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A STUDY OF THE COLLOID OBTAINED FROM
WEATHERED LIGNITE

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Cecil O. Lohn

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of
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University, North Dakota
August 2, 1932

This thesis, presented by Cecil O. Lohn in partial fulfillment of the requirements for the degree of Master of Science, is hereby approved by the Committee on Instruction in charge of his work.

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II. EXPERIMENTAL

A STUDY OF THE COLLOID OBTAINED FROM WEATHERED LIGNITE

When lignite is exposed to the action of weather it undergoes various changes, probably due to oxidation. Surface beds of lignite are often rejected by the miners as inferior coal, due to the weathered condition. But when this weathered lignite is treated with sodium hydroxide, and the resulting solution allowed to evaporate to dryness, there is left a hard, shiny substance very similar in appearance to hard coal. This dried product has been exploited under the name of Dakolite. When dispersed in water this product makes a very good wood stain.

Tests made on Dakolite show that it has colloidal properties. When the Dakolite is dispersed in water a negative hydrosol is formed, which exhibits the Tyndall effect, precipitated by electrolytes, and can be dialyzed by membranes.

The material used in this study was found in a ditch in western North Dakota. It was in a jelly-like condition when found, but on drying became a hard, shiny substance like Dakolite. It is thought that this jelly-like substance was formed by the action of alkaline waters on weathered lignite. As the alkaline waters flowed over the lignite beds a portion of the weathered lignite was disolved, and as the water evaporated the jelly-like substance was left, which on drying became a hard coal-like material.

This study was undertaken to ascertain the chemical composition and some of the colloidal properties of this substance.

Preparation of Material

Since the material contained impurities, chiefly sand, it was first dispersed in water. The sand and other insoluble matter settled, and the colloidal sol was decanted off. This sol was then flocculated with hydrochloric acid, the amount depending on the concentration of the sol. A concentrated sol takes more acid to flocculate it in proportion to its concentration than does a weak one. The flocculated sol was filtered with suction; washed several times, first with six normal hydrochloric acid, then with dilute hydrochloric acid, and finally washed thoroughly with distilled water. The purpose of the washings was to remove any impurities that may have been carried down by the flocculated colloid.

To obtain a pure dry sample for analysis, the washed flocculated colloid was dried at room temperature for twenty four hours, then in an electric oven at a temperature of 105° Centigrade for three hours. It was then ground in a mortar to a fine powder and placed in the oven again for one hour. The dry powdered sample was kept in a desiccator till used for analysis.

Nitrogen Analysis

Nitrogen was determined as organic nitrogen, ammonia nitrogen, and total nitrogen. Organic plus ammonia nitrogen subtracted from the total nitrogen gives nitrate nitrogen. The Kjeldahl method[1] was used to determine the percentage of organic nitrogen present. By oxidation of nitrogenous organic substances with concentrated sulphuric acid, containing mercuric oxide, the organic matter is destroyed and the nitrogen is changed

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[1] W. W. Scott. Standard Methods of Chemical Analysis v. 1 1927 pp. 339-341.

to ammonia, which is held by the sulphuric acid as sulphate. Concentrated sodium hydroxide is added and the liberated ammonia is distilled into a measured volume of standard hydrochloric acid. Excess acid is titrated against sodium hydroxide using Methyl Red or Alizarin Red as indicator. To get the total nitrogen, salicylic acid (or zinc dust) is added previous to the oxidation process to reduce the nitrates. Concentrated sodium hydroxide added to the sample liberates the ammonia present which on distillation is received in a measured volume of standard acid and titrated. From this known amount of ammonia the nitrogen (present as ammonia) is calculated.

The results as given in Table I show

1.233% organic nitrogen
.042% ammonia nitrogen
.264% nitrate nitrogen
1.539% total nitrogen

Scotts[2] method of combustion analysis was followed to determine the percentage of carbon and hydrogen. A standard gas heated combustion apparatus was used. The weighed sample (.2 to .3 grams) is inserted in the end of the tube near the copper oxide wire (the copper oxide wire should be red hot and the lead chromate at a dull red heat), then pure oxygen is aspirated through at the rate of three bubbles per second. The burner flames are gradually increased, starting back of the boat, and the heat is continued for two minutes after the sample ceases to glow. All burners are then turned off and 1200 cubic centimeters of

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[2] W. W. Scott, loc. cit., pp. 119-120.

Table 1
Nitrogen Analysis

Weight of sample in grams	c.c. of .1063 N HCl used	Weight of nitrogen in grams	Percent of Nitrogen
		Organic Nitrogen	
1.020	8.95	.015000	1.5000
1.021	14.12	.023014	1.5000
1.220	15.04	.018132	1.2060
1.070	10.55	.015320	1.340
		Ammonia Nitrogen	
2.792	.80	.00119	.042
		Total Nitrogen	
2.0000	19.34	.02070	1.001
2.0055	21.00	.03139	1.547
			av. 1.570

Table 2
Combustion Analysis

Weight of sample in grams	Increase in weight of $CaCl_2$ tube in grams	Increase in weight of KOH bulb in grams	Percent Hydrogen	Percent Carbon	Weight of ash in grams	Percent Ash
.2243	.0604	.5475	2.781	61.[illegible]	.0097	4.014
.2195	.0570	.5502	2.901	61.[illegible]	.0091	4.140
.2[illegible]	.0764	.6[illegible]	[illegible]	61.733	.0124	4.095
.2268	.0604	.7426	2.[illegible]	63.509	.0130	5.910
.2092	.0600	.4750	[illegible]	61.[illegible]	.0[illegible]	6.111
		av.	2.[illegible]	61.159		4.[illegible]

air aspirated through. The bulbs are allowed to come to room temperature, wiped, and weighed. The increase in weight of the calcium chloride tube is due to absorbed water, and the increase in weight of the potassium hydroxide bulb is due to absorbed carbon dioxide. Care was taken to refill the potassium hydroxide bulb with fresh thirty percent potassium hydroxide when it became saturated with carbon dioxide. Potassium permanganate added to the potassium hydroxide gives it a green color which changes to an orange-yellow color when the potassium hydroxide becomes saturated with carbon dioxide. Two trials can be made before the color changes. If the color changes while a determination is being made, the determination must be thrown out.

