investigation of the migration as well as of the stability of the suspension.

In the following experiments 2 drops of the concentrated suspension of collodion particles were added to 50 cc. of the various solutions used, and this dilute suspension served as material for the mobility measurements. The collodion particles moved towards the anode, thus indicating that they were negatively charged. Only in the presence of salts with trivalent cations, like $LaCl_3$, was the sign of charge reversed.

In these experiments it was found that the P.D. between the collodion particles and water was a minimum when the water contained no salts and was as near as possible the point of neutrality. When acid, alkali, or a salt was added the P.D. rose rapidly with increasing concentration until a maximum was reached. This maximum depended on the nature of the electrolyte added. It was high when the anion was plurivalent and the cation univalent, and low when the cation was plurivalent and the anion monovalent. The influence of acid, alkali, and salts with monovalent ions; e.g., HCl, NaOH, and NaCl, was not very different. Upon the addition of increasing concentrations of electrolytes the P.D. rose, reaching a maximum, and then dropped again upon a further rise of concentration. We will illustrate this in more detail.

The distilled water used in these experiments had a pH of about 5.8. At this pH the cataphoretic P.D. between collodion particles and water was about 22 to 30 millivolts. It was difficult to obtain more definite figures probably on account of the CO_2 error. When the distilled water was replaced by acid or alkali of different concen-

trations, the P.D. rose at first with increasing concentrations of the acid or alkali until a maximum was reached at a concentration between M/1,000 and M/500. This is shown in Fig. 1, where the ordinates
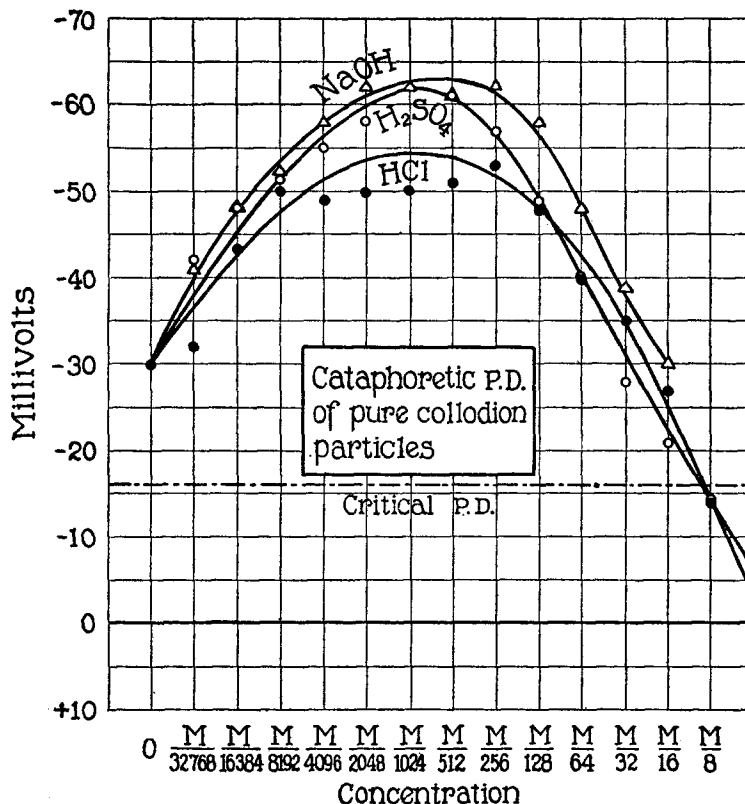

FIG. 1. Influence of acid and alkali on the cataphoretic P.D. between collodion particles and water. The original pH of water was about 5.0. The abscissæ are the concentrations of acids or alkali, the ordinates are the P.D. in millivolts. The collodion particles were negatively charged. The line marked "Critical P.D." (at 16 millivolts) is in this and the following figures the P.D. below which the collodion suspension is no longer stable.

are the P.D. and where the abscissæ are the molar concentrations of the electrolytes. The P.D. was at the maximum about 55 to 65 millivolts. With a further rise in concentrations of acid or alkali the P.D. dropped rapidly and the drop was about the same for the

acid and alkali (Fig. 1). The rise in P.D. must be due to the fact that in the case of low concentrations of NaOH an excess of OH ions and in the case of low concentrations of HCl and H_2SO_4 an excess of Cl and SO_4 ions respectively is forced into the outermost layer of water at the surface collodion-water, and that this layer moves with the collodion particles in an electric field.

