Summary

1. Blue solutions containing copper have been prepared by the following methods: (a) by dissolving copper hydroxide in concentrated alkali hydroxide; (b) by digesting copper oxide in concentrated alkali hydroxide at 80° to 90°; (c) by electrolyzing concentrated alkali hydroxide between copper electrodes with a high current density at 80° to 90°. The blue solutions obtained by these methods are identical in their behavior. The blue substance which is formed when copper oxide is added to melted potassium hydroxide may be the same as the blue component of these solutions.

2. The blue solutions do not exhibit the characteristic properties of colloidal solutions, particularly those of the solutions of colloidal hydroxide prepared by Ley.

3. Evidence is put forward which indicates that the blue color of the solutions is due to the presence of an alkali salt of cupric acid. The formation of the salt by Method b can be represented by the equation, $CuO + 2OH^- \longrightarrow CuO_2^{--} + H_2O$; by Method c by the equations, $Cu + 2 \oplus \longrightarrow Cu^{++}$, and $Cu^{++} + 4OH^- \rightleftharpoons CuO_2^{--} + 2H_2O$.

4. The solubility of alkali cuprates in alkali hydroxides, though quite low, increases rapidly with the concentration of the hydroxide. The potassium salt is apparently more soluble than the sodium salt.

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THE RELATION OF HYDROGEN-ION CONCENTRATION TO THE FLOCCULATION OF A COLLOIDAL CLAY

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In a recent study in this Laboratory of the minimum amounts of various electrolytes required to flocculate a colloidal clay solution it was found that when dipotassium phosphate was mixed with the colloidal clay in quantities just below that required to cause flocculation and the electrolyte requirement of this phosphated solution then determined, the presence of this salt required the addition of much larger quantities of the other electrolytes than did the untreated colloid.

Two possible explanations were suggested. (1) The protective action might be due to the absorption of the negative phosphate and hydroxyl ions by the negative clay particle, thus increasing its negative charge and consequently the amount of positive ions required to bring it to the isoelectric point. It is a well-established fact that the phosphate ion is held

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[1] The author wishes to express his indebtedness to Professor M. F. Miller for critically reading the manuscript and to his assistant, Franklin Davis, for the determinations of the electrolyte requirement.

very tenaciously by most soils. (2) The higher concentrations of dipotassium phosphate required for flocculation when used alone might be due to its weakly basic reaction, larger quantities being required to bring the colloid to the critical Sörensen value than in the case of a strong base such as potassium hydroxide. This would be in accord with Maschhaupt[2] and others who have shown that small amounts of an alkali tend to stabilize soil suspensions while larger amounts cause flocculation. The increased quantities of other electrolytes required in the presence of the basic phosphate might then be due to its well-known buffer action, larger quantities of either a strong base or a strong acid being required to bring the clay to the critical hydrogen-ion concentrations than in the absence of the buffer salt.

There has been no systematic study of the effect of varying hydrogen-ion concentrations upon the electrolyte requirement of soil colloids, so far as the author has been able to find, although numerous investigators have made interesting observations.

Smith[3] found that salts containing bivalent cations aided in the flocculation of clay suspensions by alum but that sodium hydroxide and sodium carbonate retarded it. Comber[4] found that clay suspensions were flocculated most readily in an alkaline medium but that the degree of alkalinity above a certain critical concentration (obtained with 0.005 *N* ammonium hydroxide) had no effect. Comber estimated the relative flocculating powers of the different electrolytes, however, by observing the rate of settling of the coagulum formed by a decided excess of the electrolyte. Numerous observations in this Laboratory as well as those of Smith,[3] Arrhenius,[5] Burton[6] and others show that the addition of certain electrolytes in excess of the minimum required for flocculation yields a coagulum that settles much more slowly than that obtained when just enough is added to bring the colloid to its iso-electric point. This matter is being investigated further in this Laboratory; preliminary results indicate that the rate of settling cannot be used as a criterion of the flocculating power of an electrolyte, but that it is a distinctly different phenomenon which is probably influenced by the change in volume of the floccules formed on flocculation. A slight excess of electrolyte increases the volume of the floccule and decreases its specific gravity and consequently retards very appreciably its rate of settling. Still larger excesses repress this swelling and cause a zone of more rapid settling. The initial swelling is probably due to the setting up of a Donnan equilibrium between the floccules formed on coagulation and the excess of electrolyte in the solution.

