CLXXXVI.—*Colloidal Platinum. Part VII. The Effect of Electrolytes upon the Cataphoretic Velocity of Platinum Particles, and its Bearing on Stability.*

By Stuart W. Pennycuick.

The electric charge is being increasingly recognised as the controlling factor in the stability of hydrophobic sols. In this paper a comparative study is made of the effect of various electrolytes upon the cataphoretic velocity of platinum particles, and upon the corresponding changes in stability. Owing to the remarkable influence of traces of certain electrolytes, it is necessary to have trustworthy details regarding, first, the purity of the preparation, and secondly, the constitution of the surface ionogen whose ionisation confers the stabilising charge. From this point of view colloidal platinum is seen, from the author's previous work, to be particularly suitable. As will be shown, the velocity measurements confirm the conclusions already drawn regarding the action of acids (J., 1929, 618) and of bases (*ibid.*, p. 623) on this colloid.

The methods of obtaining the colloid charge and the electrokinetic potential are limited to observations of the electrokinetic phenomena. Of these, cataphoresis is outstanding, and accordingly considerable attention has been paid in recent years to the accurate measurement of cataphoretic velocities (see reviews by Tuorila, *Kolloid-Z.*, 1928, **44**, 11, and by Pauli and Valkó, " Elektrochemie der Kolloide," Wien, 1929, pp. 149 and 202).

In this work, the author has utilised the macroscopic moving-boundary method, as developed by Burton (*Phil. Mag.*, 1906, **11**, 436) and improved by Landsteiner and Pauli (*Verh. d. Kongr. f. innere Medizin*, XXV Kongress, Wien, 1908) and by Mukherjee (*Proc. Roy. Soc.*, 1923, *A*, **103**, 102). The technical errors arising from this method have been discussed by Mukherjee and by Kruyt and van der Willigen (*Kolloid-Z.*, 1928, **44**, 22), who have shown that extreme precautions are necessary if trustworthy results are to be obtained, and that the common practice of using, as the overlying liquid, any electrolyte having the same conductivity as the sol, is by no means satisfactory. During migration, if the colloid particles move into a slightly different environment, important changes occur which result in velocity fluctuations. It is obvious that the ideal overlying liquid would be the intermicellar fluid; Kruyt and van der Willigen (*loc. cit.*) have attempted to isolate such a liquid by subjecting portions of the sol to centrifuging and ultra-filtration, whereas Powis (J., 1916, **109**, 734) used the clear solution obtained by filtering a coagulated sol. The majority of workers, however, have been satisfied to use comparable solutions of potassium chloride or of hydrochloric acid. The author has shown (J., 1928, 2108) that, in the case of colloidal platinum, the intermicellar liquid can be isolated by freezing out the colloid particles. If this liquid is used as the overlying fluid, therefore, these particles suffer no material change in environment during the whole of their movement, and it is believed that by this device and by the exercise of the precautions now outlined, the nearest approach yet recorded to the ideal conditions has been made.

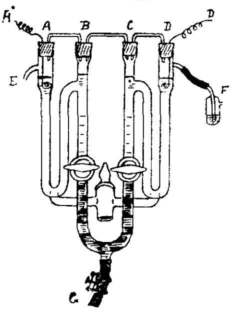
The moving boundary between the dark brown platinum sol and the clear overlying liquid is well defined, and can be followed with accuracy.

EXPERIMENTAL.

The mode of preparation of a sol has a direct influence on its charge and on its cataphoretic velocity. Accordingly, the various samples of colloidal platinum were prepared in exactly the same way (*Australian J. Exp. Biol. Med. Sci.*, 1927, **4**, 99), the following being the details: voltage 200, current 3·5 amps., sparking time (continuous) 18 minutes per 500 c.c. of water. After preparation, the sol was boiled for 25 minutes and stored for two days. The samples used had specific conductivities (κ) ranging from 10 to 15 gemmhos (see Table I).