It seems worthy of notice that the maximal P.D. was about the same in the case of H_2SO_4 and of NaOH, namely about 63 millivolts at a molecular concentration of electrolyte of about 1/1,024, while it was a little lower in the case of HCl; namely, about 55 millivolts. It may be worth while to point out that the P.D. between air bubbles and water in McTaggart's experiments was about 55 millivolts; though he does not state at which hydrogen ion concentration this P.D. was observed. The order of magnitude of the cataphoretic P.D. of air bubbles and of collodion particles in water is, therefore, not materially different so that we may say that the cataphoretic P.D. between collodion particles and water has in all probability the same origin as in McTaggart's experiments; namely, in molecular forces inherent in the water itself which push the cations of an electrolyte deeper down into the surface layer, than the anions. The collodion particles increase this effect only slightly, since the maximal P.D. between collodion particles and water is only about 70 millivolts. Such a P.D. was observed in the experiments recorded in Fig. 2.

Fig. 2 gives the results of measurements of the P.D. between the collodion particles and solutions of five different salts, $Na_4Fe(CN)_6$, Na_2SO_4, NaCl, $CaCl_2$, and $LaCl_3$, all solutions having a pH of 5.8. This experiment was intended to illustrate the relative influence of the valency of the anions and cations on the cataphoretic P.D. The P.D. rose upon the addition of salts with univalent cation (Na) to a maximal value of about 70 millivolts, but the concentration required to reach this maximum was least for $Na_4Fe(CN)_6$, a little higher for Na_2SO_4, and still a little higher for NaCl. A further increase of the concentration of the salts depressed the P.D., the curves dropping rapidly (Fig. 2). The maximum was but slightly higher in the case of $Na_4Fe(CN)_6$ than in the case of Na_2SO_4, and but slightly higher in the case of Na_2SO_4 than in the case of NaCl.

Fig. 2 shows also that the initial rise in the P.D. did not occur at all or occurred at a very low concentration when the salt added was $LaCl_3$, and that the rise was small when the salt added was $CaCl_2$;

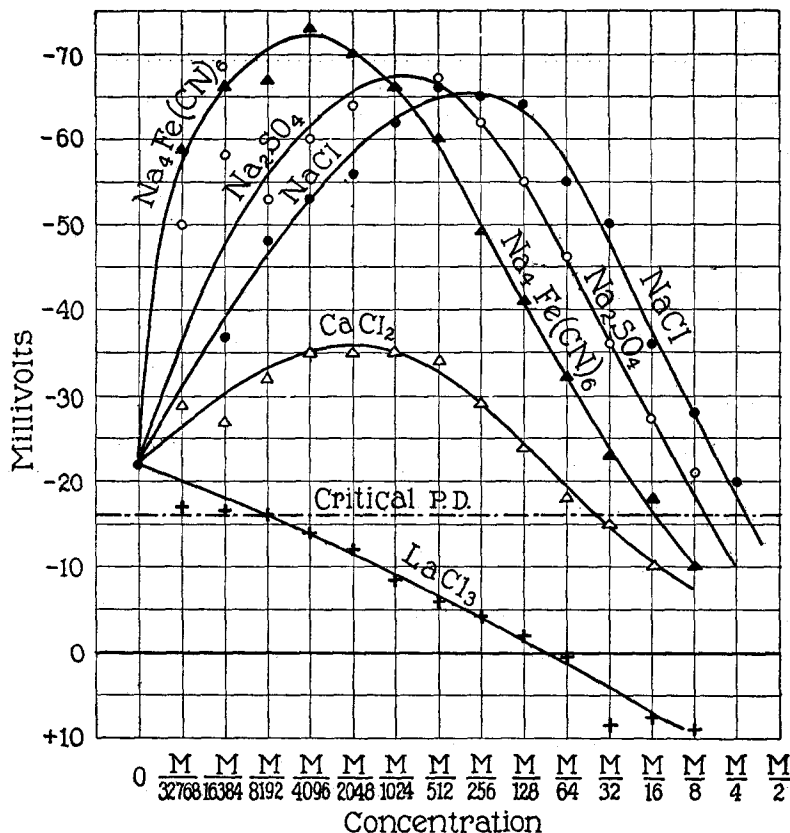FIG. 2. Influence of $Na_4Fe(CN)_6$, Na_2SO_4, NaCl, $CaCl_2$, and $LaCl_3$ on the P.D. at pH 5.8. Addition of little salt with monovalent cation raises the P.D. to about 70 millivolts and the more rapidly the higher the valency of the anion. With $CaCl_2$ only a slight rise and with $LaCl_3$ no rise occurs in the concentrations used. In concentrations above M/64 $LaCl_3$ causes a reversal of the sign of charge of the particles.