Tartar and Gailey[7] have shown that various acids precipitate sols of mastic and gamboge at the same hydrogen-ion concentration regardless of titrable acidity or the nature of the anion. In their study of the flocculating power of potassium salts all were found to precipitate at the same concentration regardless of the nature of the anion, if all solutions where brought to the same Sörensen value by means of hydrochloric acid.

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[2] Maschhaupt, *Landw. Vers. Sta.*, **83**, 468 (1913).

[3] Smith, THIS JOURNAL, **42**, 468 (1920).

[4] Comber, *J. Agr. Sci.*, **10**, 428 (1920).

[5] Arrhenius, THIS JOURNAL, **44**, 521 (1922).

[6] Burton, "Physical Properties of Colloidal Solutions," Longmans, Green and Co., **1916**, p. 151.

[7] Tartar and Gailey, THIS JOURNAL, **44**, 2212 (1922).

No comparison was made of the flocculating power of the various salts at Sörensen values much above 4.5.

Michaelis and Hirabayashi[8] found in their study of the precipitating power of various salts at various values of hydrogen-ion concentration on mastic sols that the anion was not entirely without effect. Sulfosalicylic acid had an antagonistic action. The activity of the ions was not absolute but could be determined only with reference to the Sörensen value.

In order to understand the apparent protective action of the basic phosphate upon the colloidal clay it is necessary to find out whether the phosphate ion has any specific effect in itself or whether what appears to be a specific effect is in reality due to differences in hydrogen-ion concentration. If the anion has no effect the various acids should flocculate the clay at the same hydrogen-ion concentration and a salt such as potassium chloride should flocculate at the same concentration of potassium ions as does dipotassium phosphate when compared at the same hydrogen-ion concentrations.

This study included, therefore, determinations of the minimum electrolyte requirement with (1) certain acids such as hydrochloric, sulfuric, phosphoric, acetic and citric; (2) mixtures of potassium chloride, potassium hydroxide and hydrochloric acid combined in such proportions that the potassium content was constant and the Sörensen value varied from 4 to 12 and (3) of mixtures of dipotassium phosphate, potassium hydroxide, potassium chloride and hydrochloric acid in which the potassium and phosphate contents were kept constant and the Sörensen value varied from about 4 to 12.

Experimental Part

Preparation of the Colloidal Clay.—The colloidal clay used in this study was extracted from the subsoil of the Putnam silt loam, the predominating soil type on the level prairies of northeastern Missouri, by a method developed in this Laboratory. One part of the fresh subsoil (water content 35%) was agitated in a churn of the barrel type with 5 parts of distilled water for 3 hours. The coarser particles were settled out by gravity in 10 days. All material remaining in suspension after 10 days was siphoned off and passed through a Sharples supercentrifuge, making 32,500 revolutions per minute, at the rate of 1 liter per minute. This centrifuging removed the great bulk of the noncolloidal material. This solution was then passed through the centrifuge a second time at the rate of 250 cc. per minute. The solution emerging was rather viscous, a clear, dark amber in color and apparently homogeneous. No particles could be detected with an oil-immersion microscope. The solution was distinctly acid, p_H about 5.8, and contained but very little organic matter. Other studies indicated that it was largely composed of complex alumino-silicates. It contained 4.817 g. of oven-dry material per 100 cc. It served as a stock solution which was diluted to the concentration desired (0.4%) as needed. Solutions prepared in this way are truly colloidal, showing no tendency to settle out on prolonged standing.

