5. This is exemplified by any one of the higher soaps simply on change of concentration. Thus in concentrated solution there is little else present than colloid plus cation, whereas in dilute solution both undissociated and dissociated soap are crystalloids of simple molecular weight.

6. Similarly, there is a continuous transition from typical colloidal electrolytes through slightly charged colloids to typical neutral colloids.

7. For the summary of the chief properties of the soap solutions, reference should be made to the numbered statements used as headings in the present paper. These follow from the mass of dew-point data here presented, by which Krafft's well known but erroneous results for "molecular weights" of soaps are at last superceded.

8. The ionic micelle in the case of soaps exhibits an equivalent conductivity quite equal to that of potassium ion. Its formula may correspond to $P_n^{n(-)}.mH_2O$ but more probably it is $(NaP)_x.P_n^{n(-)}.(H_2O)_m$, where P^- is the anion of the fatty acid in question.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus. Finally, our thanks are due to Miss M. E. Laing for her assistance in preparing this paper for publication, without which its appearance would still have been indefinitely delayed.

Bristol, England.

[Contribution from the Chemical Laboratory of the University of Illinois.]

THE COAGULATION OF CLAY SUSPENSIONS AND SILICIC ACID.[1]

By Otto M. Smith.

Received September 8, 1919.

An explanation is given in this paper of why many turbid river waters require at certain periods excessive amounts of coagulants for clarification and how purification may be most efficiently accomplished. The action of electrolytes commonly occurring in natural waters upon the stability of colloidal clay suspensions and silicic acid and their effect when alum is used as a coagulant, is discussed. Colloidal clay and silicic acid are more prevalent in the surface waters of the Mississippi valley[2] and the western states, and the need of research in this line has been emphasized in several papers.[3]

The experimental work was carried out along 3 well defined lines, and is discussed in the following order: 1. The removal of silicic acid

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[1] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] *Water Supply Paper* No. 236.

[3] Fuller, "Water Purification at Louisville, Ky.;" Elms, *Eng. Record,* 51, 552; Black and Veach, *ibid.,* 72, 292; and Catlett, *ibid.,* 73, 741.

from dilute solutions by electrolytes and colloids. 2. The effect of electrolytes on dilute clay suspensions. 3. The effect of silicic acid on the coagulation of clay suspensions in the presence of electrolytes.

Precipitation of Silicic Acid.

Silicic acid is not precipitated from a solution containing 184 parts per million of silica by solutions of sodium chloride, sodium carbonate, sodium hydrogen carbonate, sodium sulfate, potassium sulfate, trisodium phosphate, magnesium hydrogen carbonate, magnesium sulfate, barium chloride, calcium chloride, aluminum sulfate, ferrous sulfate, ammonium sulfate, ferric chloride and aluminum chloride, when present in a concentration of 0.07 *N*, but is precipitated by sodium, calcium and barium hydroxides and colloidal iron at a concentration of 0.099 *N*, 0.0019 *N*, 0.0019 *N* and 0.0045 *N*, respectively.

Temperature *Ca.* 23° Time, 5 minutes.

Ca.	*N*.		*N* conc.
5.5	0.18	NaOH	0.099
0.6	0.018	$Ca(OH)_2$	0.0019
0.4	0.026	$Ba(OH)_2$	0.0019
2.6	(0.6 mg.)	colloidal Fe	0.0045

These results indicate that bivalent ions have a precipitating value 50 times that of monovalent ions. Trivalent ions from the formula $1 : x : x^2$ should have a coagulating value of 2500 times that of the univalent and 50 times that of bivalent ions. Qualitative experiments with more dilute solutions indicate that the ratio between bivalent and trivalent to be about one to four. The more dilute a solution, the less marked is this precipitating effect of the cations.

Very dilute solutions—30 or 40 parts per million of silica—are not precipitated by sodium hydroxide and rather high concentrations of calcium hydroxide relative to silicic acid are necessary to obtain a precipitate within 6 hours. At these concentrations the reactions may be ionic and precipitates of calcium silicates may be thrown down. Since the hydroxides of calcium and barium precipitate silicic acid, it is desirable to know the effect of added univalent and bivalent ions upon the amount of calcium hydroxide needed.