the maximal P.D. in the latter case was 36 millivolts at a concentration of M/2,048 of the salt. After the maximum was reached the curves dropped rapidly and this drop was apparently due to the cation only. A comparison of the descending branches of the curves shows that

to bring the P.D. down from the maximum (about 70 millivolts) to *e.g.* 27.5 millivolts, the following molecular concentrations of the salts were required.

NaCl.. $M/8$

Na$_2$SO$_4$.. $M/16$

Na$_4$Fe(CN)$_6$...slightly less than $M/32$

CaCl$_2$...between $M/128$ and $M/256$

This means that the depressing action of the three Na salts is almost the same for the same concentration of cations, regardless of the anion; while the depressing effect of CaCl$_2$ is between 16 and 32 times as great as that of NaCl. This leaves no doubt that the depressing effect is due to that ion which has the opposite sign of charge to that of the collodion particle (or rather to that of the film of water moving with the particle), since the particle is negatively charged. This corresponds to the Hardy rule.

LaCl$_3$ depresses the P.D. at pH 5.8, even at low concentrations, so that at a molecular concentration of $M/64$ the P.D. is already zero (Fig. 2). With a further rise of the concentration of LaCl$_3$ the P.D. reverses its sign; the collodion particles assuming a positive and the water a negative charge. McTaggart observed the same reversal of the sign of charge of gas bubbles by trivalent cations. The cause of this reversal lies therefore primarily, if not exclusively, in forces inherent in the water itself. According to the curves in Fig. 2, neither CaCl$_2$ nor the Na salts are able to cause a reversal of the sign of charge of the collodion particle at pH 5.8 since the curves seem to become asymptotic to the axis of abscissæ for concentrations varying from $M/16$ to $M/2$ or above. The curves in Fig. 1 show that acids do not bring about a reversal in the concentrations used in the experiment.

The question arose whether other properties of the ion except its valency contribute to the depressing effect. The writer expected a difference in the depressing effects of LiCl, NaCl, and KCl. As a matter of fact, no difference in the influence of the three salts on the cataphoretic P.D. was noticed, as Fig. 3 shows. If differences existed they were within the limit of error in these experiments. These experiments were made at a pH of 4.7. Fig. 4 shows that the influence

of salts on the cataphoretic P.D. of collodion particles is about the same at a pH of 4.7 (Fig. 4) as at a pH of 5.8 (Fig. 2).

When the experiments were made at a higher alkalinity, namely, in a N/1,000 KOH solution (Fig. 5), the P.D. was already about 60 milli-volts when no salts were added and the addition of salt could only
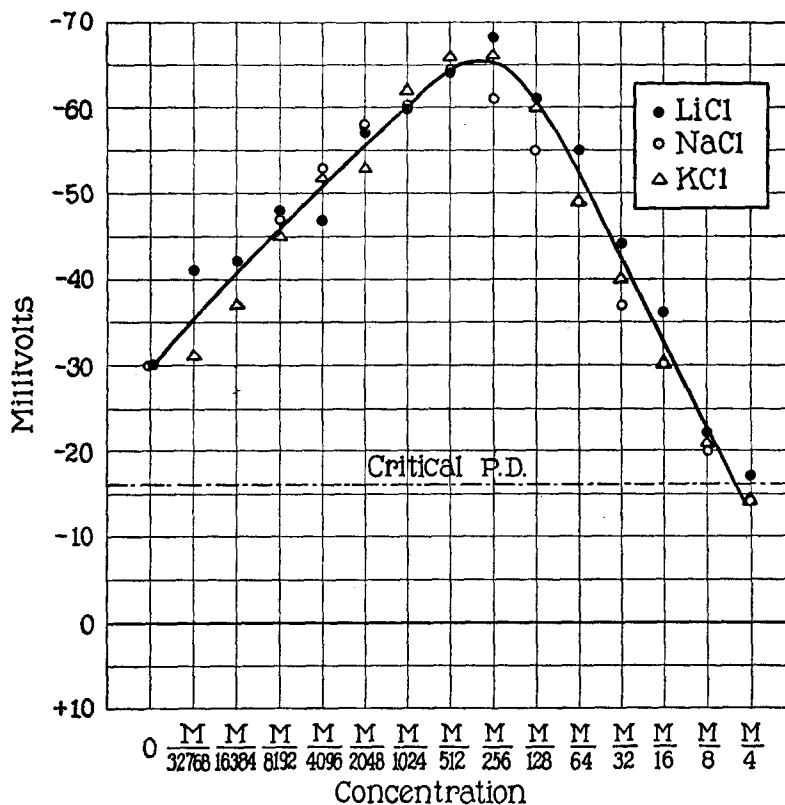

