Coagulation of Colloidal Aluminium Hydroxide by Electrolytes.

By

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1. Introduction.

Physical chemistry, in its application to the problems of biology, achieved many brilliant conquests with comparative ease, particularly by means of the theory of osmotic pressure and that of the mass-action. But the progress has been impeded by several circumstances. Particularly the colloidal nature of the substances which form living bodies seemed to present insurmountable difficulties. Yet through the combined labour of physical chemists and physiologists these difficulties are being removed one by one; and at present there is no branch of physical chemistry which is cultivated with greater ardour and, whose progress is watched with keener interest than the so-called colloid-chemistry. Of all the results obtained in this field the most definite and at the same time the most interesting from the chemical stand-point are those concerning the coagulation of colloidal solutions by electrolytes. The experimental works of SCHULZE, PICTON and LINDER, HARDY, BILTZ, FREUNDLICH and others have thrown much light on the complicated phenomena.

It is only the so-called suspension colloids which are so

sensitive to electrolytes.[1] Most inorganic colloids belong to this class, and the greater part of the experimental researches have been carried out with such. Of these the colloidal solution of arsenious sulphide is the one most frequently studied on account of the ease with which it can be obtained free from contamination, and on account of its stability. It is the positive and negative ions which cause the coagulation. Where the suspended particles are negatively charged, as is the case with arsenious sulphide, the coagulation is called forth by positive ions ; while positively charged particles such as ferric hydroxide are precipitated by negative ions. The strength of the action evidently depends on the valency of the ions, because the higher the valency the stronger the action. And the difference between the action of mono- and divalent ions, as well as that between di- and trivalent ions is enormous.

Such are some of the salient features of the results hitherto obtained. They are only quasiquantitative, because the time effects are often very pronounced in the case of coagulating colloids and preclude any exact determination. Moreover the methods hitherto employed in determining the concentration of electrolytes which call forth coagulation in a given colloidal solution leave much to be desired. Some investigators have measured the minimum concentration of the electrolytes at which distinct turbidity is observed ; others have estimated the concentration at which the coagulum separates out leaving clear supernatant liquid free from suspended particles ; while still another has determined the strength of the electrolyte solutions which so far coagulate

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1 There are intermediate forms between suspension colloids and hydrophile colloids. These may be sensitive to electrolytes as is evidently the case with legumine, whose coagulum forms the principal constituent of our food-stuff tôfu.

the colloidal solutions that none pass through filter paper of certain definite brand. But as SCHULZE pointed out more than twenty years ago, all these methods must give different values, because they are only fit, so to speak, to determine certain definite points on the curves of coagulation. This is due to the fact that coagulation comprises a whole series of changes, the magnitude of suspended particles increasing continuously with the increasing concentration of the active ion. At a certain stage the average particles begin to reflect so much light that the solution appears turbid. When the particles attain such magnitude that they can no longer remain suspended in the medium they separate out as coagulum. For complete precipitation still greater concentration of the active ion is necessary. If we could determine the average magnitude of the particles as a function of the concentration of the ion concerned, a clear idea of the phenomena might be obtained. Indeed it may not be impossible to accomplish this by means of the ultramicroscope. It will however be a very laborious task; and the results, being obscured by various unavoidable sources of errors, may not correspond to the pains taken. But if we could find a specific property of the colloidal solution which varied continuously with the growing magnitude of the suspended particles, we might employ it as an index of the degree of coagulation; and by measuring this property we might attain our object much more readily.

The inner friction or viscosity of colloidal solutions is evidently a specific property corresponding to the foregoing description, and being in general quite easy of measurement, seems to be particularly well fitted for the study of the problem under discussion. In order to test this supposition the coagulation of

colloidal aluminium hydroxide by various electrolytes has been studied with the aid of the viscosimeter, and the results obtained fulfil the expectation to a remarkable degree as is shown in the following pages.

2. The Colloidal Solution of Aluminium Hydroxide.

The colloidal solution of aluminium hydroxide employed in the following experiments is the one first prepared by the English chemist, WALTER CRUM,[1] more than half a century ago. He obtained a basic acetate of aluminium as a fine insoluble crystalline powder by heating a concentrated solution of aluminium acetate. On prolonged boiling with water the basic salt goes into solution, the acetic acid being given off with the steam, while aluminium hydroxide remains in the colloidal state. All the soluble impurities can be removed by thoroughly washing the basic acetate. When the boiling is carried out in a large platinum vessel, care being taken to exclude contamination from the air, it is possible to get rid of the acetic acid almost completely. In this way a remarkably pure solution of colloidal aluminium hydroxide can be prepared with great ease. It is slightly opalescent, but almost clear to the transmitted light, somewhat viscous and oily to the touch when concentrated. This solution is very stable. Kept in a vessel of hard Jena-glass it has remained apparently quite unaltered in its appearance and properties during the lapse of more than three years. Parallel experiments carried out with this old solution and with a solution newly prepared agreed in all particulars.

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1 Journ. Chem. Soc. London, 4, (1853), 216.

