

CCCLVIII.—*The Electrokinetic Potential and its Relation to the Rate of Coagulation of Colloids. Part I.*

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THE stability of a colloid is generally recognised to depend upon (1) the size of its particles, (2) their electrical charge, and (3) their state of solvation. In the case of lyophobic sols, solvation is very small, and hence stability is determined mainly by the other two factors. Hardy (*Proc. Roy. Soc.*, 1900, **66**, 110) first suggested that a colloid is coagulated when its electrical charge is reduced to zero: when the particles are electrically charged they repel one another and hence cannot coalesce, but when the charge is removed there is nothing to prevent their aggregation. As the aggregates become larger, their Brownian movement becomes more sluggish and finally stops altogether; at this stage they begin to settle under the action of gravity.

The cataphoretic measurements of Ellis (*Z. physikal. Chem.*, 1912, **80**, 597) and of Powis (*ibid.*, 1915, **89**, 186) showed conclusively that Hardy's view is not quite correct. Powis observed that, in an oil emulsion, the drops begin to coalesce when their electrokinetic potential is reduced to about 0.030 volt by the addition of an electrolyte, and from Burton's measurements of the cataphoretic velocity of a copper oxide sol, he showed that this sol becomes unstable when its potential falls to about 0.021 volt. It was therefore suggested that a colloid becomes unstable when its electrokinetic potential falls below a certain critical value which Freundlich ("Colloid and Capillary Chemistry," English transl., 1926, p. 418) now terms the "first critical potential." Later investigations by Powis (*J.*, 1916, **109**, 734), however, were not in agreement with this view, for the coagulation of arsenious sulphide sol started at a potential of about 0.026 volt when salts of multivalent kations (*e.g.*, Ba⁺⁺, Al⁺⁺⁺, and Th⁺⁺⁺⁺) were used, but at much higher potentials (0.044 and 0.050 volt) when potassium chloride and hydrochloric acid were used; he therefore suggested that the last two reagents had a salting-out effect on the colloid.

Recently Kruyt and Willigen (*Z. physikal. Chem.*, 1927, **130**, 170) observed that with potassium ferrocyanide an arsenious sulphide sol is coagulated when its cataphoretic velocity is higher than that of the original sol. Since the rate of cataphoresis depends both on the electrokinetic potential and on the dielectric constant of the dispersion medium, they thought that the colloid is coagulated at a low potential but the high velocity is due to an increase

in dielectric constant owing to the presence of electrolyte in high concentration. Mukherjee and his co-workers (*J. Indian Chem. Soc.*, 1928, **5**, 735; *Nature*, 1928, **122**, 960) noted a similar behaviour of this sol in presence of potassium chloride as coagulator, but found differences according to the mode of preparation of the sol : during coagulation one type showed a higher, and another type a lower cataphoretic velocity than the corresponding original sol ; further, he pointed out that an increase in dielectric constant alone could not explain the observed facts unless an improbably high value were assigned to it.

The foregoing data pertain to the region of slow coagulation, and no measurements are on record of the electrokinetic potential of a colloid in the zone of rapid coagulation where the potential is generally believed to be nearly zero. Freundlich (*op. cit.*, p. 432) distinguished between these two types and thought it probable that the comparatively quick transition from one to the other was connected with the electrical properties of the micelles, agreeing with Zsigmondy's assumption that in the region of rapid coagulation the micelles are almost completely discharged and are near their isoelectric point. He thus distinguished two critical potentials, the first (see above) which must be attained in order that flocculation may be definitely started, and a second, immediately at the zero potential of the double layer, at which the slow coagulation velocity passes into the rapid. The present work was undertaken with the view of measuring the electrokinetic potential of colloids in the zone of rapid coagulation, and the results with sols of arsenious sulphide and ferric oxide are now described.