FIG. 3. Influence of LiCl, NaCl, and KCl on the P.D. at pH 4.7.

raise the P.D. to its usual maximum of about 70 millivolts. This slight rise occurred in Na_2SO_4 and $Na_4Fe(CN)_6$, but to a less amount in NaCl. In concentrations of M/256 and less, all the salts had only a depressing effect.

To bring the P.D. down to 35 millivolts in N/1,000 KOH, an approx-imate concentration of M/16 NaCl, of M/32 Na_2SO_4, of a little less

than M/64 $Na_4Fe(CN)_6$, and of approximately M/1,500 $CaCl_2$ was required. The depressing ion is therefore again the cation as was to be expected, since the collodion particle or rather the water film moving with it is negatively charged.
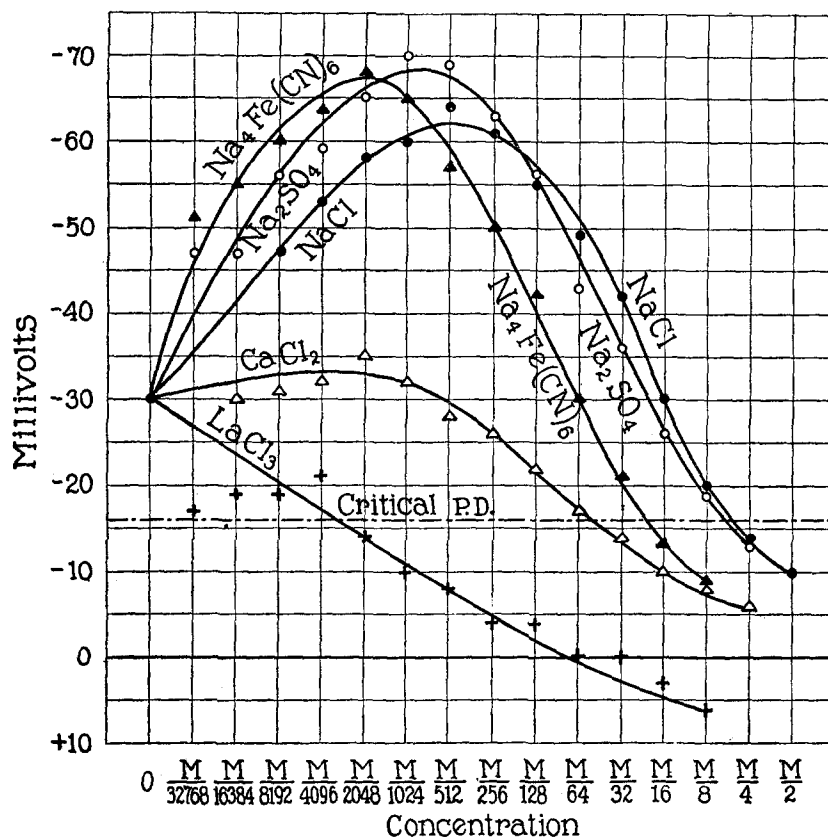

FIG. 4. Similar to Fig. 2 except that the pH was 4.7.