The coagulation of such a solution of colloidal aluminium hydroxide by various agents was observed by WALTER CRUM and described in the following terms:

"A solution containing $\frac{1}{4}$ percent of alumina is converted into a transparent jelly, when mixed with half its bulk of water acidulated with $\frac{1}{2500}$ of sulphuric acid. The jelly has therefore only $\frac{1}{600}$ of its weight of alumina, and $\frac{1}{7500}$ of sulphuric acid.

"By pressure in a bag the liquid part of this jelly was readily separated, and the solid was reduced to $\frac{1}{60}$ or $\frac{1}{70}$ of its original volume. Pure water did not dissolve this residue, neither did an excess of sulphuric acid, even at a boiling heat. On examination it was found that the solid portion had imbibed almost the whole of the sulphuric acid. It existed there in the proportion of about 1 equivalent of acid to 15 of alumina.

"The coagulating power of the various agents may be ascertained with tolerable accuracy by employing an aluminous solution so dilute as to contain not more than 1 part of alumina in 800 of water, and shaking it in a phial with about half its volume of a coagulating solution. In this manner it was found that 1 atom of citric acid (tribasic) coagulates as powerfully as 3 atoms of sulphuric acid, and tartaric acid (bibasic) as much as 2. 2 atoms of oxalic acid are required to produce the same effect as 1 of sulphuric acid. Of muriatic and nitric acids, not less than 300 equivalents must be employed to produce an effect equal to that of 1 equivalent of sulphuric acid—the volume of the acid being always $\frac{1}{2}$ that of the aluminous solution. No acid has the power of redissolving the coagulum.

"Of the other acids which have been tried, the chromic, molybdic, racemic, suberic, salicylic, benzoic, gallic, lactic, cinnamic, butyric, valerianic, carbazotic, camphoric, uric, meconic,

comenic and hemipinic acids all coagulate the solution ; but their exact power has not be ascertained.

" The acetic, formic, boracic, arsenious, and cyanuric acids do not coagulate, at least when moderately concentreted.........

" The alkalies have a strong coagulating power. About 2 equivalents of potash produce an effect equal to 1 of sulphuric acid, and the same is the case with soda, ammonia, and lime. The coagulation takes place before the acetic acid which remains in the aluminous solution is fully saturated ; for when the alkali, in a very dilute state, is added with caution, the coagulum which it produces has still an acid reaction. This coagulum, like that from sulphuric acid, is insoluble in any acid, whether cold or hot, as well as in pure water. It dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated by an acid, the ordinary terhydrate of alumina is thrown down.

" Large quantities, however, of the acetic salts (ready formed) may be added before they coagulate the aluminous solution. When the solid part of the coagulum produced by a strong solution of acetate of soda was afterwards freed from that salt by pressure, it redissolved in pure water, and the solution was again coagulated by a fresh addition of the salt. An experiment with acetate of lime gave the same result.

" The nitrates and chlorides coagulate also with great difficulty.

" Solutions of sulphate of soda, magnesia, and lime coagulate as readily as a liquid containing the same quantity of sulphuric acid in the free state. On examining one of these mixtures, the sulphuric acid was found in the solid part of the coagulum, as before, and the alkali in the fluid part, united with the

acetic acid which had remained in the aluminous solution after boiling.

"The digested solution of alumina which has not been deprived of its acetic acid by boiling, requires about twice as much sulphuric acid to coagulate it as does the boiled solution, and thirty or forty times as much alkali. The coagulation is complete before the acetic acid is entirely saturated.

"One of the most characteristic properties of the digested and altered acetate of alumina is its loss of the power of acting as a mordant. The ordinary acetate, as is well known, forms a yellow opaque precipitate with decoction of quercitron. That which has been thoroughly digested is merely coagulated by that decoction—the colour of which is but little altered, and the coagulum is translucent. The same effect is produced with decoctions of logwood, brazilwood, etc."

This description shows how well the solution is suited to the experimental study of the phenomena of coagulation of a colloidal solution by electrolytes. The solution employed in the greater part of the present study is an old one made by Prof. IKEDA. On analysis it was found to contain 0.457% of alumina. It was diluted 4.4 times, so that the solution actually employed contained 0.1 per cent (or more exactly 0.104%) of alumina.

When the electrodes of a secondary battery of 120 volts were inserted in the two branches of a U-tube filled with the more concentrated solution of alumina, the liquid near the negative electrode became milky in about half an hour, while that in the vicinity of the opposite electrode lost its opalescence and became quite clear. This observation proves beyond doubt that the suspended particles of aluminium hydroxide are positively charged. The same has already been found to be true for the

colloidal solutions of ferric and aluminium hydroxide prepared by dialysis. Hence coagulation phenomena similar to those observed in the latter solution are to be expected in the present study.

3. The Method of Measurement.

The apparatus and the method of measuring viscosity employed in this work are those recommended by OSTWALD; they are too well known to require description. A capillary tube of a rather wide bore was purposely chosen for the viscosimeter in order to minimise the effect of small particles which might separate out from the solution and adhere to the side of the tube. This had the unfortunate result of making the flow of the liquid too rapid and so the correction to be applied on account of the kinetic energy acquired by it became unduly large. But as it is quite useless to aim at any high degree of exactness in a work of this nature, this correction has been neglected. The omission is the more justifiable as the viscosity is measured not for its own sake but only as an index to the degree of coagulation, and so only relative values are to be considered. For the same reason the time of flow was measured with an ordinary watch, the readings being taken to the second.