To 5 cc. of a dialyzed silicic acid solution, containing 625 parts per million of silica, there was added 0.5 cc. of a 0.1 *N* solution of the above electrolytes and the silicic acid precipitated by the addition of calcium hydroxide. Precipitation resulted when 0.3 cc. of calcium hydroxide was added to solutions of barium, calcium, magnesium, iron and aluminum, more than this being required in all other cases. The result was not influenced by sodium chloride at these concentrations. It is evident that the precipitating value of the cation depends upon its valence and that the hydroxyl has some influence.

Accordingly the concentration of the hydroxyl ion necessary before silicic acid is precipitated by calcium hydroxide from its solution in water alone or when any of the salts mentioned above are present, was determined and found to correspond to between a P_H[1] of 8.6 and 9.5. Silicic acid may act as a buffer in the manner of large complex organic molecules because there appears to be little relationship between the normality or alkalinity of the solution and the concentration of the hydroxyl ion.

The optimum conditions, according to the theory of coagulation, for precipitation of negatively charged silicic acid, should be: (1) an amount of trivalent cations or positively charged colloids sufficient to neutralize exactly the negative charges; (2) a minimum amount of univalent cations, protective or stabilizing colloids; and (3) the same P_H value as that at the iso-electric point. Just what conditions must be defined in order to locate the iso-electric point, have not been discovered. Flemming[2] designated it in terms of normality of the solution, but it seems preferable to express it by the concentration of the hydrogen ion.

Since the above tests indicate that the optimum P_H value for the precipitation of silicic acid is approximately 9.0, the maximum amount of silicic acid ought to be removed when the reaction is carried out at this point, and in order to determine this value more accurately and in the absence of bivalent cations, aluminum hydroxide was precipitated in the silicic acid solution by sodium hydroxide and aluminum chloride, and the relationship observed between the removal of silicic acid, the concentration of the hydroxyl ion and the character of the precipitate.

The acid was prepared by bringing the solution of sodium silicate to a P_H value of 6.5 by the addition of hydrochloric acid. This solution contained 4 mols of silicon dioxide to one mol. of sodium chloride. Two dilutions were used: 87 and 232 parts per million of silicon dioxide. To the silicic acid solution were added water to produce the proper dilution, aluminum chloride and 0.1 N sodium hydroxide solution, which was added drop by drop with constant shaking. After shaking at frequent intervals and standing 48 hours, the reaction was practically complete. The solution was filtered and silicic acid determined in the filtrate. It was noticed in precipitating aluminum from a solution of aluminum chloride, silicic acid and sodium chloride, that the manner of adding the reagents and the relative ratio of aluminum to silicic acid markedly influenced the character and amount of the precipitate.

Poor removal of silicic acid is associated with a turbid colloidal solution and a sticky gelatinous precipitate which is very difficult to filter while a good removal is usually obtained when the precipitate is well flocked and settled quickly from a clear solution which exhibited little

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[1] Determined by the colorimetric method of Clark and Lubs, $P_H = -\log C_H$.

[2] *Z. physik. Chem.*, 41, 443 (1902).

Tyndall effect. In the absence of silicic acid a flocculent precipitate of aluminum hydroxide was produced in a dilute solution of aluminum chloride by $0.1\,N$ sodium hydroxide solution or in a dilute solution of sodium hydroxide by $0.0003\,N$ aluminum chloride regardless of the manner of adding reagent or presence of sodium chloride. If the above solution contained 87 parts per million of silica as colloidal silicic acid, on adding $0.1\,N$ sodium hydroxide drop by drop, a precipitate formed at the end of one hour, depending upon the amount of aluminum chloride in the solution, but if an equivalent amount of $0.1\,N$ or stronger sodium chloride was added all at once no precipitate formed. The later solution showed a very strong Tyndall effect and gradually deposited a small amount of very fine precipitate. One solution was made from which very little precipitate settled at the end of a month. The same effect was produced when sodium hydrogen carbonate or carbonate was used instead of hydroxide.

With calcium hydroxide an excellent precipitate formed regardless of the manner of adding the reagent. There are evidently some complex substances formed under these conditions, which are intimately connected with the sodium ion and the silicic acid. Perhaps the silicic acid in the presence of sodium ions is acting as a protecting colloid preventing in some manner passage of aluminum hydroxide from the colloid into the crystalline condition. In any event, the importance of this fact is quite valuable in obtaining well flocked precipitates. A high ratio of silicic acid to aluminum tends to produce colloidal solutions while the reverse ratio produces nicely flocked precipitates. The magnitude of the Tyndall effect is inversely related to the removal of the silicic acid and the character of the flock or precipitate.