When the experiments were made at higher hydrogen ion concentrations, e.g. in N/1,000 HCl (Fig. 6), the particles had nearly their maximal charge without the addition of salt, since the P.D. was about 64 millivolts. Hence the addition of NaCl has no augmenting effect while Na_2SO_4 has a slight augmenting effect to 72 millivolts. At concentrations below M/256 the salts depress the charge of the par-

ticles.   Since the particles are always negatively charged the depressing effect increases markedly with the increasing valency of the cation, as was to be expected.   To depress the charge to 27.5 millivolts, a
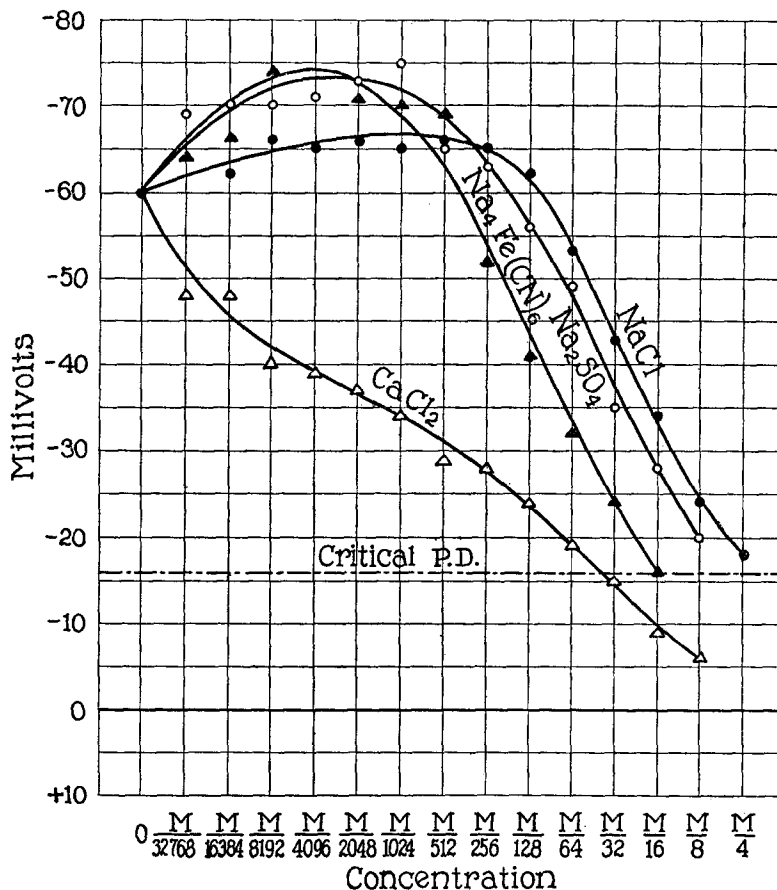
FIG. 5. Influence of salts on the cataphoretic P.D. at pH 11.0.   Without salt the P.D. was already near the maximum and hence the addition of salt had only a slight augmenting effect on the P.D.

concentration of M/16 NaCl, M/256 CaCl$_2$, and M/16,384 LaCl$_3$ is required.   In this acid solution LaCl$_3$ diminished the P.D. but did not bring about a reversal of the charge; perhaps for the reason that the original P.D. due to the acid was too high at the beginning.