As the temperature exercises considerable influence on viscosity, the apparatus was immersed in a thermostadt with glass sides. The temperature was kept constant at 25°, and the greatest fluctuation during the whole period of the work, which lasted several months, did not exceed $\frac{1}{5}$ of a degree.

To make a measurement, 2 c.c. of the colloidal solution and an equal volume of an electrolyte solution were introduced into

the wider tube of the viscosimeter, and mixed thoroughly. Then the mixture was sucked up into the bulb. The measurement of the time of flow was repeated several times with one and the same mixture, and the mean was taken. As a rule single determinations did not differ by more than a second. Between two observations with different mixtures the apparatus was heated with concentrated sulphuric acid, washed thoroughly with distilled water, and dried.

The following details of a series of observations made with potassium sulphate as electrolyte will give an idea of how the work was carried out.

TABLE 1.

Concentration of SO_4K_2 in equivalent normal.	Time of flow in seconds.	Mean t
0	26, 25, 25, 24, 25, 24.5, 25, 25.	25
0.0005	27, 26, 25.5, 26.	26
0.0007	28, 28, 28, 28.5.	28
0.0010	42, 42, 42, 41.5, 41.5.	42
0.0025	42, 42, 41, 42, 42.5.	42
0.0050	42, 41.5, 42, 42, 41.5.	42
0.050	40, 42, 42.5, 42, 42.	42

The viscosity of the aluminous solution, containing 0.05% of alumina and free from electrolyte, differed but slightly from that of pure water. If we take the ratio of the time of flow of various mixtures to that of the solution to which no electrolyte has been added we get relative viscosities η.

TABLE 2.

Concentration of SO_4K_2	0	0.0005	0.0007	0.001	0.0025	0.005	0.05
t	25	26	26	42	42	42	42
η	1.00	1.04	1.12	1.68	1.68	1.68	1.68

These numbers show clearly that with the concentration of 0.001 molar of potassium sulphate the coagulation was complete and the further addition of the electrolyte had no effect. It is also to be noted that the coagulation began at a concentration as low as 0.0005 and was considerable at 0.0007. In this way we get a tolerably good idea of the degree of coagulation effected by different concentrations of the electrolyte.

4. The Influence of Temperature.

In order to be able to make generalisations which should hold good over a wide range of temperature we had to study the influence which temperature exercises on the phenomena of coagulation. As a typical electrolyte, potassium sulphate was chosen, and the viscosity was further measured at three different temperatures, viz. 6°, 40°, and 60°. The results obtained are contained in the following tables.

TABLE 3.

Temperature = 6°.

Concentration of SO_4K_2	0	0.0005	0.0025	0.004	0.05
t	42	43	70	71	71
η	1.00	1.02	1.66	1.69	1.69

TABLE 4.

Temperature $= 40°$.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	20	21	32	32	32
η	1.00	1.05	1.60	1.60	1.60

TABLE 5.

Temperature $= 60°$.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	15	16	24	24	24
η	1.00	1.06	1.60	1.60	1.60

The absolute values of viscosity vary considerably with the temperature, but the values of η remain nearly constant. For the sake of easier comparison all the results including those at 25° are collected in the next table.

TABLE 6.

Value of η.

Temperature \ Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
6°	1.00	1.02	1.66	1.69	1.69
25°	1.00	1.04	1.68	1.68	1.68
40°	1.00	1.05	1.60	1.60	1.60
60°	1.00	1.06	1.60	1.60	1.60

As may be seen, the general course of coagulation with the increasing concentration of the electrolyte remains nearly the

same at different temperatures. And if it were not too venture-some we might say that the higher the temperature the lower will be the concentration of the electrolyte necessary to cause noticeable coagulation. The relative viscosity of the completely coagulated solution tends to decrease with the rising temperature. But as the general features remain the same between 6° and 60°, we may draw pretty general conclusions from observations at the single chosen temperature of 25°.

5. Effect of the Concentration of the Colloidal Solution.

As has been demonstrated by CRUM the electrolyte is de-composed in the act of coagulation, the anion being retained by the gel formed. Hence the concentration of the electrolyte which causes complete coagulation must vary with the concentration of the colloidal solution. In order to test this point the follow-ing measurements were made.

TABLE 7.

Concentration of the colloidal solution=0.025% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	25	26	33	34	34
η	1.00	1.04	1.32	1.36	1.36

TABLE 8.

Concentration of the colloidal solution=0.0125% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	24	24	28	29	29
η	1.00	1.00	1.17	1.21	1.21

TABLE 9.

Concentration of the colloidal solution = 0.005% alumina.

Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
t	23	23	26	26	26
η	1.00	1.00	1.13	1.13	1.13

In order to facilitate the comparison, all the values of η are collected in the following table together with the results obtained with 0.05% colloidal solution. (See § 3).