Method of Determining the Minimum Electrolyte Requirement.—Since the amount of an electrolyte required to flocculate a colloid is

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[8] Michaelis and Hirabayashi, *Kolloid.-Z.*, 30, 209 (1922).

generally influenced by the rate of mixing, it was found necessary to mix the electrolyte and the colloid as quickly and as uniformly as possible. This was accomplished by means of a device made as follows: a glass tube about 3 cm. in diameter and 17 cm. long was tightly fitted about half way into the small end of a rubber stopper 35 mm. in diameter; both were then inserted in the small end of the chimney of an ordinary, study lamp. Small bits of paraffin were placed both inside and outside the inner tube and then melted, while the chimney was held upright. This served to fasten the inner tube securely in place and to make a water-tight junction between the stopper, the inner tube and the chimney. The inner tube was calibrated to hold 50 cc. In making a determination the proper quantity of electrolyte was measured into the inner tube and enough distilled water added to make the final volume 50 cc. Fifty cc. of the colloid of twice the final concentration desired was then transferred with a pipet into the space between the outside of the inner tube and the chimney. A stopper was then placed in the large end of the chimney and the latter quickly inverted thrice. The colloid and electrolyte were very quickly and thoroughly mixed in this way. The solution was then poured into a 100cc. test-tube and allowed to stand undisturbed at room temperature for 24 hours, when observations were taken. The electrolyte requirement was first located between rather wide limits by preliminary trials. Then with the approximate concentration known, a series was prepared composed of 0.1 milliequivalent intervals, in the case of the stronger mixtures, and 0.5 milliequivalent intervals in the case of the poorer flocculants. Results could be easily duplicated within these limits. After the minimum concentration had been determined at least twice, the hydrogen-ion concentration of the supernatant liquid was measured electrometrically and its conductivity determined.

Results with Acids

The results obtained with the various acids show that while the requirement varies widely if expressed in terms of milliequivalents per liter, or total titrable acidity, all of the acids used flocculate at approximately the same hydrogen-ion concentration. Such differences in Sörensen values as appear in Table I are due partly at least to the fact that in the case of the weak organic acids the electrolyte requirement could not be consistently located at closer intervals than 0.5 milliequivalents. The differences are rather small and indicate that the variation in the flocculating power of the acids is due largely to differences in their ability to supply free hydrogen ions. Citric acid is a possible exception. The values obtained with this acid were repeatedly confirmed and in every case a higher concentration of hydrogen ions was necessary than with any other acid. In the last column of Table I are given the differences in Sörensen values obtained with the critical concentration of the acids with and without any colloid present. The differences are significant and uniform in the case of the stronger acids and rather small with the weak organic acids which is probably due to a replenishing of the hydrogen ions removed by the colloid by further ionization of the undissociated acid. With the strong acids ionization is very nearly complete from the start.

TABLE I

RESULTS WITH ACIDS

Acid	Milliequivalents required	P_H with colloid	P_H without colloid	Difference
HCl	0.48 ± 0.02	3.9	3.5	0.4
H_2SO_4	.50 ± .02	3.9	3.5	.4
H_3PO_4 (as monobasic acid)	.73 ± .016	3.7	3.3	.4
H_3PO_4 (as tribasic acid)	2.20 ± .05	3.7	3.3	.4
Acetic	5.5 ± .5	3.8	3.7	.1
Citric	6.5 ± .5	3.2	3.1	.1

Results with Potassium Chloride

The potassium chloride mixtures with Sörensen values less than 6 were obtained by adding graded amounts of hydrochloric acid to constant quantities of a standard potassium chloride solution and diluting to constant volume. The mixtures with Sörensen values greater than 7 were obtained by combining standard solutions of potassium chloride and potassium hydroxide in different proportions, thus varying the hydrogen-ion concentration but keeping the potassium content constant.