The electrokinetic potential of colloids coagulated by the addition of electrolytes was measured by the electroendosmotic method. Perrin's modification of Helmholtz's equation for electroendosmosis is

$$V = qE\epsilon D/4\pi L\eta \dots \dots \dots (1)$$

where V is the volume (in c.c.) of the liquid flowing per second through the capillary of cross-section q and length L , E is the potential difference between the two ends of the capillary tube, ϵ the potential of the double layer, D the dielectric constant of the medium, and η its viscosity. If, instead of a single capillary, a porous diaphragm is used, we may regard it as a bundle of capillaries of effective cross-section q and length L . Now $E = iR$, where i is the current and R the resistance, and $R = L/q\kappa$, where κ is the specific conductivity of the liquid filling the pores of the diaphragm. Substituting these values in (1), we have

$$V = i\epsilon D/4\pi\eta\kappa \dots \dots \dots (2)$$

E X P E R I M E N T A L.

Arsenious Sulphide Sol.

The sol was prepared by stirring a nearly half-saturated solution of arsenious oxide into an equal volume of saturated hydrogen sulphide solution. Hydrogen sulphide was then passed through the mixture for nearly 3 hours to ensure that all the oxide had been converted into sulphide, excess of the gas was removed by bubbling hydrogen through the liquid, and the sol was stored in Pyrex-glass bottles in the dark.

The equicoagulating concentration of the different electrolytes was determined as follows. A 16-c.p. lamp was placed inside a wooden box provided with a narrow slit through which the glowing filaments could be seen, and the tube containing the colloid-electrolyte mixture was held in front of the slit. As coagulation proceeded, the filaments appeared fainter and finally could not be seen. The concentration of each electrolyte was so adjusted that this stage was reached in 25—30 seconds after mixing, equal volumes of electrolyte solution and sol being used in each case.

The electroendosmotic measurements were carried out in the form of apparatus previously described (J., 1926, 2605; 1928, 711). About 15 minutes after the addition of the electrolyte the flask was vigorously shaken, and the colloid allowed to settle. The clear solution at the top was decanted into a beaker, and the coagulum transferred to the U-tube, which was then rotated in a centrifuge until the coagulum settled at the bottom and occupied a certain volume fixed by two marks one on each limb of the U-tube. The tube was then filled with the solution from which the colloid had separated, and placed in a beaker containing water at 15°. Two platinised platinum electrodes were introduced, one in each limb of the U-tube, and the total resistance (R) between them was measured. A difference of potential (E) was then applied between the electrodes. This was measured by a voltmeter and could be maintained constant within ± 1 volt by means of an adjustable resistance. The specific conductivity (κ) of the solution filling the U-tube and diaphragm was also determined at 15°.

It will be seen from equation (2) that, other factors remaining constant, the velocity of electroendosmosis should be directly proportional to the current. This was tested by varying E for the same filling of the U-tube, and the following results show that V/i is fairly constant within the range investigated.

| Conc. of BaCl ₂ . | i , amp. | V (c.c. per 30 secs.). | V/i . |
|------------------------------|------------|--------------------------|---------|
| 0.0037N | 0.0045 | 0.021 | 4.66 |
| „ | 0.0091 | 0.0438 | 4.81 |
| „ | 0.014 | 0.065 | 4.64 |

It also follows from equation (2) that when i remains constant V should be independent of the amount of material packed in the same volume, provided the specific conductivity of the solution does not change with the degree of packing. This was proved by making the precipitate obtained from different volumes of the same arsenious sulphide sol occupy a definite volume, the current being maintained constant by adjustment of E :

| Vol. of sol (c.c.). | Final conc. of $MgCl_2$. | i , amp. | V (c.c. per 30 secs.). |
|------------------------|------------------------------|------------|-----------------------------|
| 80 | 0.002N | 0.0058 | 0.045 |
| 60 | " | " | 0.044 |
| 40 | " | " | 0.044 |

It can be inferred from this that the specific conductivity of the electrolyte inside the diaphragm is independent of its packing and hence, in all probability, has the same value as the solution in bulk.

In the following experiments 50 c.c. of arsenious sulphide sol were always mixed with 50 c.c. of the electrolyte solution. In some preliminary experiments the electrokinetic potential ϵ was measured at different intervals after the addition of electrolyte to the colloid, but the value was the same whether measured within an hour or 24 hours after such addition. In most of the cases in Table I the measurements were taken within $1\frac{1}{2}$ hours after the addition of the electrolyte. A zero in the second column denotes that coagulation was instantaneous.