TABLE 10.

% Al_2O_3 \ Concentration of SO_4K_2	0	0.0005	0.0025	0.005	0.05
0.05	1.00	1.04	1.68	1.68	1.68
0.025	1.00	1.04	1.32	1.36	1.36
0.0125	1.00	1.00	1.17	1.21	1.21
0.005	1.00	1.00	1.13	1.13	1.13

Within the experimented range, the concentration of the electrolyte, which causes complete coagulation, appears to be the same for the colloidal solutions of different concentrations. In order to observe the effect above mentioned the concentration had to be varied within far wider range. Hence any generalisation from the observations made on the aluminous solution containing 0.05% Al_2O_3 will apply to all the solutions whose concentrations are not very large.

The value of $\eta-1$ for the completely coagulated solution is not quite proportional to the concentration, as might have been

expected, but varies more slowly. Even when the viscosity of pure water instead of the respective aluminous solution is taken as the standard of comparison, strict proportionality does not obtain. But this is after all not very strange, because the apparent viscosity observed in the these experiments can not be a very simple function of the number of suspended particles.

The simplest empirical equation, which represents the relation, will have the form :

$$\eta_{lim} - 1 = a\,c^{\beta}$$

where c stands for the concentration of the colloidal solution, and a and β are constants. In the present case it has been found by trial that $a=10$ and $\beta=0.9$.

Concentration c.	0.05	0.025	0.0125	0.005
$\eta_{lim}-1$ (found).	0.68	0.36	0.21	0.13
$\eta_{lim}-1$ (calculated).	0.68	0.36	0.20	0.09

6. The Effect of Time.

As the colloidal solution is essentially an unstable system and its coagulation is generally a change to a more stable state, time must exercise some effect on the phenomena. This has been confirmed in the case of arsenious sulphide. But in the present case no marked effect was observed. This is well shown by the constancy of the viscosity of various solutions, partially or completely coagulated, during the time in which repeated measurements of the time of flow were made. Yet when a completely coagulated solution is allowed to stand for a comparatively long time the viscosity gradually diminishes. For example, in a solution whose relative viscosity was initially 1.76, it became after

66 hours 1.68 and after 22 hours more, 1.64. To what this diminution is due can only be surmised.

No particular attention was paid to the mode of mixing the colloidal solution with that of the electrolyte.

7. Coagulative Power of Various Electrolytes.

In the foregoing investigations we have seen that the relative viscosity η of the colloidal solution is nearly independent of temperature and not much influenced by time. On the other hand it has been found to be a function of the concentration of the colloidal substance, and it might well be affected by the previous history of the solution. The aluminous solution employed throughout the following experiments was of the same origin and concentration (0.05% of alumina); hence the values of η observed are strictly comparable. We are thus in a position to study the effect of the nature and concentration of various electrolytes on the coagulation of the colloidal aluminium hydroxide.

Most of the substances employed were purified by recrystallisation, but some could be obtained only in such small quantities that they had to be used as they were. Of the alkalies, caustic soda was made from metallic sodium, while the others were the ordinary materials of the laboratory. The solutions of $Ag(CN)_2K$, PO_4Na_3 and the like were prepared by adding the components in proper proportions. Mellithic acid was prepared from mellithrite. The colouring matters were ordinary samples, while the solution of egg-albumin was obtained by dialysing the white of hen's eggs.

The results of the measurements arranged in the order of the increasing valency of the negative ions of the electrolytes are contained in the following table. The concentrations are given in equivalent normal.

TABLE 11.

No.	Concentr. / Substance	0.00017	0.00025	0.0005	0.00072	0.001	0.0017	0.0025	0.005	0.05
1	$NO_3 K$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
2	$ClO_3 K$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
3	$MnO_4 K$	—	—	—	—	1.00	1.00	1.00	1.04	1.20
4	$Cl K$	—	—	—	—	1.00	1.00	1.00	1.00	1.53
5	$Br K$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
6	$I K$	—	—	—	—	1.00	1.00	1.00	1.00	1.74
7	$CNS K$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
8	$CN K$	—	—	—	—	—	1.00	1.32	1.84	1.88
9	$Ag(CN)_2 K$	—	—	—	—	1.00	1.00	1.08	1.16	1.48
10	$NO_3 H$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
11	$Cl H$	—	—	—	—	1.00	1.00	1.00	1.00	1.00
12	Picric acid	1.00	1.00	1.00	—	1.08	—	—	1.60	(1.88)[1]
13	$HO Na$	—	—	—	—	—	1.08	1.22	1.74	1.84
14	$HO K$	—	—	—	—	—	1.00	1.04	1.30	1.88
15	$(HO)_2 Ba$	—	—	—	—	—	1.00	1.00	1.04	1.88
16	$SO_4 K_2$	—	1.00	1.04	1.58	1.68	1.68	1.68	1.68	1.68
17	$CrO_4 K_2$	—	1.00	1.00	1.00	1.00	1.00	1.17	1.75	1.75
18	$Cr_2O_7 K_2$	—	1.00	1.00	1.00	1.00	1.08	1.58	1.75	1.75
19	$B_4O_7 Na_2$	—	1.00	1.00	1.12	1.20	1.32	1.36	1.40	1.68
20	$Pt(CN)_4 K_2$	1.00	1.00	1.00	1.00	1.00	1.04	1.16	1.52	1.72
21	$CO_3 Na_2$	—	1.00	1.00	1.00	1.00	1.00	1.26	1.79	1.79
22	$SO_4 H_2$	—	1.00	1.58	1.58	1.58	1.58	1.58	1.58	1.58
23	Succinic acid	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
24	Na Succinate	1.00	1.00	1.00	1.00	1.00	1.26	1.58	1.68	1.68
25	Oxalic acid	1.00	1.05	1.06	1.08	1.10	1.26	1.26	1.26	1.26
26	NH_4 Oxalate	1.00	1.02	1.10	1.15	1.21	1.23	1.26	1.26	1.26
27	K Oxalate	1.00	—	1.00	1.04	1.10	1.32	1.32	1.32	1.32