TABLE II

EFFECT OF HYDROGEN-ION CONCENTRATION ON FLOCCULATION OF CLAY BY MIXTURES

KCl			K_2HPO_4		
Milli-equivalents K required	P_H	$K \times 10^{-4}$	Milli-equivalents K required	P_H	$K \times 10^{-4}$
0	3.90	..	1.2 ± 0.1	4.24	2.38
0.4 ± 0.05	4.50	1.25	1.5 ± .1	4.26	2.60
0.5 ± .05	4.80	1.38	2.5 ± .1	4.35	3.65
0.6 ± .05	5.20	1.43	16 ± 1	5.71	19.5
0.9 ± .05	5.22	1.74	21 ± 1	7.29	24.4
1.4 ± .05	5.40	2.14	21 ± 1	7.59	25.5
1.5 ± .05	5.82	2.26	21 ± 1	7.81	26.0
1.8 ± .05	6.19	2.54	21 ± 1	8.00	24.4
10.0 ± .1	7.45	14.05	21 ± 1	8.18	24.8
14 ± .5	8.72	19.05	19 ± 1	8.38	22.8
	9.64	18.41	18 ± 1	9.11	21.1
	10.53	18.20	19 ± 1	10.04	21.4
	11.02	18.20	23 ± 1	10.60	23.7
	11.24	18.42	23 ± 1	10.90	24.6
	11.46	19.70	24 ± 1	11.03	26.2
			28 ± 1[a]	8.01	33.3

[a] Contained 42 milliequivalents of PO_4^{---}.

The data given in Table II and plotted in Fig. 1 show that the electrolyte requirement increases gradually with a decrease in hydrogen-ion concentration until the neutral point is approached, then rises very quickly to a constant value. Variations in Sörensen values between 8 and 12 (the maximum attained with a potassium hydroxide solution) had no effect whatever upon the minimum electrolyte requirement. Solutions made up of 9 parts of potassium chloride and only 1 part of potassium hydroxide flocculated at the same concentration of potassium ions as with solutions of potassium hydroxide alone, although 10 times as much potassium hydroxide was required as with potassium chloride alone.

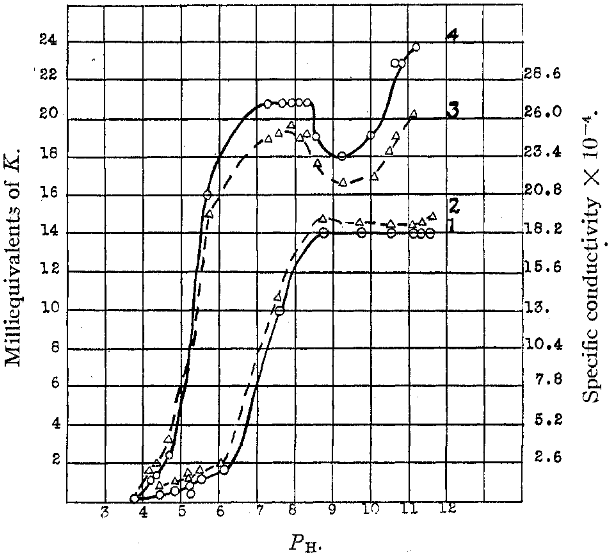

Fig. 1.—The effect of hydrogen-ion concentration upon the electrolyte requirement of a colloidal clay. (1) Electrolyte requirement with KCl. (2) Conductivity with KCl. (3) Electrolyte requirement with K_2HPO_4. (4) Conductivity with K_2HPO_4.

The specific conductivity of the supernatant liquid when plotted against Sörensen value yields a curve which follows the flocculation curve very closely at all points.

Results with Dipotassium Phosphate

All stock solution mixtures used in this study were made 0.2 *N* in both potassium and phosphate (allowing phosphate ion a valence of 3). The more acid mixtures were obtained by adding various quantities of hydrochloric acid to the proper combination of dipotassium phosphate and potassium chloride. The more alkaline mixtures were made by increasing the proportion of potassium hydroxide to potassium chloride added to a fixed quantity of dipotassium phosphate. The average data from a large number of carefully duplicated determinations are given in Table II and are presented graphically in Fig. 1. The phosphate curve shows a sharp change from a zone of low electrolyte requirement to a zone of high electrolyte requirement similar to the potassium chloride curve. It differs from the latter curve in three respects: (1) the break in the phosphate curve occurs at a much higher concentration of hydrogen ions; (2) the electrolyte requirement averages about $^1/_3$ higher than with potassium chloride; (3) the curve is not linear after it reaches the maximum but shows a secondary minimum at P_H 9.5.