It is often stated that H and OH ions have a greater effect on the
P.D. than other ions. This was not the case in our experiments. A
comparison of Fig. 1 and Fig. 2 shows that HCl, H₂SO₄, and NaOH
act very much like NaCl or Na₂SO₄ on the P.D. The reason that in
N/1,000 HCl or NaOH the addition of a salt no longer raises the P.D.
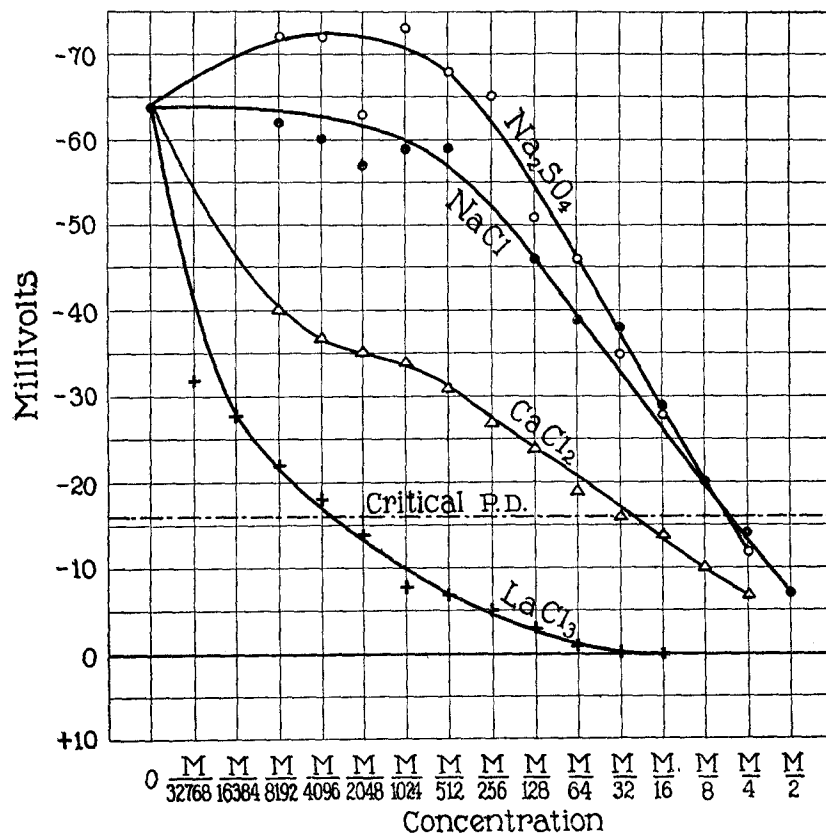
FIG. 6. Influence of salts on the P.D. at pH 3.0. (See legend of Fig. 5.)

is because the P.D. is already near the maximum before the salt is
added, so that only the depressing effect of the salt becomes noticeable.

The idea that H and OH ions act more strongly than other mono-
valent ions is probably based on experiments with amphoteric elec-
trolytes (where acids and alkalies bring about differences in ioniza-
tion), but is apparently not true in the case of chemically inert sub-

stances like collodion.   The statement that H ions act like Na ions
on the cataphoretic P.D. of collodion particles is also borne out by the
fact that acids do not depress the P.D. more than do Na ions, as a
comparison of Figs. 1 and 2 shows.   A reversal of the P.D. was ob-
served when LaCl₃ was added but not when HCl or NaCl were added
to the solution.

All these experiments prove, however, that it is necessary to measure
the hydrogen ion concentration of the solution since otherwise the
results are not strictly reproducible and comparable.

<div align="center">III.</div>

The Critical P.D. for the Precipitation of Collodion Particles from Aqueous Solutions.

The question arose whether this cataphoretic P.D. or some other
P.D. was responsible for the stability of suspensions of collodion
particles in water.   It can be shown that the stability of a suspension
of collodion particles free from protein depends on the cataphoretic
P.D., since precipitation always occurs below the same critical cata-
phoretic P.D. of about 16 millivolts.

When the stock suspension of collodion particles was shaken up to
produce an equal distribution of particles and 1 drop of this suspen-
sion was added to 10 cc. of distilled water (of pH 5.8), the new sus-
pension was milky when shaken up and remained so for several days.
During this time the larger particles all settled and only a cloudy gray
suspension was left, which gradually, after the still further settling
of larger particles, gave way to a bluish opalescent suspension which
lasted for many weeks ("permanently").   In this case the settling was
a slow process.   When 1 drop of the stock suspension was put into
10 cc. of an aqueous salt solution (also of pH 5.8) it was noticed that
there existed a critical concentration of the salt, varying according
to the nature of the salt, below which the suspension behaved as it did
in distilled water, while in the next higher concentration a rapid,
complete settling of the whole mass of collodion occurred in 12 hours
or less, leaving not an opalescent but an entirely clear aqueous solution.

It was therefore comparatively easy to determine at which concen-
tration the slow settling was replaced by a rapid settling caused by

coalescence of the small particles into larger ones. It was found that at the concentrations of salts where the rapid settling occurred, the cataphoretic P.D. between particles and aqueous solution fell below the value of about 16 millivolts; regardless of the nature of the electrolyte used for precipitation. When the P.D. was above this value, the suspension was as stable as if no electrolyte had been added; and the stability was no greater at a P.D. of 60, or 70 millivolts, than at a P.D. of 50, or 25 millivolts.