For the measurement of cataphoretic velocities, a modified Landsteiner–Pauli apparatus was used throughout. It was thoroughly cleaned before each determination. As the results with sodium hydroxide are of great importance, and as measurements with bases are often avoided, the method of making cataphoretic measurements in the absence of carbon dioxide is described. Samples of the platinum sol and of the intermicellar fluid (frozen sol) are brought into two conductivity cells of low cell constant. The intermicellar fluid, which has the higher conductivity (owing to previous boiling and evaporation), is diluted with conductivity water until it shows the same specific conductivity as the platinum sol. The required amount of sodium or barium hydroxide is introduced into each cell in the absence of carbon dioxide (J., 1927, 2600), and the conductivities are brought to exactly the same values: as the platinum particles remove some of the base, the colloid solution requires more alkali than the sample of intermicellar fluid, and hence it is not sufficiently accurate simply to add equal quantities of base to the two solutions. The solutions are then introduced into the cataphoresis tube shown in Fig. 1. To keep the solutions carbon-dioxide free, the air-tight connexions *A*, *B*, *C*, and *D* are fitted. The apparatus, previously washed with conductivity water, is dried by passing a warm carbon dioxide-free air stream in at *E* and out through bubblers at *F* and *G*. The conductivity cells are fitted with tubes so that the solutions can be blown into the cataphoresis apparatus under a small head of carbon dioxide-free air. The platinum sol is introduced at *G*, until it rises 1 mm. or so above the taps, whilst the overlying solution is introduced at *E*. By careful manipulation the transference may be accomplished without any contamination whatsoever with carbon dioxide.

FIG. 1.



When acids and salts are to be used, simplifying modifications at once suggest themselves. In preparing comparable solutions in the presence of salts, the knowledge of the surface actions as previously developed (J., 1929, 618) was always utilised with the object of providing a perfectly uniform environment for the

TABLE I.

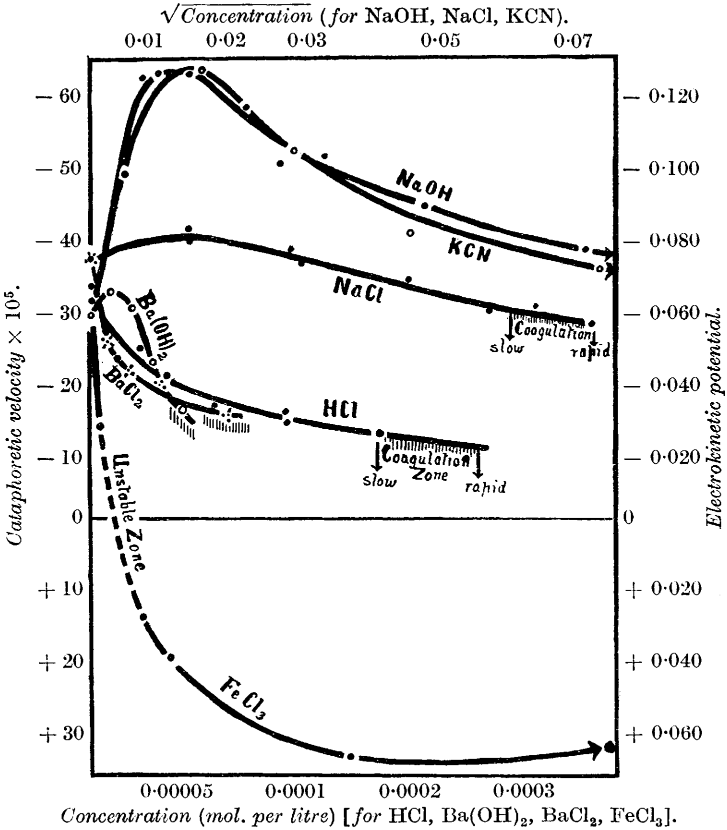
Pure platinum sols at 25°.