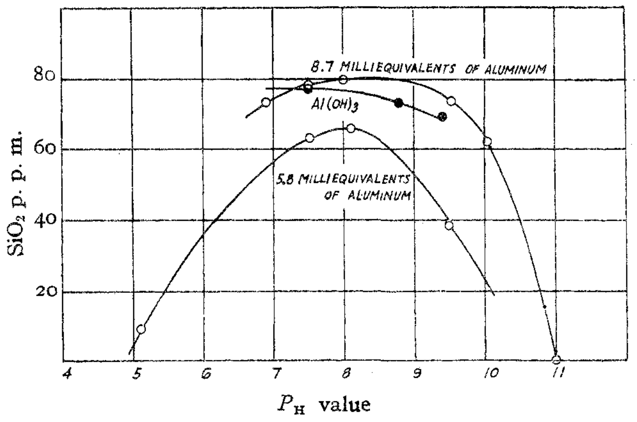

Fig. 1.—Comparison between the P_H value, the precipitation of silicic acid and the amount of $Al(OH)_3$ in the solid phase.

Thus in plotting the curves, Fig. 1, Table I, only the higher concentrations of aluminum salt are used; the lower values are inaccurate because of the formation of colloidal solutions. There is shown in Fig. 1 a third curve, obtained by precipitating the aluminum with ammonia in the absence of silicic acid.

Table I.

Removal of Silicic Acid[a] by Aluminum Hydroxide of Various Hydrogen Ion Concentrations.

Temperature *ca.*23°. Time, 48 hours.

Millequivalents of Al.	SiO_2 precipitated.	SiO_2 in solution.	P_H.
8.73	73	14	6.8
8.73	79	8	7.5
8.73	79	8	8.0
8.73	74	13	9.6
8.73	0	87	11.0 no ppt.
5.82	9	78	5.2 colloidal
5.82	63	24	7.5
5.82	65	22	8.2 colloidal
5.82	38	49	9.5

[a] Concentration of SiO_2 is 87 parts per million.

A study of data and curves indicates (1) that silicic acid is best precipitated at a P_H value of 8.0 to 8.5, (2) that the amount of silicic acid precipitated follows closely the amount of aluminum hydroxide in the solid phase, and (3) that below a P_H value of 4.0 the concentration of the hydrogen ion shifts the reaction so far to the right in the equation:

$$H^+ + AlO_2^- + H_2O \leftrightarrows Al(OH)_3 \; AlO^+ + \leftrightarrows HO^- + H_2O,$$

and that above a P_H value of 11.0 so far to the left that the solid aluminum hydroxide phase is unstable and disappears.

In the region below these curves the tendency to form colloidal solutions is quite marked and the gelatinous nature of the precipitate and the magnitude of the Tyndall effect generally varies inversely with the amount of aluminum ions added to the system and directly as the hydrogen ion concentration departs in either direction from a P_H value of 8.25.

The precipitation of silicic acid by aluminum sulfate may probably be explained by (1) the neutralization of the charge on the silicic acid complex by the aluminum ion, (2) by the neutralization of the negatively charged silicic acid by positively charged aluminum hydroxide, (3) by the solid aluminum hydroxide adsorbing the silicic acid or (4) by the formation of an insoluble chemical compound.

The Coagulating Action of Electrolytes on Clay Suspensions.

If sodium carbonate or an acid be added to a clay which has just enough calcium to keep the colloidal matter in the gel form, it may react according to the following equation:

$$\text{Ca gel} + Na_2CO_3 = CaCO_3 + \text{Na}_2\text{ gel}$$

or

$$\text{Ca gel} + \text{Acid} = \text{Salt} + \text{H}_2\text{ gel}$$

Much valuable information is available in the ceramic researches on the action of salts on clay suspensions. The work of many investigators on clay slips (a suspension of clay in water whose consistency is that of thick cream) indicates that sodium, potassium and lithium hydroxides, carbonates, silicates and sulfides generally have a high dispersive or stabilizing power while the most active coagulating agencies are the salts of the bivalent and trivalent cations especially in the presence of a high concentration of hydroxyl ions.