The existence of such a critical P.D. for the precipitation of suspensions agrees with the observations of Powis[7] as well as of Northrop and De Kruif.[8] Powis has made it probable that the stability of oil emulsions in aqueous solutions is destroyed when the cataphoretic P.D. between oil droplets and water is depressed below the critical value of about 30 millivolts. Northrop and De Kruif have shown that certain bacteria agglutinate when their cataphoretic P.D. is depressed by electrolytes below a critical value of 15 millivolts.

Table I gives the results of experiments on the precipitation of suspended particles of collodion by electrolytes. In one series of experiments the pH was 5.8, in a second 11.0, and in a third 3.0. In the second column of Table I are given the minimal concentrations at which precipitation was observed, i.e., in which the solution became completely clear in less than 18 hours, at about 20°C., while in the fourth column are found the maximal concentrations at which the suspensions remained "permanently" stable, i.e. opaque for days and opalescent for weeks; in other words, where the salt caused no coalescence of particles. No attempt was made to locate the critical concentration more accurately than within the limits of concentrations given in the table, since it would probably not have been of any use in an attempt to define more sharply the real quantity of importance; namely, the critical P.D. between particles and solution. In Column 3 are found the P.D. between particles and solution at the minimal concentrations where precipitation occurred, and in the fifth column are found the P.D. of the maximal concentrations where the suspension remained stable.

[7] Powis, F., Z. physik. Chem., 1914-15, lxxxix, 186.

[8] Northrop, J. H., and De Kruif, P. H., J. Gen. Physiol., 1921-22, iv, 639.

It may be pointed out that the precipitating action of acids like HCl or H_2SO_4 is of the same order of magnitude as that of Na salts but not of the order of magnitude of La salts. This agrees with the

TABLE I.

Cataphoretic Charge and Stability of Suspensions of Particles of Collodion.

1.	2. Minimum concentration required for precipitation.	3. P.D. in millivolts.	4. Maximal concentration at which suspension remains stable.	5. P.D. in millivolts.
pH 5.8				
LiCl..........................	M/2	(10)	M/4	17
NaCl..........................	M/2	10	M/4	14
KCl..........................	M/4	14	M/8	21
Na$_2$SO$_4$..........................	M/4	13	M/8	19
Na$_4$Fe(CN)$_6$..................	M/16	13	M/32	21
MgCl$_2$..........................	M/16	11	M/32	15
MgSO$_4$..........................	M/16	15	M/32	19
CaCl$_2$..........................	M/32	14	M/64	17
LaCl$_3$..........................	M/2,048	14	M/4,096	21
pH 11.0				
NaCl..........................	M/2		M/4	18
Na$_2$SO$_4$..........................	M/4		M/8	20
Na$_4$Fe(CN)$_6$..................	M/16	16	M/32	24
CaCl$_2$..........................	M/32	15	M/64	19
pH 3.0				
NaCl..........................	M/2	7	M/4	14
Na$_2$SO$_4$..........................	M/4	12	M/8	(Lost.)
CaCl$_2$..........................	M/32	16	M/64	19
LaCl$_3$..........................	M/2,048	14	M/4,096	18
H$_2$SO$_4$..........................	M/4		M/8	14

statement made in an earlier part of the paper that the acids act like salts with monovalent cation (*e.g.*, NaCl) on the P.D.

The average of all the P.D. values for the minimal concentrations at which precipitation occurred was 13 millivolts, while the average of all the P.D. at the concentrations at which the suspensions remained stable was 18.5 regardless of the pH. This suggests as the probable

critical value for the P.D. where precipitation commences about 16 millivolts. The actual P.D. evaluated from the mobility by cataphoresis are probably accurate only within ± 2 millivolts of this value, which explains some of the slight deviations from this value in Table I.

These measurements confirm the conclusion reached by Powis as well as by Northrop and De Kruif that there exists a critical P.D. for the stability of suspensions, this critical P.D. being about 16 millivolts for collodion particles in aqueous solutions. When the P.D. falls below this value, the particles upon colliding are no longer repelled electrostatically but may adhere to each other and coalesce (i.e. agglutinate or coagulate) into larger particles which rapidly sink to the bottom of the test-tube. This coalescence of the colliding particles is due to forces of attraction between certain chemical groups of their molecules. If the P.D. is larger than 16 millivolts the particles will repel each other upon colliding with sufficient force to prevent coalescence. If this critical value is once exceeded the stability of the suspension is not increased when the charge is increased. I have noticed that there is no difference in the rate of settling of a suspension of the collodion particles when the charge varies between 20 and 70 millivolts.