Sol.	κ.	$[H_2Pt(OH)_6]$.	$u \times 10^5$.	ζ.
D (unboiled)	5·7	16×10^{-6}	33·3	0·062
D (boiled 25 mins.)	14·2	41 ,,	32·0	0·060
D ,, ,, ...	15·0	43 ,,	30·8	0·058
E (unboiled)	3·7	11 ,,	38·6	0·072
E (boiled 25 mins.)	11·2	32 ,,	37·0	0·069
F ,, ,, ...	9·7	28 ,,	30·7	0·057
F ,, ,, (old)	11·4	33 ,,	27·8	0·052
G (boiled 25 mins.)	12·0	34 ,,	36·4	0·068

moving particles. In all cases the solutions were prepared in the conductivity cells, and then transferred to the apparatus.

Results.—The distance between the electrodes was 74 cm., and the voltage 135 (less in a few cases). Each result is the average of several determinations. The error is of the order 6—7%, which is considered satisfactory for this type of measurement. Unless otherwise stated, all velocity values recorded are negative, this sign being omitted for the sake of convenience.

FIG. 2.



The results for the pure platinum sols are set out in Table I, and curves for sols containing this and other electrolytes appear in Fig. 2.

Interpretation of Results.—The criticisms of McBain (*J. Physical Chem.*, 1924, **28**, 706), Burton (*Colloid Symposium Monographs*, 1926, **4**, 132), and Kruyt and van der Willigen (*Z. physikal. Chem.*, 1927, **130**, 170) undoubtedly show that the theoretical relation between cataphoretic velocity and electrokinetic potential, which was developed some 30 years ago, rests upon very insecure grounds. Nevertheless, because of convenience and long usage, practically every investigator in this field prefers to interpret cataphoretic results in terms of electrokinetic potential ζ.

In this paper the cataphoretic velocities (u) themselves are recorded, and it is these which are stressed, but for the sake of comparison the ζ values also are recorded. As colloidal platinum particles are spherical (Diesselhorst and Freundlich, *Physikal. Z.*, 1916, **17**, 117), the usual Helmholtz–Smoluchowski equation, $\zeta = 4\pi\eta u/DH$, must be replaced by the corrected equation $\zeta = 6\pi\eta u/DH$ (Debye and Hückel, *ibid.*, 1924, **25**, 49). For the dilute solutions of electrolytes used, η may be taken as the viscosity of water (0·00893 at 25°), and D as 81, the dielectric constant of water; ζ and u/H then become proportional and the equation may be written $\zeta = (6\pi\eta/D)\ (u/H) = ku/H$. In this paper u is always given as the velocity (cm. per sec.) for a potential gradient of 1 volt per cm., whence $H = 1$, and $\zeta = ku$. The value of the proportionality factor k is 187·1. The ζ values so calculated are shown in Fig. 2 and in the table.

Discussion of Results.

The Pure Sols.—The cataphoretic velocities of the pure sols, as shown in Table I, exhibit variations in spite of the similarity of the method of preparation. For the boiled sols, $u \times 10^5$ ranges from 27·8 to 37·0 cm./sec./volt/cm. The free acid content, as obtained from the specific conductivity [assumed all to be due to $H_2Pt(OH)_6$], ranges from 28×10^{-6} to 43×10^{-6} equiv. The source of charge is undoubtedly the platinic acid, but it is evident from the irregularity of the figures that no simple relationship holds between cataphoretic velocity and concentration of free acid. The unboiled sols have the smallest acid content but the greatest velocities; and as the acid content increases (by boiling or ageing), the charge as revealed by cataphoretic velocity decreases. The absence of the simple relation between velocity and acid concentration which will be shown to hold for the surface-inactive acids, such as hydrochloric and nitric, is evidently due to the surface activity of the $Pt(OH)_6$ anion. An increase in the $H_2Pt(OH)_6$ concentration then has a double effect: the hydrogen ion decreases the surface ionisation, whilst the $Pt(OH)_6$ ion increases the number of surface ionogens and hence the charge. The total action is complicated by the changes in surface area, state of aggregation, etc., which must occur when the sol is boiled or aged.