TABLE I.

 $(D = 81; \eta = 0.0116.)$

| Conc. of electrolyte. | Time of coag. | $V \times 10^4$ (c.c.). | i (amp.). | $\kappa \times 10^4$. | $\epsilon \times 10^3$ (volts). |
|--------------------------|------------------|----------------------------|----------------|------------------------|------------------------------------|
| 0.0009N- $AlCl_3$ | 25—30 secs. | 16.3 | 0.0034 | 1.94 | 15.1 |
| 0.0018 " | 0 | 8.6 | 0.0039 | 2.64 | 9.4 |
| 0.0036 " | 0 | 5.4 | 0.0051 | 3.28 | 5.6 |
| 0.015 " | 0 | 0 | 0.0130 | 8.17 | 0 |
| 0.0005N- $Th(NO_3)_4$ | 25—30 secs. | 15.1 | 0.0029 | 1.65 | 13.9 |
| 0.001 " | 0 | 8.6 | 0.0034 | 2.16 | 8.9 |
| 0.00184N- $BaCl_2$ | 25—30 secs. | 15.8 | 0.0058 | 3.22 | 14.2 |
| 0.00368 " | 0 | 14.6 | 0.0090 | 5.20 | 13.7 |
| 0.00196N- $SrCl_2$ | 25—30 secs. | 14.8 | 0.0057 | 3.48 | 14.6 |
| 0.00390 " | 0 | 14.0 | 0.0090 | 5.51 | 14.0 |
| 0.00205N- $MgCl_2$ | 25—30 secs. | 14.8 | 0.0058 | 3.63 | 15.0 |
| 0.0041 " | 0 | 14.9 | 0.0099 | 6.06 | 14.8 |
| 0.0038N- $C_6H_5-NH_3Cl$ | 25—30 secs. | 23.4 | 0.0077 | 5.08 | 25.0 |
| 0.0080 " | 0 | 10.2 | 0.0267 | 29.2 | 18.1 |
| 0.013N- CN_5H_5, HNO_3 | 25—30 secs. | 21.5 | 0.015 | 15.2 | 35.3 |
| 0.068N-KCl | 25—30 secs. | 6.5 | 0.0175 | 71.8 | 43.2 |
| 0.070N- KNO_3 | 25—30 secs. | 16.9 | 0.044 | 73.6 | 45.8 |

The first five salts in Table I are seen to coagulate the sol within 25—30 seconds when its potential reaches 14—15 millivolts. This constancy of the potential, however, disappears altogether when salts of univalent kations are considered, for the same rate of coagulation occurs at 25—46 millivolts for different salts. In general, the higher the coagulating concentration of a univalent kation the greater is the electrokinetic potential. It will also be noticed that, even with the salts of the multivalent kations, when their individual concentrations are increased to twice the value of their equicoagulating concentrations the potential changes to different extents: the bivalent kations diminish it slightly, whereas the ter- and quadri-valent kations reduce it to about 9·1 millivolts. The results also show that in the zone of rapid coagulation ϵ is not zero but is variable, *e.g.*, 8·9 for thorium nitrate and 18·1 for aniline hydrochloride.

Electrokinetic Potential in Mixtures of Electrolytes.—It was first observed by Freundlich and Scholz (Freundlich, *op. cit.*, p. 460) that during the coagulation of arsenious sulphide sol by magnesium chloride, the presence of lithium chloride in small quantities retards the coagulation markedly, and a higher concentration of magnesium chloride is required to coagulate the colloid. This kind of ionic antagonism has also been observed for different pairs of ions and for various colloids by other investigators (*e.g.*, Mukherjee and Ghosh, *J. Indian Chem. Soc.*, 1925, **1**, 213; Sen, *ibid.*, 1926, **3**, 81; *J. Physical Chem.*, 1925, **29**, 517; Dhar and co-workers, *ibid.*, 1925, **29**, 435, 659; 1926, **30**, 649; Weiser, *ibid.*, 1924, **28**, 232; Alexander, "Colloid Chemistry," Vol. 1, p. 613). In all these cases nothing is known as to the potential at which the colloid is coagulated, but it has been tacitly assumed that it remains the same for mixtures as for the individual electrolytes. Table II contains the results of some measurements (carried out exactly as above) in which mixtures of electrolytes were used, the rate of coagulation being approximately the same for each mixture.