The above agrees with the statements of Mayer, Schaffer and Terroine[1] that the addition of a trace of alkali decreases the size of the negative suspended particles and Hardy's conclusions that the coagulation of a negative sol varies directly as the valence of the cation and that the action of the anion obeys the regular ionic laws.

The above observations were obtained from rather concentrated clay suspensions where the ultimate end was the formation of a stable fluid slip of the highest clay content. In water purification, on the other hand, the aim is the removal of a very small amount of colloid material from a large amount of water. It is clearly evident from a study of dilute clay suspensions and colloidal silicic acid that the physical state of the substances and their chemical properties must be taken into consideration, and the factors which influence them, *i. e.*, (1) degrees of dispersion, (2) the presence of the protective colloids and adsorbed substances, (3) magnitude and kind of electric charge, (4) the liquid or dispersing medium, (5) the ionic content of the liquid, (6) the concentration, (7) the temperature and (8) the speed of reaction of added substances.

Washed potters clays were used in making the suspensions. Tennessee ball clay Nos. 1 and 3 remained longest in suspension. Ashley rates the latter as having a relative colloid content of 95 to 100%. The clay was freed from large particles and soluble salts by washing with distilled water and running the suspension through a Sharples supercentrifuge; the desired end being a suspension as nearly like that in surface waters, but free as possible from electrolytes. These suspensions had turbidities of 400 to 420 and coefficients of fineness of 0.79 to 0.81. Standards for determining turbidities were prepared from original clay suspensions and checked with a standardized turbidimeter.

Fine particles of various sizes in suspension do not settle uniformly leaving a clear supernatnant liquid, but are deposited in layers or zones. Those particles of approximately the same diameter will settle together leaving a turbid suspension of finer particles above. In a suspension one

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[1] *Compt. rend.*, **145**, 918 (1907).

can observe 2 or 3 of these zones of widely different turbidities and rates of sedimentation. Within a zone the turbidity is fairly uniform, but different zones vary as much as 100% within a vertical distance of 1/2 inch.

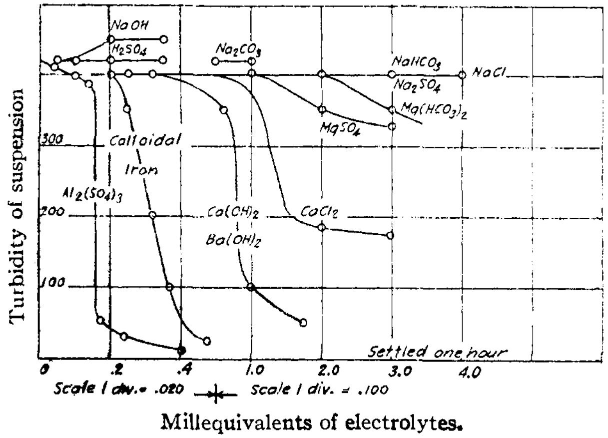

Fig. 2.—Effect of electrolytes on the coagulation and settling of clay suspensions.

It was necessary to determine the turbidity of a suspension without disturbing the liquid. A beam of parallel rays of light 3/16 inch in diameter from a stereoptican equipped with a 500-watt lamp was projected through the standard and sample, parallel to and 1/2 inch below the surface of the liquid in the bottles, and the turbidity determined by observing the intensity of this beam of light.

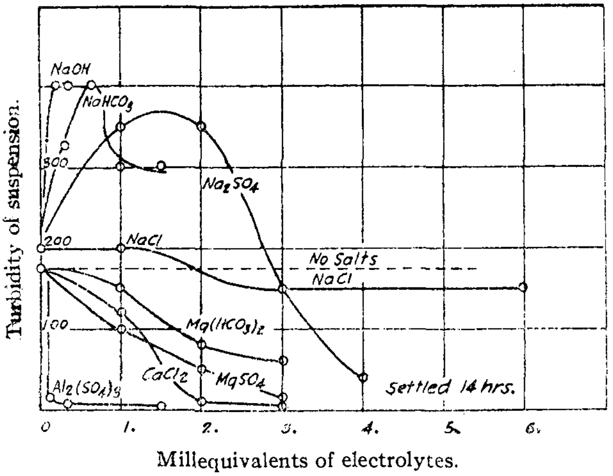

Fig. 3.—Effect of electrolytes on the coagulation and settling of clay suspension.