The results recorded for $u \times 10^5$ by other workers with pure platinum (Bredig) sols are 30 (Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, **26**, 1339), 21 (Burton, *Phil. Mag.*, 1906, **11**, 425), 24 (Svedberg, *Nova Acta Upsala*, 1907, [IV, 2] 190), and 20—40 (Cotton and Mouton, *Compt. rend.*, 1904, **138**, 1692). Although all the results are very roughly of the same order of magnitude, variations would be expected for the reasons outlined above. (For comparison with other sols, see Pauli and Valkó, *op. cit.*)

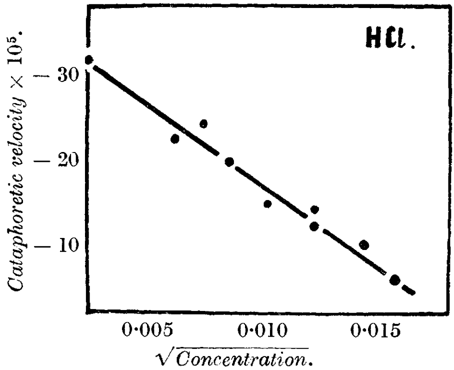
The Critical Potential.—The idea that all coagulations occur at a critical potential (critical velocity) was developed by Powis (*loc. cit.*; *Z. physikal. Chem.*, 1915, **89**, 186), using oil drops and arsenious sulphide sols. The negative results of Mukherjee (*Nature*, 1928, **122**, 960), the confirmatory results of Kruyt and Briggs (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 384) and of Ghosh (J., 1929, 2693), and the indefinite conclusions of Tuorila (*Koll.-Chem. Beih.*, 1928, **27**, 44) and of Kruyt and van der Willigen (*loc. cit.*) leave the question open as to whether the critical potential has any general significance.

From the results now recorded, it is evident (i) that coagulation always occurs before the cataphoretic velocity has been depressed to zero, and (ii) that with hydrochloric acid, barium hydroxide, barium chloride, ferric chloride, and calcium chloride (not shown), coagulation occurs at a velocity between 10×10^{-5} and 15×10^{-5}. Hence with these electrolytes we may speak of a critical velocity (or potential). On the other hand, sodium chloride and hydroxide and potassium chloride (not shown) show coagulation velocities of quite a different order. These conclusions are in general accord with those of Powis and of Ghosh (*loc. cit.*) on arsenious sulphide, and of Freundlich and Zeh (*Z. physikal. Chem.*, 1925, **114**, 65) on both arsenious sulphide and ferric hydroxide sols. There appears to be strong evidence for the view that, with electrolytes which coagulate at low concentrations, a critical potential exists below which the sols are unstable, but that where a large concentration of electrolyte is required, coagulation occurs at a much higher potential.

Hydrochloric Acid.—It has been established that colloidal platinum is an acidoid sol, and that the ionisation of the surface hexahydroxyplatinic acid is the source of charge and of stability. Coagulation by surface-inactive acids, such as the common inorganic acids, is then interpreted as due to the repression of the surface ionisation or of the ionic double layer. The slope of the hydrochloric acid curve (Fig. 2) is in keeping with this view. Further confirmation is at hand, for, by the application of the Debye–Hückel theory (*Physikal. Z.*, 1923, **24**, 185), it follows that if no abnormalities occur, the addition of an electrolyte should cause a decrease in the velocity which is directly proportional to the square root of the concentration, and actually when these two variables are plotted against one another, the curve (Fig. 3) shows that the linear relationship holds.

These conclusions are in agreement with the results obtained with the acidoid mastic sol, where it has been shown that coagulation by inorganic acids is a plain case of ionic repression (Michaelis, "The Effect of Ions in Colloidal Systems," 1925, 67).

FIG. 3.



Barium Chloride.—On the addition of this salt, the cataphoretic velocity decreases rapidly, and coagulation occurs at a relatively low concentration. Here the outstanding action, and the one which ultimately leads to coagulation, is the ionic exchange of hydrogen contra-ions for barium ions from solution. Because of this interfering action, the velocity–$\sqrt{\text{concentration}}$ curve does not yield a straight line.