The above data show clearly that on addition of potassium chloride to the other salts the potential at which coagulation takes place is much higher than the mean value (14·6 millivolts) when the salts of the multivalent kations were used singly. Further, as the concentration of potassium chloride is increased in the mixtures, the potential also increases. From this it can be concluded that the rate of coagulation of arsenious sulphide sol in these mixtures of electrolytes does not depend on the electrokinetic potential. This statement, however, involves the assumption that the dielectric constant of the dispersion medium does not change, but, as the total concentration of the electrolytes in the mixtures never exceeds

TABLE II.

| Conc. (N). | | $V \times 10^4$ (c.c.). | i (amp.). | $\kappa \times 10^4$. | $\epsilon \times 10^3$ (volts). |
|--|-------|----------------------------|-------------|------------------------|------------------------------------|
| <i>Mixtures of BaCl₂ and KCl.</i> | | | | | |
| BaCl ₂ . | KCl. | | | | |
| 0.00184 | 0.000 | 15.8 | 0.0058 | 3.22 | 14.2 |
| 0.00184 | 0.001 | 19.5 | 0.0074 | 4.57 | 19.5 |
| 0.00184 | 0.002 | 21.5 | 0.0090 | 5.84 | 22.6 |
| 0.0019 | 0.004 | 23.4 | 0.014 | 8.75 | 23.7 |
| <i>Mixtures of MgCl₂ and KCl, also MgCl₂ and LiCl.</i> | | | | | |
| MgCl ₂ . | KCl. | | | | |
| 0.002 | 0.000 | 14.8 | 0.0058 | 3.63 | 15.0 |
| 0.002 | 0.002 | 21.6 | 0.0099 | 6.02 | 21.3 |
| 0.0021 | 0.004 | 24.1 | 0.014 | 8.78 | 24.5 |
| MgCl ₂ . | LiCl. | | | | |
| 0.002 | 0.004 | 24.1 | 0.0135 | 8.72 | 25.2 |
| <i>Mixtures of AlCl₃ and KCl.</i> | | | | | |
| AlCl ₃ . | KCl. | | | | |
| 0.0009 | 0.000 | 16.3 | 0.0034 | 1.94 | 15.1 |
| 0.0009 | 0.001 | 17.4 | 0.0055 | 3.26 | 16.7 |
| 0.0009 | 0.002 | 20.0 | 0.0074 | 4.62 | 20.2 |
| 0.0009 | 0.004 | 21.7 | 0.0103 | 6.94 | 23.7 |
| <i>Mixtures of Th(NO₃)₄ and KCl.</i> | | | | | |
| Th(NO ₃) ₄ . | KCl. | | | | |
| 0.0005 | 0.000 | 15.1 | 0.0029 | 1.65 | 13.9 |
| 0.0005 | 0.004 | 21.3 | 0.0111 | 6.12 | 19.0 |
| 0.0005 | 0.008 | 24.5 | 0.0189 | 10.8 | 22.7 |

0.01N, the dielectric constant should not differ appreciably from that of pure water.

There are two ways in which the addition of potassium chloride to the above salts could increase ϵ —(1) by increasing the thickness of the double layer, and (2) by increasing the electric charge of the colloid. According to Gouy (compare Freundlich, *op. cit.*, p. 252) and Chapman (*Phil. Mag.*, 1913, **25**, 475), however, the thickness of the diffuse double layer diminishes on the addition of an electrolyte; hence, an increase in ϵ on the addition of potassium chloride must be ascribed to the second cause, and, since arsenious sulphide is known to adsorb potassium chloride (compare Dhar and Weiser, *loc. cit.*), the increase in charge may be due to the adsorption of the chloride ion.

Ferric Hydroxide Sol.