Reagents were added to 100 cc. portions of the clay suspension and thoroughly mixed by shaking for one minute; the samples were then allowed to remain perfectly quiet at room temperature and the turbidity of the liquid determined at appropriate intervals. All results are expressed as turbidities in parts per million and milligram equivalents per liter, except in the case of silicic acid, which is in parts per million of silica.

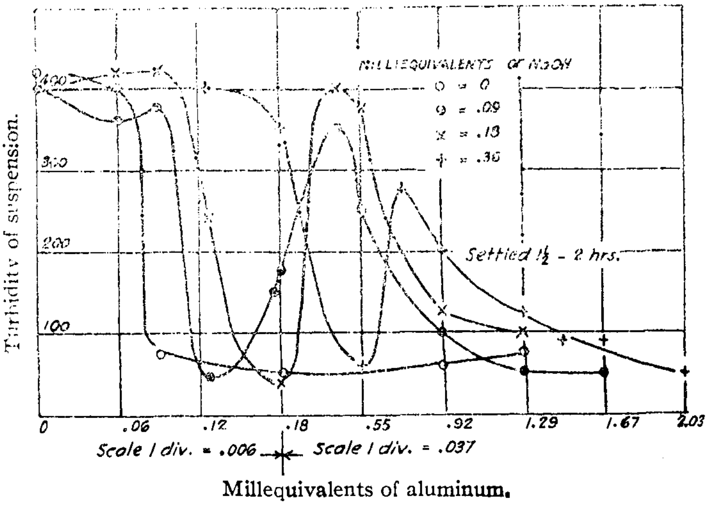

Fig. 4.—Effect of NaOH on the coagulation of a clay suspension by $Al_2(SO_4)_3$.

The action of salts on the coagulation of clay suspensions is shown in Figs. 2 and 3, and their action when the suspensions were coagulated by aluminum sulfate in Figs. 4, 5 and 6. These figures show in graphic form data from many experiments.

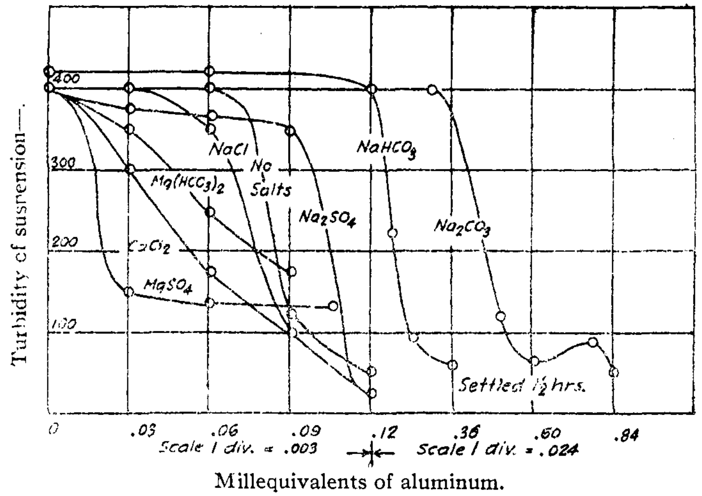

Fig. 5.—The effect of the addition of one millequivalent of electrolytes on the coagulation of clay suspension by $Al_2(SO_4)_3$.

The salts arranged according to their efficiencies as coagulants are aluminum sulfate, calcium and barium hydroxides, calcium chloride, magnesium sulfate and magnesium and calcium hydrogen carbonates. The coagulative powers of calcium and barium hydroxides are practically the same and the ratio of aluminum to calcium and barium ions is about five to one. Sodium chloride has little effect until its concentration becomes large. Sulfuric acid has no apparent effect up to a concentration of 0.35 millequivalents, but higher amounts coagulate the colloid. Sodium hydroxide, carbonate, acid carbonate and sulfate have at first a stabilizing influence followed by a coagulating effect, the hydroxide showing this action the greatest and the sulfate the least. The coagulating effect of anions seems to be an inverse function of their valences, since sodium sulfate disperses and sodium chloride does not.