The critical potential for this and comparable salts lies between —0·020 and —0·030 volt. The corresponding value of ζ recorded by Powis for oil drops and arsenious sulphide is —0·025 volt.

Sodium Hydroxide.—From a study of the reactions of colloidal platinum in basic solutions (J., 1929, 623), the author has concluded that univalent bases have the important property of reacting with surface non-ionogenic groups (probably oxides) to form further stabilising ionogens. It was, in fact, in order to test this conclusion that the present experiments were undertaken. The remarkable increase in the cataphoretic velocity on the addition of sodium hydroxide completely confirms the view that fresh surface ionogens are formed. From the curve in Fig. 2 (where, for convenience, the concentration is replaced by its square root), it is seen that when $5{\cdot}3 \times 10^{-6}$ equiv. of base has been added (free sodium hydroxide = 33×10^{-6} equiv.), the cataphoretic velocity is more than doubled; on further addition of base, the velocity remains practically constant over a considerable range; and at higher concentrations it begins to decrease. The important stabilising and peptising action of univalent bases is undoubtedly connected with this increase in charge. The flat maximum in the curve is probably related to the view (Hevesy, *Kolloid-Z.*, 1917, **21**, 129) that the electrokinetic potential of colloid particles cannot exceed a certain maximum, *viz.*, approx. 0·105 volt ($0{\cdot}070 \times 3/2$). At all events the very high value of ζ here obtained, 0·120 volt, is not exceeded by any other colloid system.

The important charging action of the hydroxyl ion was first emphasised by Perrin (*J. Chim. physique*, 1904, **2**, 601), and has since been demonstrated for various negative suspensions—for emulsions by Ellis (*Z. physikal. Chem.*, 1912, **78**, 321; **80**, 597), and for kaolin by von Buzágh (*Kolloid-Z.*, 1929, **48**, 33) and Dubrissay, Trillat, and Astier (*Compt. rend.*, 1929, **189**, 41). These workers all find an increase in ζ on the addition of univalent bases. The explanation in terms of an increase in surface ionogens can be extended to include all the known observations. The streaming potential against ordinary glass shows no such maximum (Ellis, *loc. cit.*; Powis, *Z. physikal. Chem.*, 1915, **89**, 91; Elissafoff, *Z. physikal. Chem.*, 1912, **79**, 385): the high initial ζ indicates that the sodium hydroxide from the hydrolysis of the sodium silicate has already given the glass its maximum charge.

The cataphoretic velocity of the platinum particles at the coagulation point (in the case of sodium hydroxide) is remarkably high, *viz.*, $36{\cdot}8 \times 10^{-5}$ ($\zeta = 0{\cdot}069$), *i.e.*, higher than the initial velocity of the particles. Sodium hydroxide coagulation figures for other acidoid sols have not yet been recorded.

Barium Hydroxide.—On the addition of barium hydroxide, the cataphoretic velocity shows an extremely small initial increase, in striking contrast to the results obtained with univalent bases. This small increase cannot be ascribed to the lack of formation of surface ionogens, for it has been shown that platinum sols take up 4 or 5 times as much barium hydroxide as sodium hydroxide. There is little doubt that both the low value of the maximum and the subsequent rapid decrease in the cataphoretic velocity are intimately connected with the strong inter-attractive forces between the colloid particle and the ion of higher valency. This, in fact, is the interpretation of the " valency rule."

The shape and the position of the curve show that the charging and stabilising action of the hydroxyl ion are here very soon outweighed by the coagulating action of the bivalent barium ion. Barium hydroxide will therefore have no pronounced action as a peptising agent.

The only example in the literature where a similar maximum for a bivalent base is recorded is that of Dubrissay, Trillat, and Astier (*loc. cit.*) for kaolin.