The first difference noted is probably due to the fact that the monohydrogen orthophosphate (HPO_4^{--}) ion is strongly absorbed by the colloid while the chloride ion is not. The absorption of the ion, HPO_4^{--} should affect the electrical charge on the particle similarly to the hydroxyl ion. Consequently, much less hydroxyl ion is necessary to bring the colloid to the zone of higher electrolyte requirement in the presence of the ion HPO_4^{--}. With dipotassium phosphate alone, 28 milliequivalents of potassium ion was required for flocculation; with the first 5 mixtures of dipotassium phosphate, potassium hydroxide and chloride in the higher requirement group, 21 milliequivalents of potassium ion was required as compared with 14 for the mixtures of the chloride and hydroxide. This indicated the possibility that the dipotassium phosphate was ionizing into the ions K^+ and $KHPO_4^-$. Conductivity measurements show, however, that the supernatant liquid over the colloid flocculated by 28 milliequivalents of dipotassium phosphate was 33.3×10^{-4}, almost twice as great as that of the mixtures of potassium chloride and hydroxide, while that of the mixtures of all 3 salts, was about $^1/_3$ higher than the mixtures of chloride and hydroxide. It is quite evident then that a higher concentration of potassium ions is present in the phosphate mixtures. This higher requirement is necessary to overcome the effect of the monohydrogen orthophosphate.

The secondary minimum at P_H 9.5 is rather difficult to account for. Conductivity measurements of the various alkaline mixtures at a concentration of 20 milliequivalents per liter show no break at P_H 9.5, which indicates that the break obtained in the flocculation curve is not due to changes in the degree of dissociation with an increase in the P_H value.

Both the conductivity and the hydrogen-ion concentrations were measured after the solutions had been mixed for 24 hours. Wendt and Clarke[9] obtain a somewhat similar break in titrating phosphoric acid with calcium hydroxide. Additions of the basic solution made the solution more acid, due probably to molecular rearrangement. This break disappeared on standing. Some such reaction may be responsible for the apparent abnormality in the phosphate flocculation curve. It may not have been de-

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[9] Wendt and Clarke, This Journal, **45**, 882 (1923).

tected in the hydrogen-ion concentration measurements because these measurements were not made until 24 hours after mixing. A qualitative test shows that quite appreciable quantities of aluminum go into solution in weakly alkaline media. In the presence of phosphates the insoluble aluminum phosphate might be formed. The values obtained were repeatedly confirmed so there seems to be little reason to doubt that a higher concentration of potassium ion is required to flocculate the colloidal clay in the presence of the phosphate ion than in the presence of the chloride ion even when compared at the same hydrogen-ion concentration.

Discussion

Considerable recent work on colloids tends to show that many of the so-called specific effects attributed to the ion of the same sign as the colloid are in reality due to differences in the hydrogen-ion concentration and that if the efficiencies of the different salts of the same metal are compared at the same hydrogen-ion concentration these so called specific differences will disappear. The data presented in this paper indicate that this view is not strictly true with colloidal clay when phosphate salts are used. Differences are encountered which seem to be due to the specific action of the phosphate ion. The situation is apparently complicated in the case of colloidal clay by the formation of insoluble phosphates with the metals liberated by the potassium ion in the basic exchange.

The apparent protective action observed at the beginning of these studies seems to be due both to the buffer action of the phosphate, and to some secondary reactions peculiar to the phosphate ion.

Summary

1. Hydrochloric, sulfuric, phosphoric and acetic acids flocculated colloidal clay at about the same Sörensen value but greater acidity was required with citric acid.

2. Changes in Sörensen value from 6.2 to 8 increased the electrolyte requirement 10-fold in the case of mixtures of potassium chloride and hydroxide. Further increases in alkalinity were without effect.

3. Dipotassium phosphate mixtures showed a similar variation in flocculating power with changes in hydrogen-ion concentration. The phosphate curves differ, however, from the chloride curves in three respects: (1) the break occurs in more acid mixtures, (2) the electrolyte requirement is higher, (3) the curve shows a second minimum in alkaline mixtures.

The results indicate that the flocculating power of potassium salts is influenced by the nature of the anion even when compared at the same Sörensen values. Secondary reactions seem to be responsible.

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