This sol was prepared by pouring a concentrated solution of ammonium carbonate in small quantities at a time into a vigorously stirred ferric chloride solution, until a permanent precipitate was formed. At this stage some fresh ferric hydroxide solution was added to peptise the precipitate. The sol was then dialysed until the external water gave scarcely any precipitate with silver nitrate.

The sol became dilute during dialysis and was therefore concentrated somewhat by evaporation at 60—70° for about an hour.

The equicoagulating concentrations of the different electrolytes were determined in the following manner. The concentration of an electrolyte was so adjusted by trial that when the colloid was centrifuged at about 1000 r.p.m. for 10 minutes after the addition of the electrolyte it left a clear solution at the top; if the concentration of the electrolyte happened to be less than this value by 5%, it could not bring about a separation of the colloid even on standing for 24 hours in a test-tube. In Table III the equicoagulating concentrations of the electrolytes are marked with an asterisk: the next higher concentrations coagulated the colloid almost instantly. The procedure was otherwise exactly the same as already described. The minus sign before the values of ϵ indicates that the colloid had become negatively charged.

TABLE III.

| Conc. (N) of electrolyte. | $V \times 10^4$ (c.c.). | i (amp.). | $\kappa \times 10^4$. | $\epsilon \times 10^3$ (volts). |
|--------------------------------|-------------------------|-------------|------------------------|---------------------------------|
| <i>Potassium oxalate.</i> | | | | |
| 0.0065* | 21.5 | 0.0088 | 8.2 | 32.5 |
| 0.007 | 16.8 | 0.0092 | 8.7 | 25.5 |
| 0.0105 | 8.2 | 0.0133 | 11.6 | -11.6 |
| <i>Potassium sulphate.</i> | | | | |
| 0.0066* | 21.3 | 0.0088 | 8.3 | 32.5 |
| 0.0071 | 18.4 | 0.0090 | 8.8 | 29.1 |
| 0.0109 | 5.2 | 0.0133 | 11.9 | 7.5 |
| 0.0190 | 3.0 | 0.0214 | 20.7 | -4.7 |
| 0.0285 | 6.5 | 0.0283 | 30.8 | -11.5 |
| <i>Aniline sulphate.</i> | | | | |
| 0.008* | 23.0 | 0.0083 | 7.0 | 31.4 |
| 0.0085 | 21.5 | 0.0089 | 7.4 | 29.0 |
| 0.01 | 14.3 | 0.0098 | 8.0 | 18.9 |
| <i>Potassium ferricyanide.</i> | | | | |
| 0.00065* | 21.5 | 0.0081 | 7.0 | 30.2 |
| 0.00075 | 15.0 | 0.0090 | 7.6 | 20.5 |
| 0.001 | 0 | — | — | 0 |
| <i>Potassium chloride.</i> | | | | |
| 0.10* | 7.6 | 0.0376 | 103.0 | 33.7 |
| <i>Sodium hydroxide.</i> | | | | |
| 0.0075* | 22.0 | 0.0085 | 7.5 | 31.5 |
| 0.0084 | 18.3 | 0.0106 | 9.0 | 25.2 |
| 0.0144 | 24.7 | 0.0180 | 13.2 | -29.3 |

Examination of Table III shows that for the same rate of coagulation the potential at which potassium chloride coagulates the sol is about 34 millivolts, whereas for the other five substances it is

between 30.2 and 32.5 millivolts. In 0.1*N*-potassium chloride solution, however, the possibility of an increase in the dielectric constant of water must be taken into account, and, moreover, evolution of gas bubbles makes the results somewhat inaccurate. Allowing for these disturbing factors, it may be concluded that all the above salts coagulate ferric hydroxide sol at a potential of about 32 millivolts. The behaviour of this sol may therefore be said to be in agreement with the current conception of a "critical potential."