Since the collodion particles are generally negatively charged, it was to be expected that only the cation of the salt should be responsible for the precipitation. This is corroborated by the fact that the precipitating efficiency of salts increases rapidly with the valency of the cation. Thus for NaCl, CaCl₂, and LaCl₃ the precipitating efficiency measured by the reciprocal value of the minimal concentration required for precipitation (Column 2, Table I) is as 1:16:1,024. This valency effect is considerably greater than it would be if the P.D. responsible for the stability were due to the Donnan effect.

The question has often been raised whether that ion of a salt which has the same sign of charge as the colloidal particle will not counteract the precipitating action of the other ion. The molecular precipitating concentrations for NaCl, Na₂SO₄, and Na₄Fe(CN)₆ are M/2, M/4, and about M/16 respectively. In M/2 NaCl and M/4 Na₂SO₄ the concentration of cations is practically identical. If the anion had an inhibiting effect on precipitation, the concentration of Na₂SO₄

required for precipitation should be higher than $M/4$ which is not the case. The precipitating concentration of $Na_4Fe(CN)_6$ is even lower than that to be expected if only the Na ion acted.

It follows from this that the force preventing coalescence of the colloidal particles into larger aggregates which settle rapidly is the *cataphoretic* and no other potential difference between the particles and the aqueous solution, and that there is a critical value for this P.D. which in the case of collodion particles is about 16 millivolts. As soon as the cataphoretic P.D. falls below this value the collodion particles will coalesce. The depressing and precipitating action of a salt on the negatively charged collodion particles depends practically exclusively on the cation of the salt and increases rapidly with the increase in the valency of the cation. There exists no peptization effect of plurivalent anions.

SUMMARY AND CONCLUSIONS.

1. When collodion particles suspended in water move in an electric field they are, as a rule, negatively charged. The maximal cataphoretic P.D. between collodion particles and water is about 70 millivolts. This is only slightly more than the cataphoretic P.D. found by Mc-Taggart to exist between gas bubbles and water (55 millivolts). Since in the latter case the P.D. is entirely due to forces inherent in the water itself, resulting possibly in an excess of OH ions in the layer of water in contact and moving with the gas bubble, it is assumed that the negative charge of the collodion particles is also chiefly due to the same cause; the collodion particles being apparently only responsible for the slight difference in maximal P.D. of water-gas and water-collodion surfaces.

2. The cataphoretic charge of collodion particles seems to be a minimum in pure water, increasing as a rule with the addition of electrolytes, especially if the cation of the electrolyte is monovalent, until a maximal P.D. is reached. A further increase in the concentration of the electrolyte depresses the P.D. again. There is little difference in the action of HCl, NaOH, and NaCl or LiCl or KCl.

3. The increase in P.D. between collodion particles and water upon the addition of electrolyte is the more rapid the higher the valency

of the anion. This suggests that this increase of negative charge of the collodion particle is due to the anions of the electrolyte gathering in excess in the layer of water nearest to the collodion particles, while the adjoining aqueous layer has an excess of cations.

4. In the case of chlorides and at a pH of about 5.0 the maximal P.D. between collodion particles and water is about 70 millivolts, when the cation of the electrolyte present is monovalent (H, Li, Na, K); when the cation of the electrolyte is bivalent (Mg, Ca), the maximal P.D. is about 35 to 40 millivolts; and when the cation is trivalent (La) the maximal P.D. is lower, probably little more than 20 millivolts.

5. A reversal in the sign of charge of the collodion particles could be brought about by LaCl₃ but not by acid.

6. These results on the influence of electrolytes on the cataphoretic P.D. between collodion particles and water are also of significance for the theory of electrical endosmose and anomalous osmosis through collodion membranes; since the cataphoretic P.D. is probably identical with the P.D. between water and collodion inside the pores of a collodion membrane through which the water diffuses.

7. The cataphoretic P.D. between collodion particles and water determines the stability of suspensions of collodion particles in water, since rapid precipitation occurs when this P.D. falls below a critical value of about 16 millivolts, regardless of the nature of the electrolyte by which the P.D. is depressed. No peptization effect of plurivalent anions was noticed.

The mobility measurements required for the determination of the P.D. were made by Mr. M. Kunitz.