1. This value corresponds not to the concentration 0.05 but to 0.01.

No.	Concentr. / Substance	0.00017	0.00025	0.0005	0.00072	0.001	0.0017	0.0025	0.005	0.05
28	Tartaric acid	1.00	—	1.00	1.27	1.63	1.72	1.84	1.84	1.84
29	Malonic acid	1.00	—	—	—	—	—	—	—	1.00
30	Fumaric acid	1.00	—	—	—	1.00	1.68	1.68	1.68	1.68
31	Maleic acid	1.00	—	—	—	—	—	—	—	1.00
32	Na Maleate	1.00	—	—	—	—	1.00	1.16	1.74	1.89
33	Itaconic acid	1.00	—	—	—	—	—	—	—	1.00
34	Na Itaconate	1.00	—	—	—	—	1.00	1.16	1.63	1.68
35	$PO_4 H_3$	—	—	—	—	1.00	1.05	1.05	1.05	1.74
36	$PO_4 H Na_2$	—	—	—	—	1.00	1.00	1.79	1.89	1.89
37	$PO_4 Na_3$	—	—	—	—	1.00	1.00	1.89	1.95	1.95
38	$Fe(CN)_6 K_3$	1.00	1.36	1.84	1.88	1.92	1.96	1.96	1.96	2.00
39	Citric acid	—	—	—	1.00	1.39	1.74	1.84	1.84	1.84
40	K Citrate	—	—	—	1.00	1.74	1.75	1.85	1.90	1.90
41	$Fe(CN)_6 K_4$	1.08	1.52	2.16	2.20	2.20	2.24	2.24	2.24	2.24
42	Mellithic acid	1.00	1.16	1.42	2.00	2.00	2.00	2.05	2.05	2.05

An inspection of the foregoing table reveals the following facts. In the cases where the coagulation takes place, the relative viscosity shows a noticeable rise only when the concentration of the electrolytes reaches certain values. From this point the viscosity increases with the increasing concentration to a certain limit, and then ceases to be influenced by the further addition of the electrolyte. Sometimes the increase of viscosity with increasing concentration is gradual, while in other cases it is quite sudden. Again the limiting value, to which the relative viscosity tends, shows considerable difference in different cases. A diagram, in which the logarithm of the concentration is taken as the abscissa and the relative viscosity as the ordinate, brings these facts most clearly into view. Ammonium
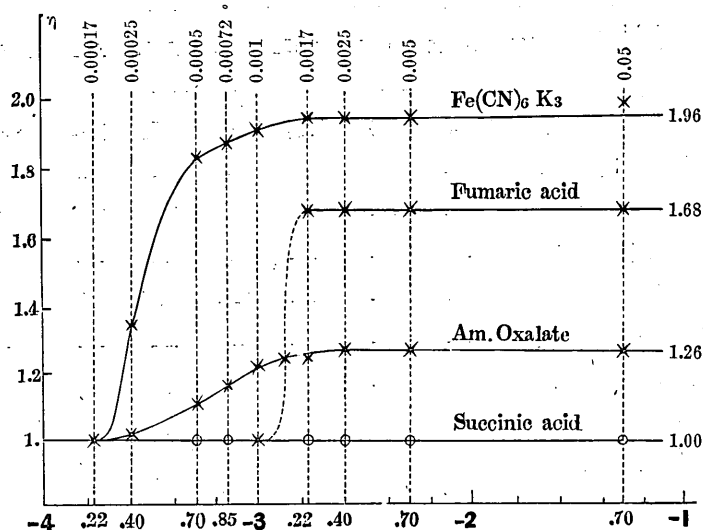
oxalate (26),[1] potassium ferricyanide (38), and fumaric acid (30) are chosen as typical cases and represented in the annexed diagram. In the case of ammonium oxalate, incipient coagulation took place at the very low concentration of 0.0002, the concentration at which complete coagulation was effected was 0.0025 and the final value of the relative viscosity was very low being only 1.26. In the case of potassium ferricyanide the concentration of the incipient coagulation was about the same, but complete coagulation was reached at the somewhat lower concentration of about 0.0015, while the limiting value of the relative viscosity was as high as 1.96. In the case of fumaric acid no coagulation was observed at 0.001 while at 0.0017 it was already complete. The limiting value of η is here middling, being 1.68.