Effect of Sensitising Agents on the Critical Potential.—Kruyt and Van Duin (*Koll.-chem. Beih.*, 1914, **5**, 269) observed that the concentrations of a uni- and of a ter-valent kation required to coagulate an arsenious sulphide sol are lowered by the addition of phenol or isoamyl alcohol. Freundlich and Rona (*Biochem. Z.*, 1917, **81**, 1871) showed that non-electrolytes such as camphor, thymol, and urethane make a ferric hydroxide sol sensitive to the action of electrolytes. Wo. Ostwald ("Grundriss der Kolloidchemie," 1st Edtn., 1909, p. 441) pointed out that non-electrolytes are likely to affect the stability of a colloid by changing the dielectric constant and thereby affecting the electric charge. The measurements of Freundlich (*op. cit.*, p. 464) and of Mukherjee and co-workers (*J. Indian Chem. Soc.*, 1928, **5**, 697) show that the cataphoretic velocity of a colloid diminishes on the addition of non-electrolytes. The following measurements with sols of arsenious sulphide and ferric hydroxide were undertaken with a view to ascertain how far a change in the rate of coagulation brought about by the addition of sensitising agents such as thymol, amyl alcohol, etc., produces a concomitant change in the potential of the double layer. The experiments were conducted in the same way as described previously, a given volume of a mixture of electrolyte and sensitiser being mixed with an equal volume of colloid. Corrections were made for the changes in viscosity of the solutions in the case of urethane, phenol, and amyl alcohol. The results are in Table IV, and V , i , κ , and ϵ are expressed in the same units as before.

The rate of coagulation of ferric hydroxide sol is accelerated by the addition of thymol, urethane, and amyl alcohol, and corresponding to this acceleration there is also found a lowering of ϵ . The results obtained with arsenious sulphide sol are, however, different: phenol and amyl alcohol accelerate its rate of coagulation in potassium chloride solution and retard it in strontium chloride solution, but the potential does not show a corresponding change—this is not surprising, since it has already been shown in the case of arsenious sulphide that for the same rate of coagulation ϵ may have different values.

TABLE IV.

| Solution. | $V \times 10^4$. | i . | $\kappa \times 10^4$. | $\epsilon \times 10^3$. |
|--|-------------------|--------|------------------------|--------------------------|
| <i>Ferric hydroxide sol.</i> | | | | |
| KCl, 0.1N | 7.6 | 0.0376 | 103.0 | 33.7 |
| Urethane, 14% } KCl, 0.1N | 7.0 | 0.042 | 92.0 | 31.0 |
| Thymol, half satd. } KCl, 0.1N | 7.0 | 0.0427 | 109.0 | 28.8 |
| C ₆ H ₁₁ ·OH, half satd. } KCl, 0.1N | 6.7 | 0.0415 | 96.0 | 27.9 |
| K ₂ SO ₄ , 0.0066N | 21.3 | 0.0088 | 8.3 | 32.5 |
| C ₆ H ₁₁ ·OH, half satd. } K ₂ SO ₄ , 0.0066N | 17.6 | 0.0084 | 7.7 | 29.0 |
| Urethane, 14% } K ₂ SO ₄ , 0.0066N | 15.0 | 0.0074 | 6.8 | 27.9 |
| Thymol, half satd. } K ₂ SO ₄ , 0.0066N | 19.5 | 0.0088 | 8.2 | 29.3 |
| <i>Arsenious sulphide sol.</i> | | | | |
| KCl, 0.07N | 13.5 | 0.041 | 79.0 | 42.1 |
| C ₆ H ₁₁ ·OH, half satd. } KCl, 0.07N | 11.8 | 0.039 | 75.0 | 40.8 |
| Phenol, 10% } KCl, 0.07N | 14.0 | 0.042 | 79.4 | 44.9 |
| SrCl ₂ , 0.002N | 13.4 | 0.0055 | 3.80 | 15.0 |
| C ₆ H ₁₁ ·OH, half satd. } SrCl ₂ , 0.002N | 12.0 | 0.003 | 2.1 | 15.1 |
| Phenol, 10% } SrCl ₂ , 0.002N | 13.0 | 0.0052 | 3.5 | 14.8 |

Discussion.