Sodium Chloride.—Sodium chloride and also potassium chloride show two interesting features : a definite maximum in the velocity–concentration curve, and an abnormally high velocity at coagulation. Similar maxima for univalent salts are recorded by Ivanitzkaja and Proskurnin for colloidal arsenious sulphide and vanadium pentoxide (*Kolloid-Z.*, 1926, **39**, 15), by Thiessen and Heumann for gold (*Z. anorg. Chem.*, 1929, **181**, 379), and by Powis for oil emulsions (*loc. cit.*). They are generally interpreted in terms of the charging action (adsorption) of the negative ion, usually the chlorine ion. In the case of colloidal platinum, the results with hydrochloric acid show that this ion is not surface-active, and there is no reason to believe that such activity would develop in the case of its salts. The author considers that the explanation of the initial increase in the cataphoretic velocity is to be found in the hydrolytic cleavage of the salt. The collective evidence for this view is shortly to be presented elsewhere.

The high velocity at coagulation, *viz.*, 25×10^{-5} ($\zeta = 0{\cdot}050$), is not unique. Similar high values for univalent salts have been recorded with colloidal arsenious sulphide (Freundlich and Zeh; Powis; Kruyt and van der Willigen; *locc. cit.*), and also for oil emulsions (Limburg, Dissertation, 1924). Owing to the low platinum content, the salting-out effect suggested by Powis has in this case little significance; and there is nothing in the records to indicate, as suggested by Kruyt and van der Willigen, that variations in the dielectric constant of such a weak electrolyte as $0{\cdot}005N$-sodium chloride would play an interfering part.

Potassium Cyanide.—The potassium cyanide curve corresponds very closely to that of a univalent base. Owing to the very high hydrolysis of this salt the result is not surprising. The hydrolysis is doubtless increased by the removal of some potassium hydroxide by the platinum surface, and here we have a rather obvious, but extreme case of hydrolytic cleavage. The well-known surface activity of the cyanide ion may also play some part. It will be noticed that the maximum electrokinetic potential for sodium hydroxide (0·120 volt) is not exceeded.

Ferric Chloride.—Ferric chloride shows a first coagulating zone when the negative velocity is decreased to about -12×10^{-5}

cm. per sec., and the sol then remains unstable over a range of ferric chloride concentration, but when this reaches $0{\cdot}00004M$, and the velocity becomes $+ 15 \times 10^{-5}$, the charge is reversed and the sol again becomes stable. For higher saline concentration, well above $0{\cdot}004M$, the sol behaves as a typical positive sol. The existence of an unstable zone and of a negative and a positive critical potential are clearly shown by the curve.

Coagulation Zones.—The shaded portions of the various curves represent the coagulation zones, *i.e.*, the concentrations between slow and rapid coagulation. It has been usual to distinguish between two critical potentials, one for slow and one for rapid coagulation, and to assume that, whilst the former may have a relatively large value, the latter is approximately zero. The slopes of the curves at and near coagulation show that this is not the case, but that the potential at rapid coagulation is only slightly less than that at slow. This is confirmed by the actual measurements. The velocity at slow coagulation is obtained in the normal manner, the experiment being completed before the particles have had time to coalesce; and that at rapid coagulation can also be directly measured if the necessary amount of salt, *and no more*, is added. For example, if a sol is made $101 \times 10^{-6}M$ with respect to barium chloride, an extremely fine but quite definite precipitate can be noticed with a magnifying glass. This settles so very slowly that its cataphoretic velocity may be measured in the normal manner. The final point on the barium chloride curve was obtained with such a coagulated sol. The settling cannot altogether be neglected, and therefore such values are, if anything, a little too low. The fact that such points fall in the continuation of the curves brings out the interesting feature, *viz.*, that the coagulated agglomerates move with the same velocity (and therefore have the same potential) as the individual particles immediately before coalescence.