For a complete characterisation of an electrolyte with respect to its coagulative power on a chosen colloidal solution a curve such as shown in the foregoing diagram is necessary. But for

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1. The numbers in the brackets refer to the number in Table 11.

the purpose of comparison of various electrolytes among themselves, it will be more convenient to chose certain characteristic points on the curves, than to employ the curves themselves; and the distinct points which are particularly well fitted for the purpose seem to be those above mentioned, viz. : the concentration of the incipient coagulation, and the lowest concentration at which complete coagulation takes place.

The smallest concentration of an electrolyte at which coagulation actually begins can not of course be determined with great precision. Moreover, its experimental value depends on the exactness of the method of measurement. In the present investigation the method employed is a rather rough one, therefore the values found can only be approximate. Yet they may serve as the basis of a broad comparison.

In Table 12 the electrolytes are classified according to the magnitude of the concentration under consideration.

In the first column are placed the electrolytes whose coagulative power is very slight, since they fail to cause even incipient coagulation at the comparatively high concentration of $\frac{1}{20}$ normal. They are all electrolytes with monovalent anions. The organic acids included are indeed dibasic, but they are all so weak that their dissociation hardly proceeds beyond the first stage, and if the free divalent anion be present at all it must be in such a minute quantity that they do not affect the colloidal solution in any noticeable degree.

In the second column are contained only two halides, potassium chloride and iodide. It is a rather curious fact that the coagulative power of the bromide is so weak and does not lie between those of the two halides. To exclude any mistake the measurements were repeated, but with the same result.

TABLE 12.

above	between	between	below
0.05	and	0.005	and	0.001
$NO_3 K$	Cl K	$Mn O_4 K$	Picric acid
$ClO_3 K$	I K	CN K	K oxalate
Br K		$Ag (CN)_2 K$	Tartaric acid
CNS K		HO Na	Citric acid
$NO_3 H$		HO K	K Citrate
Cl H		$(HO)_2 Ba$	$SO_4 K_2$
Succinic acid		$CrO_4 K_2$	$SO_4 H_2$
Malonic acid		$Cr_2O_7 K_2$	Oxalic acid
Maleic acid		$Pt (CN)_4 K_2$	NH_4 Oxalate
Itaconic acid		$CO_3 Na_2$	$Fe (CN)_6 K_3$
		$B_4O_7 Na_2$	Mellithic acid
		Na Succinate	$Fe (CN)_6 K_4$
		Na Maleate	
		Na Itaconate	
		Fumaric acid	
		$PO_4 H_3$	
		$PO_4 HNa_2$	
		$PO_4 Na_3$	

In the third column are included electrolytes with mono-valent anions. Of these the permanganate is the weakest and its position is rather doubtful. Three are alkalies, which have a pretty strong coagulative power, as first pointed out by CRUM. The remaining two are potassium cyanide and potassium silver-cyanide. Why they act comparatively so strongly is not known. Of the other twelve electrolytes belonging to this class, nine have divalent anions, the remaining three being phosphoric acid and its salts. Phosphoric acid, although it is tribasic, may not

be dissociated to such an extent that the trivalent anion PO_4''' exists in any significant concentration; but in the solution of trisodium phosphate this must undoubtedly be the case.

In the last class, whose members have such a strong action on the colloid that they produce incipient coagulation at a concentration below $\frac{1}{1000}$ equivalent normal, there is only one electrolyte with monovalent anion, viz., picric acid. Of the anions of the remaining eleven electrolytes, six are divalent, three are trivalent, one is tetravalent and one may be hexavalent.

According to SCHULZE, the coagulative power of an electrolyte is chiefly determined by the valency of its ions. On the whole, this rule holds in the present case; though there are several noteworthy exceptions. The other chemical and physical properties of the anion seem to exercise considerable influence on the coagulative power.

When we take the lowest concentration of the electrolytes necessary for complete coagulation as the basis of comparison, we get the results shown in Table 13.

This mode of comparison comes nearer to the methods employed by former investigators, particularly SCHULZE and FREUNDLICH, because what they measured may also be looked upon as the lowest concentrations of complete coagulation.

Among fifteen electrolytes which require greater concentrations than $\frac{1}{20}$ equivalent normal, there is only one whose anion is polyvalent, i. e. phosphoric acid.