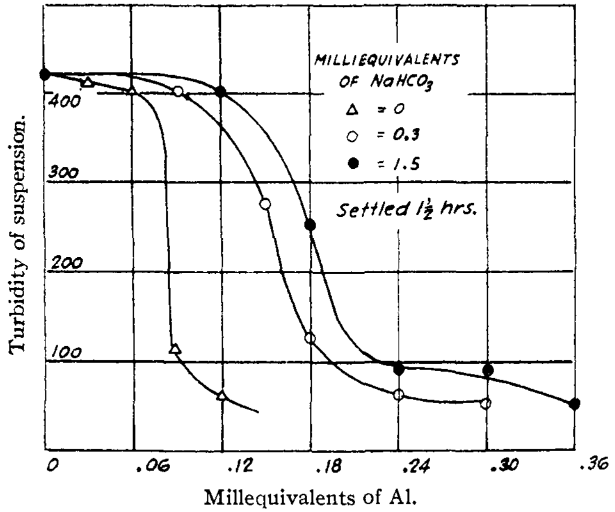

Fig. 6.—Effect of $NaHCO_3$ on the coagulation of clay suspension by $Al_2(SO_4)_3$.

It is noticeable that this order is similar to that given above where the clay suspension was coagulated by the salt alone. Salts containing the bivalent cations, *i. e.*, calcium chloride, calcium hydrogen carbonate, magnesium sulfate and magnesium hydrogen carbonate, aid in the coagulation by alum and increase the rate of reaction; sodium chloride aids slightly; while sodium hydroxide, carbonate, hydrogen carbonate and sulfate prevent coagulation and retard the rate of reaction. In general, the magnitude of the effect is proportional to the concentration of the salts, but in the case of sodium hydroxide and carbonate, this is by no means true. With a given sodium hydroxide content and the addition of graded amounts of alum, there is first dispersion then coagulation, followed by a second disperse phase (not as stable as the first) and coagulation. See Fig. 4.

A third disperse state was not obtained by increase of alum or sodium hydroxide. As the content of sodium hydroxide is increased, additional amount of aluminum sulfate must be added in order to produce coagulation and to combat the dispersive action of the hydroxide or sodium compound. The concentration of chemicals necessary to produce coagulation does not vary with the alkalinity of the solution. Coagulation seems to be a function of the concentration of the hydroxyl ion and alkali metal ion as well as the cation and its valence. The monovalent ion of the alkalies in the presence of high hydroxyl ion concentration or *vice versa,* is intimately connected with dispersive or protective action in the coagulation of clay suspensoids and probably with the peculiar (protective) effect of silicic acid in preventing the formation of aluminum hydroxide. If calcium is substituted for sodium these peculiar effects are not produced.

Effect of Silicic Acid on Coagulation.

The effect of silicic acid on the coagulation of clay suspensions by aluminum sulfate is in all cases to retard the reaction and more aluminum sulfate is required to coagulate than before, regardless of the presence or absence of electrolytes. This is shown in Tables II and III, and Fig. 7.