The Cause of Coagulation.—The recognition of colloid particles as great multivalent ions was first emphasised by Billiter (*Z. physikal. Chem.*, 1903, **45**, 307) and Duclaux (*J. Chim. physique*, 1907, **5**, 29); but the practical demonstration that colloid systems are strong electrolytes is due to the work of Pauli and of Bjerrum (*Z. physikal. Chem.*, 1924, **110**, 656). In the light of this view, the condensed double layer of Helmholtz, Lamb, and Smoluchowski has become replaced by the diffuse double layer or ionic atmosphere of Gouy (*J. Physique*, 1910, **9**, 457) and of Debye and Hückel (*loc. cit.*). Accordingly, the source of colloid stability is the ionisation of the surface ionogens, whose contra-ions (" gegen-ionen ") extend into the solution as an ionic atmosphere. Any increase in the ionic concentration, *e.g.*, on addition of acids to acidoid sols, causes an attenuation of the ionic atmosphere, or a displacement of the " electrical centre of gravity " of the contra-ions towards the colloid surface. The cataphoretic velocity and the electrokinetic potential are accordingly decreased, and at some critical value coagulation ensues. If there be no interfering reactions, the Debye–Hückel theory requires that the average density of the ionic atmosphere be proportional to the square root of the concentration of coagulating ion, and in the simplest cases this has been confirmed. With all salts, however, the kationic interchange is superimposed on the above relation, and the simple linear law does not hold. With univalent bases the production of fresh surface ionogens acts in the opposite direction to the effect due to the increase in concentration of the contra-ions; hence the maximum in the curve. For these cases the complete relation between cataphoretic velocity and electrolyte concentration is still lacking. The valency rule is also directly interpreted in terms of the theory.

Any decrease in the cataphoretic velocity leading to coagulation has usually been explained in terms of the "adsorption" of the oppositely charged ion, but, although this hypothesis has been of service, ultimately it will have to be abandoned, for it fails to explain even the simplest case, *viz.*, the coagulation of an acidoid sol by an acid, the work with platinum (and also with mastic) having shown that the colloid particles do not remove (or adsorb) any of the coagulating acid. Where other ions, *e.g.*, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, are the active coagulating agents, the more definite explanation in terms of ionic interchange is to be preferred.

In spite of numerous speculations, we have no complete answer to the question, " Why does coagulation ensue before the colloid is completely discharged ? " The work with colloidal platinum shows that there are no abrupt changes (beyond instability) at the coagulation point. This has also been emphasised by Ellis and by Powis with oil emulsions. We can only assume that, when the ionic atmosphere has been sufficiently attenuated, the repulsion which existed when the two particles approached under their Brownian movement is no longer sufficient to keep them from adhering. The latter effect is probably largely a capillary one, and is not solely due to changes in interfacial tension, as is often supposed. Perrin's work with mastic and gamboge, and that of Ellis and of Powis with oil emulsions, shows that at coagulation the droplets do not run together but adhere in clusters. Peptisation experiments with platinum are in accord, for on addition of sodium hydroxide to a sol which has been coagulated with sodium chloride, peptisation follows readily, and no severe treatment is necessary to draw the adhering particles apart.

Conclusion and Summary.

Colloidal platinum is a typical hydrophobic acidoid sol. In the presence of air, the surface appears to contain oxide and acid only.

The changes in the cataphoretic velocity of the particles have been measured in the presence of certain electrolytes.

The effect of inorganic acids is interpreted as a direct repression of the diffuse ionic atmosphere, and the linear relation of Debye and Hückel is found to hold.

Univalent bases react with the surface oxide to form fresh stabilising ionogens, and the cataphoretic velocity accordingly passes through a maximum. Bivalent bases show a very weak maximum.

Hydrochloric acid, barium hydroxide, and barium, calcium, and ferric chlorides show a critical velocity and critical potential.

Poor coagulants, such as univalent salts and univalent bases, show a maximum in the velocity–concentration curve, and an abnormally high velocity (and potential) at coagulation.

Ferric chloride shows two critical velocities, one negative and the other positive.

The coagulation process in the presence of electrolytes is discussed in terms of the results obtained.

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