In the next column are found five electrolytes with monovalent anions, the remaining four having divalent ones. In the third column are placed nine electrolytes with divalent anions and five electrolytes with trivalent anions. In the last column

TABLE 13.

above 0.05	between 0.05 and 0.005	between 0.005 and 0.001	between 0.001 and 0.00025
$NO_3 K$	$CN K$	$CrO_4 K_2$	$SO_4 K_2$
$ClO_3 K$	$HO Na$	$Cr_2 O_7 K_2$	$SO_4 H_2$
$MnO_4 K$	$HO K$	$CO_3 Na_2$	Mellithic acid
$Cl K$	$(HO)_2 Ba$	Na Succinate	$Fe (CN)_6 K_4$
$Br K$	Picric acid	NH_4 Oxalate	
$I K$?	$B_4O_7 Na_2$?	Oxalic acid	
$CNS K$	$Pt (CN)_4 K_2$	K Oxalate	
$Ag (CN)_2 K$	Na Maleate	Fumaric acid	
$NO_3 H$	Na Itaconate	Tartaric acid	
$Cl H$		$PO_4 H Na_2$	
$PO_4 H_3$		$PO_4 Na_3$	
Succinic acid		K Citrate	
Malonic acid		Citric acid	
Maleic acid		$Fe (CN)_3 K_3$	
Itaconic acid			

are two having divalent anions, while one has tetravalent and the remaining one has an anion of possible hexavalency. Thus the rule of SCHULZE is here brought out much more clearly than in Table 12.

The limiting value of relative viscosity is also a characteristic quantity for an electrolyte with respect to its coagulative power. But it is perhaps more rational to compare the increase of viscosity $\eta_{lim} - 1$ caused by various electrolytes. The lowest value was found in the case of oxalic acid and ammonium oxalate, being only 0.26. The highest value was reached in potassium ferricyanide, and is about five times as large being 1.24.

As the value of $\eta_{lim}-1$ depends on the concentration of the colloidal solution, it is not very well fitted for the characterisation of an electrolyte. But perhaps it might be possible to eliminate this' effect by employing the empirical equation given at the end of § 5:

$$\eta_{lim}-1=a\,c^{\beta}.$$

It is not improbable that the empirical constant β retains its value for different electrolytes and that a alone varies with different cases; but this point must be left for further study.

Another fact deserves mention in this place. The values of $\eta_{lim}-1$ for electrolytes with particularly well developed coagulative power, are also high. Thus strong electrolytes with trivalent anions have $\eta_{lim}-1$ between 0.9 and 1.0, while in one electrolyte with tetravalent anion it is as high as 1.24.

What the different values of $\eta_{lim}-1$ may mean physically and chemically it is difficult to say. They point no doubt to some difference in the physical structure of the coagulum. Microscopic observation may reveal in what the difference lies.

In order to study the effect of the valency of ions on the coagulative power, it is necessary to compare electrolytes of chemically allied natures but of different valencies. For this purpose we chose potassium salts of cyanogen complexes, $Ag\,(CN)_2\,K$ (9), $Pt\,(CN)_4\,K_2$ (20), $Fe\,(CN)_6\,K_3$ (38), and $Fe\,(CN)_6\,K_4$ (41). The relation between η and the concentration of the electrolytes is shown in the annexed diagram. All the three aspects of the coagulative power, which we have been discussing, are brought so clearly before the eye, that it is needless to dilate upon them in this connection. In short, the rule of SCHULZE finds the
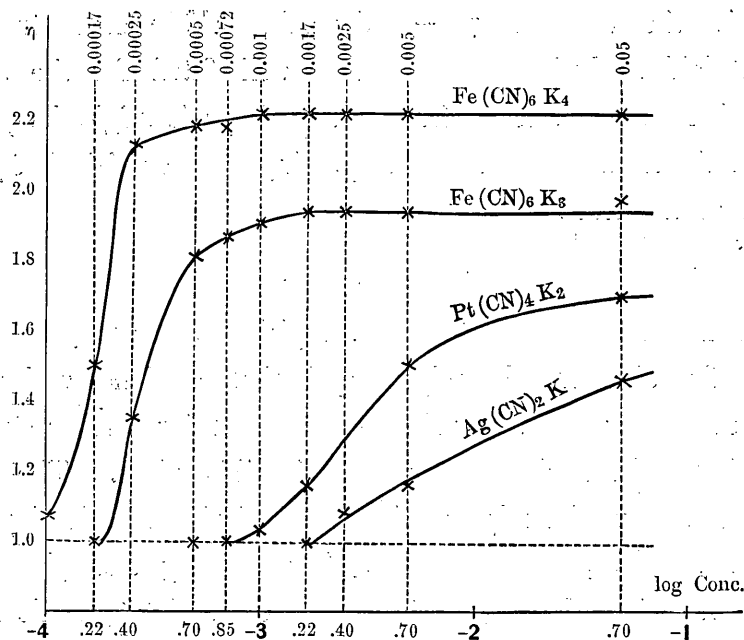
fullest cofirmation in all details. As to the quantitative relation proposed by HARDY and WHETHAM,[1] it may be tested in the following manner. The concentration necessary for complete coagulation is :

$Pt(CN)_4 K_2$	$Fe(CN)_6 K_3$	$Fe(CN)_6 K_4$
0.1	0.0015	0.0005

If n be the valency of the anion, then the nth root of the concentration ought to have one and the same value.

$Pt(CN)_4 K_2$	$Fe(CN)_6 K_3$	$Fe(CN)_6 K_4$
0.3	0.11	0.15

The order of the numbers is the same, but the difference is too great to be ascribed to experimental error.

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1. Journal of Physiology, 24, (1899), 301.