The behaviour of ferric hydroxide sol so far investigated is in agreement with the theory of a critical potential. For a given rate of coagulation arsenious sulphide sol also shows a constant potential, provided multivalent kations are employed for coagulation, but this regularity disappears completely when salts of univalent kations or their mixtures with multivalent kations are used. The investigations of Kruyt and Willigen (*loc. cit.*) and of Mukherjee and his co-workers (*loc. cit.*) further show that in solutions of potassium ferrocyanide and chloride, arsenious sulphide is coagulated even when its cataphoretic velocity is higher than that of the original sol. Freundlich (*op. cit.*, p. 419) suggests that this anomaly is in some way connected with the hydration of the sol, but this is doubtful, for, if it were so, the anomaly should have been still more prominent in the more hydrophilic ferric hydroxide sol, whereas actually the behaviour of this sol is quite normal.

This apparently anomalous behaviour of arsenious sulphide sol is capable of the following explanation. It is assumed that the force with which two particles of the sol attract each other varies inversely as the distance according to a power much higher than in the case of the electric repulsion due to the presence of the double

layer. According to Gouy (*loc. cit.*), Chapman (*loc. cit.*), and Debye and Hückel (*Physikal. Z.*, 1924, **25**, 49), the movable side of the electric double layer is diffuse; in the absence of any electrolyte this layer has considerable thickness. Now two particles can approach each other unhindered until their ionic atmospheres begin to interpenetrate, but they will then experience a repulsive force. On progressive addition of an electrolyte the thickness of the diffuse layer is continuously reduced, and the particles can approach increasingly closer to each other without experiencing any repulsive force until finally they come so close that the attractive force just overcomes the electric repulsion. The colloid will begin to coagulate in the neighbourhood of this concentration of electrolyte. A diminution in the thickness of the diffuse layer should produce a corresponding decrease in ϵ , provided the charge on the particles remains constant. Now, the increased cataphoretic velocity of arsenious sulphide sol brought about by addition of potassium chloride and ferrocyanide shows that the sol adsorbs Cl^- and $\text{Fe}(\text{CN})_6^{4-}$ ions strongly; hence, in these cases a decrease in ϵ due to a diminution of the thickness of the double layer can be more than counterbalanced by an increase in the charge of the colloid due to the adsorption of anions. In the region of concentration of electrolyte where coagulation just begins, a slight increase in concentration will enable the particles to approach a little closer to each other; this, however, would produce a considerable increase in the force of attraction between the particles and hence increase the rate of coagulation greatly. This accounts for the enormous increase in the rate of coagulation for a small increase in the concentration of electrolyte although ϵ does not change much. The anomalous behaviour of a colloid is therefore to be attributed to a strong preferential adsorption of an ion having the same charge as the colloid. Further work with other colloids is in progress along these lines.

Summary.

1. Measurements of the electrokinetic potential (ϵ) of arsenious sulphide sol in presence of equicoagulating concentrations of different electrolytes show that for the multivalent kations the potential fluctuates between 13.9 and 15.1 millivolts, whereas for univalent kations it varies within wide and higher limits.

2. For nearly the same rate of coagulation, addition of small quantities of potassium or lithium chloride to various multivalent electrolytes increases ϵ markedly, and the higher the concentration of potassium chloride the greater the value of ϵ . For salts of univalent kations and their mixtures with multivalent kations there is therefore no simple relation between the electrokinetic potential

and the rate of coagulation of the sol. Further, an increase in dielectric constant cannot account for the observed increase in the rate of electroendosmosis.

3. Using chloride, sulphate, oxalate, and ferricyanide of potassium, sodium hydroxide, and aniline sulphate as coagulators, it has been shown that ferric hydroxide sol becomes unstable when its potential falls to about 32 millivolts.

4. In presence of electrolytes the rate of coagulation of ferric hydroxide sol is accelerated by the addition of thymol, urethane, and amyl alcohol, and corresponding to this acceleration there is a decrease of potential. In arsenious sulphide sol, on the other hand, an acceleration or retardation of the coagulation velocity is not accompanied by a corresponding change in the potential.

5. An attempt has been made to account for this peculiar behaviour of the latter sol by postulating (i) the existence of a force of attraction between its particles which varies inversely with the distance according to a power higher than that involved in the electric repulsion due to the presence of the electric double layer, and (ii) a strong preferential adsorption of the ion having the same charge as the colloid.

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