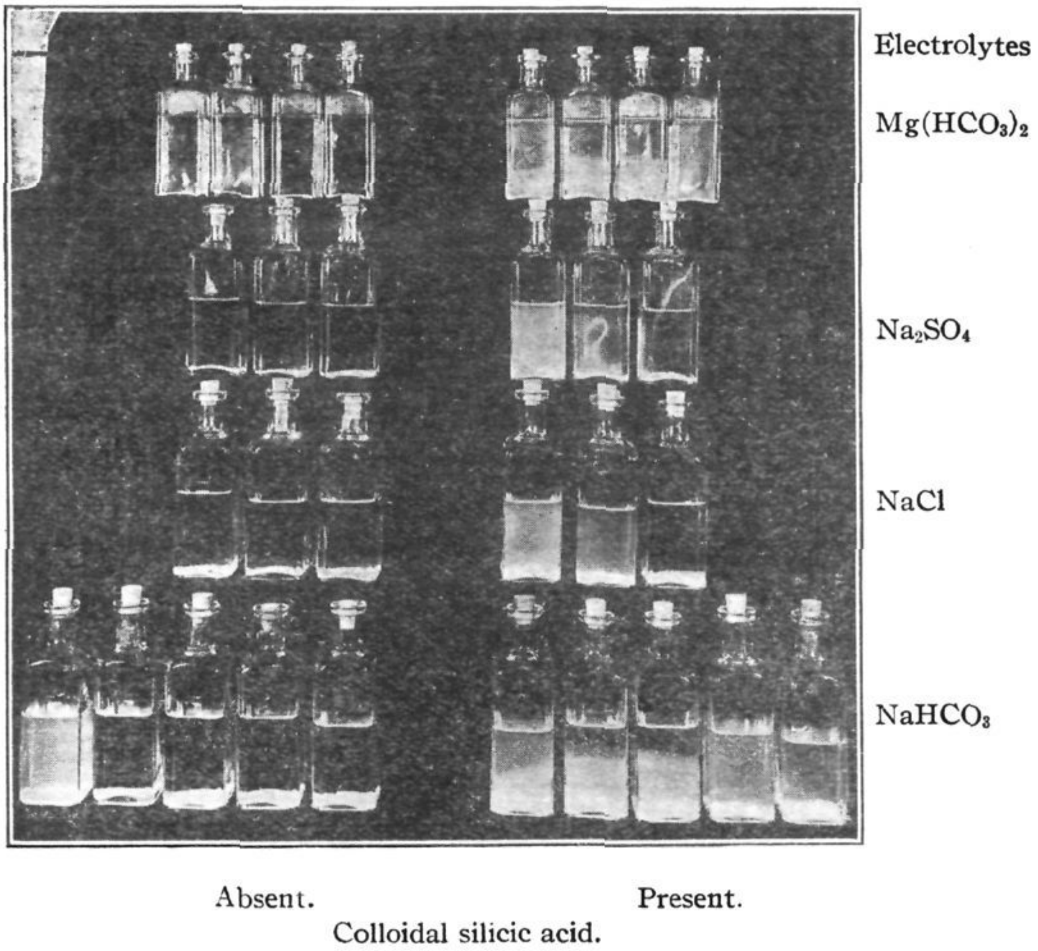

Fig. 7.—The effect of silicic acid on the coagulation of clay suspensions by $Al_2(SO_4)_3$.

The photograph was taken 5 days after the addition of the aluminum sulfate; 62 parts per million of silicic acid (SiO_2) was added to the samples on the right.

The aluminum consumed is a function of the silicic acid added, but the mathematical relationship is not a simple one and varies with the clay used. This relationship is shown in Table II. In general, the amount of aluminum required to coagulate per unit amount of silicic acid added, is larger at low than at high concentrations. Silicic acid does not seem to stabilize or disperse the clay particles, as its presence does not influence the rate of sedimentation. In this respect it differs from the alkali salts.

Applications.

Removal of Silicic Acid from Water to be Used for Boiler Purposes.—The experiments on natural waters indicate that silicic acid could be most economically removed by aluminum hydroxide formed in the reaction of aluminum sulfate with calcium hydroxide in a solution whose P_H value is 8.0 to 9.0 and that the precipitation is more or less directly related to the ratio of (Ca + Mg) : Na. The higher this ratio the more complete is the removal. In one particular case by the proper treatment with aluminum sulfate and lime it was possible to reduced the silicic acid content from 82.6 to 30 parts per million with 6 grains per gallon of aluminum sulfate and the necessary amount of lime to soften.

TABLE II.

Retarding Effect of Silicic Acid on the Coagulation of Clay Suspension by $Al_2(SO_4)_3$.

Silicic Acid (SiO_2) Added.

Mg. equivalents of Al.	0 p. p. m.		12.4 p. p. m.		37.2 p. p. m.	
	1 hr.	24 hrs.	1. hr.	24 hrs.	1 hr.	24 hrs.
0.03	400[a]	200	...	...	...	...
0.09	175	5	350	100	...	...
0.12	30	5	325	50	350	100
0.15	...	...	200	25	350	100
0. 8	...	...	75	5	350	100
0.21	...	...	40	5	212	40
0.24	...	...	40	5	100	30
0.27	...	...	...	...	50	20

The Amount of $Al_2(SO_4)_3$ Necessary to Produce a Definite Clarification in One Hour in the Presence of Silicic Acid.

SiO_2 added. P.p.m.	$Al_2(SO_4)_3$ added to reduce turbidity to 50 p. p. m. Mg. equivalents.
0	0.115
12.4	0.200
24.8	0.240
37.2	0.270
49.6	0.330

[a] Turbidity of clay suspension.

TABLE III.

Retarding Effect of 62 p. p. m. Silicic Acid on the Coagulation of Clay Suspensions by $Al_2(SO_4)$ in the Presence of Electrolytes.

Milligram Equivalents of Salts.