When the concentration is large enough, even electrolytes with the weakest coagulative power can cause considerable increase in the relative viscosity as is illustrated by the following observations on nitric acid.

TABLE 14.

Concentration	0	0.05	0.5	2.5
η	1.00	1.00	1.40	1.52

But when the concentration of an electrolyte is so large, the viscosity is generally increased to some extent even without coagulation taking place. Hence it will be necessary to apply proper correction to obtain more exact results. In the present investigation we have limited ourselves to the study of more dilute solutions.

Although it seemed highly improbable that positive ions should exercise any considerable coagulative power on the colloidal aluminium hydroxide, we studied the effect of the nitrates of the following six cations,

Na,   Ag,   Ba,   Co,   Ni, UO_2,

in order to reach experimental certainty on the subject. Up to the concentratien of $\frac{1}{20}$ equivalent normal the results were quite negative. Thus we are naturally led to the conclusion that it is anions which cause the coagulation.

The fact, that succinic, maleic, and itaconic acid are quite inactive up to the highest concentration tested, while their sodium salts exercise considerable coagulative power even in tolerably dilute solutions, is in accordance with this conclusion. But the

most interesting fact of all is that the coagulative power of
fumaric acid is so well developed while the stereoisomeric maleic
acid is quite inactive. The dissociation constant of maleic acid
considered as a monobasic acid is indeed far greater than that
of fumaric acid, being 0.00117 as against 0.000093 ; but in the
dissociation constant[1] with respect to the second hydrogen ion
the relation is reversed, being only 0.00000039 for maleic acid
and 0.000018 for fumaric acid. These latter constant were found
for 100°. At 25° their values may be somewhat different, yet
the order of magnitude will remain nearly the same. This
explains why the dissociation constant as monobasic acid cal-
culated from the electrolytic conductivity remains very nearly
constant for maleic acid, while it increases, though at first very
gradually, with increasing dilution for fumaric acid. Hence the
concentration of the divalent anion must be very much greater
in the solution of fumaric acid than in that of maleic acid.
This accounts for the great difference in the coagulative power
of the two acids.

The coagulative power of tartaric acid has been found to be
markedly greater than that of fumaric acid ; this may be looked
upon as the consequence of the greater dissociation constant of
the second hydrogen ion for this acid, the constant being 0.000059
or more than three times larger than that of fumaric acid.
This doubtless also applies to oxalic acid.

The indifferent organic substances, ethyl alcohol, phenol and
mannite, were tested, and found to lack coagulative power, at
least in not too high concentrations. Such is doubtless the case

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1. W. A. SMITH : Zeits. für physik. Chem., **25**, (1898), 241.

with most organic substances which form real (not colloidal) solutions and do not undergo electrolytic dissociation.

Mannite solution, to which boric acid had been added, was also found quite inactive, although it formed complex acids of considerable strength.[1] Boric acid itself exerts no coagulative action.

CRUM observed the coagulating action of some decoctions of certain dye-stuffs. The solutions of many colouring matters are colloidal, and when the suspended particles have negative electric charge, this is to be expected, particularly according to the observations of BILTZ.[2] We made observations on the solutions of helianthin, fuchsin, and eosin, and also on that of tannin; and found their coagulative power very strong as shown in the following table.

TABLE 15.

Substance \ Concentr.	0.00017	0.00025	0.0005	0.001	0.005	0.01
Eosin	1.04	—	2.08	—	2.12	2.12
Fuchsin	1.00	1.00	1.00	1.02	1.60	1.88
Helianthin	1.04	1.40	—	1.84	—	2.08
Tannin	1.00	1.00	1.04	—	1.36	1.84

It is known that eosin has cathodic cataphoresis and the same is probably the case with other substances in the table.

It was also observed that the colloidal solution of aluminium

1. MAGNANINI: Zeits. für physik. Chem., 6, (1890), 58.
2. Berichte d. deutschen chemischen Gesellschaft, 37, (1904), 1113.

hydroxide was coagulated by saliva. This is doubtless due to the protein present in it. We have tested the coagulative power of egg-albumin and obtained the following result.

TABLE 16.

Concentration	0.0108	0.0431	0.431%
η	1.07	1.11	1.35

Summary.

1.   The measurement of viscosity was found to be particularly well fitted for the study of the coagulation phenomena of the colloidal solution of aluminium hydroxide.

2.   The degree of coagulation was found to increase in some cases suddenly and in others more gradually with the increasing concentration of the electrolytes.

3.   Only anions were found to exercise coagulative power. This is in accordance with the rule of HARDY, for the colloidal solution shows anodic cataphoresis.

4.   The coagulative power of the anions increased rapidly with the increasing valency, in confirmation of SCHULZE's rule.

5.   The final degree of coagulation caused by the increasing concentration of various electrolytes differed considerably in different cases, and seemed to be characteristic of the action of each electrolyte.

6.   Neither the concentration of the colloidal solution nor

the temperature, nor duration of the experiment seemed to affect in any marked degree the general relations found.

The foregoing study was undertaken and prosecuted under the guidance of Prof. IKEDA to whom my best thanks are due.

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