Milli-equivalent of Al.	1.5 $NaHCO_3$.		2 NaCl.		2 Na_2SO_4.		2 $Mg(HCO_3)$.
	Dialyzed Silicic Acid—p. p. m. as SiO_2.						
	0	62	0	62	0	62	62
0.03	...	...	350	350	400	400	400
0.06	400	400	...	350	...	400	400
0.09	...	...	350	325	75	400	...
0.12	...	...	...	325	...	350	350
0.15	...	...	...	...	25	25	...
0.18	400	400	35	125	...	...	300
0.21	...	...	...	...	10	10	...
0.30	5	400	35	15	...	...	...
0.39	65	350	...	...	...	...	...
0.60	65	300	...	...	...	...	...

Readings expressed as turbidity. Time, 3 hours.

The Coagulation of Waters Containing Colloidal Clay.—The stability of a suspension of clay seems to be intimately and directly connected with amount of monovalent cations and bivalent anions present. Thus the alum needed to coagulate will be greater the larger the concentration of sodium ions except in the case when the anion is mainly chlorine. Less alum will be needed as the ratio of the calcium and magnesium ions to the sodium ion increases. As the silicic acid content increases more alum will be required to coagulate. In concentrations up to 20 parts per million, from 0.015 to 0.03 milligram equivalents of aluminum per 10 parts of silica is needed to cancel the influence of the silicic acid.

Water containing bivalent ions when treated with alum gives a sharp abrupt reaction; an increase of 0.03 milligram equivalents of aluminum coagulates but when silicic acid or alkalies are present, other factors being constant, a much larger amount of alum is necessary to produce the same clarification and the abruptness of the reaction becomes less as the amount of the silicic acid and alkalies approaches a certain maximum where the magnitude of the change produced per unit amount of alum is much smaller than in the former case (see Fig. 6). This phenomenon is exactly similar to that which occurs when "colloidal waters" are coagulated by alum and lime.

These experiments justify the addition of an excess of calcium hydroxide and allowing it to react with the water for some time (8 to 12 hours) before the addition of the alum or ferrous sulfate. This procedure has been effective in purification of water from the Arkansas River at Little Rock, Arkansas, where the suspended material is in a colloidal state and consists largely of a very finely dispersed clay in a concentration of 200 to 400 p. p. m.

Summary.

1. Dilute solutions of dialyzed and undialyzed silicic acid behave towards electrolytes in the same manner as concentrated solution with the exception that proportionally more reagent is needed.

2. The optimum hydrogen ion concentration for the precipitation of the aluminum hydroxide and the removal of silicic acid by aluminum hydroxide is a concentration of 1×10^{-8}.

3. The limiting values of the hydrogen ion concentration, between which the solid aluminum hydroxide phase is present, are 1×10^{-4} and 1×10^{-11}.

4. The presence of silicic acid prevents the formation of a precipitate of aluminum hydroxide, when the sodium hydroxide, equivalent to the aluminum chloride present, is added all at once. The silicic acid probably acts as a protective colloid preventing precipitation of the aluminum hydroxide. The presence of bivalent cations destroys this protective power.

5. The action of electrolytes on clay suspensoids is the same in dilute as in concentrated suspensions.

6. Sodium hydroxide, hydrogen carbonate, carbonate and sulfate stabilize or disperse clay suspensions at one concentration and coagulate at another.

7. The ratio of the coagulating power of calcium and barium hydroxides to aluminum hydroxide is about 1 to 5.

8. Coagulation of clay suspensions is aided by the bivalent and hindered by monovalent cations in the presence of acid carbonate, carbonate, sulfate and hydroxyl anions.

9. Silicic acid retards coagulation of clay suspensoids.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MT. UNION COLLEGE.]

A SURFACE TENSIMETER FOR SMALL QUANTITIES OF LIQUIDS.

BY C. C. KIPLINGER.

Received November 12, 1919.

An instrument for measuring surface tension which requires only a drop or two of the liquid under examination has been developed in our laboratories as an aid in the identification of organic liquids. It comprises a piece of capillary glass tubing 18 cm. long, about 1 mm. internal and 4 mm. external diameter. This is broken very carefully from a long piece by making a minute cut in the glass with a carborundum crystal, then breaking as usual, using all possible precautions to get a clean cut and a right-angled fracture. Several tubes should be broken and the