Two trials were made using pure Benzoic acid to see that the apparatus was working all right. The first trial gave values of 66.38% carbon and 4.94% hydrogen and the second one 66.31% carbon and 5.03% hydrogen. As the theoretical percentage of Benzoic acid is 68.81 for carbon and 4.75 for hydrogen the above results are sufficiently close to assume the apparatus is working all right. Several determinations were then made on the moisture free colloid. Some trials gave values ranging as low as fifteen percent carbon, but the color in the potassium hydroxide bulbs had turned before the determinations were complete. Also if the oxygen is bubbled through too fast there is incomplete absorption. The five trials on the same sample (a sample is the amount of dried colloid obtained from the washed flocculated sol. When another portion of the colloid is dispersed, flocculated, washed, and dried it is a different sample.) as shown in Table 3 gave an average carbon content of 61.949%, and a hydrogen content of 2.824%. The ash was weighed each time and the average percentage of ash was 4.056. A different sample of colloid gave values ranging as high as 65.% carbon, and nearly 3.% hydrogen. The ash content also was a little higher.

By adding the percentages of Carbon, Hydrogen, Nitrogen and ash and subtracting from 100% we get 29.583% which is assumed to represent the organic oxygen in the substance.

Carbon	Percentage Composition	Atomic Weight	Atomic Ratios
Carbon	61.949	12.	5.162
Hydrogen	2.824	1.008	2.801
Oxygen	29.582	16.	1.849
Nitrogen	1.589	14.008	.1134
Ash	4.056	——	——

Multiplying each ratio by ten gives us an approximate formula of $C_{51}H_{28}O_{18}N$. The ash is not taken into consideration in arriving at this formula; it is also assumed that the substance is a single compound, which it most likely is not.

General Tests

When a portion of the dried colloid was heated in a hard glass test tube water vapor and a white sublimate collected on the side of the tube. A gas (probably methane), that burned at the mouth of the tube, was evolved. A tarry odor was also present.

To determine the amount of volatile matter[3] present a weighed sample of the dried colloid was slowly heated (in a covered crucible) for three minites; then with the full flame for seven minites. The three trials as shown in Table 3 gave an average of 41.700% volatile matter. Taking the percentage of ash as 4.232 (which is the average of all the ash determinations) leaves 54.068% fixed carbon. These determinations were based on a moisture free sample.

Table 3

Volatile Matter

Trial Number	Weight of sample in grams	Weight of volital matter in grams.	Percent of volatile matter
1.	.9298	.3868	41.600
2.	1.2328	.5144	41.726
3	.7974	.3331	41.773
			Average 41.700%

A part of the washed floculated colloid was hydrolyzedby boiling for six hours with twnety percent hydrochloric acid; another part was boiled with 1:1 sulphuric acid.

The purpose of the hydrolysis was to break up any complex proteins to simple proteins and to reduce any polysaccharides to monosaccharides, which could be tested for.

Various t ests for proteins and sugars were made upon the hydrolyzed portions but they were all negative.

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[3] W. W. Scott. Standard Methods of Chemical Analysis. v. 2. 1927. pp. 1618-1619.

Millons test[4] for proteins showed there was no hydroxy phenyl group (C_6H_4OH) present.

The Xanthoproteic reaction[5] for proteins showed there was no phenyl group (C_6H_5) present.

Van Slyke's[6] nitrous acid test showed no simple aliphatic proteins present.

Bromine water made alkaline with sodium hydroxide did not react with either the hydrolyzed portions or the colloidal sol itself, which also shows no aliphatic proteins present.

Fehlings[7], Benedicts[8], and BarFoeds[9] tests on the hydrolyzed portions were all negative, showing no sugars were present.

We saw by the combustion analysis that the percentage of ash was 4.036. An analysis was now made to determine the composition of the ash. As the ash had a reddish hue (which seemed to vary in different samples) a qualitative test for iron was made. The ash was dissolved in one tenth normal hydrochloric acid. Potassium ferrocyanide added to a portion of the solution gave a blue color, while potassium ferricyanide gave a green color, showing ferric iron was present. The amount of iron was then quantitatively[10] determined. A weighed sample of thoroughly ashed colloid was treated with hot water and twenty percent hydrochloric acid. The

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[4] Hawk and Bergeim. Practical Physiological Chemistry, 1931, p. 126
[5] Ibid., p. 126.
[6] Ibid., p. 91.
[7] Ibid., p. 55.
[8] Ibid., p. 53.
[9] Ibid., p. 55.
[10] American Public Health Association. Standard Methods of Water Analysis. pp. 46-47.

solution was filtered into a fifty cubic centimeter Nessler tube, two drops of potassium permanganate were added, then distilled water to the mark. A standard was prepared similarly, then five cubic centimeters of thiocyanate were added to the standard and unknown at the same time. Care was taken to add an equal volume of acid to both the unknown and standard to prevent any error due to iron in the acid. The four trials as shown in Table 4 gave an average iron content of 3.283% of the ash or 0.130% of the colloid. The average percentage of ash was 3.910.

Table 4

Iron Content of Ash

Trial Number	Weight of sample in grams.	Weight of ash in grams	Percent of ash	Weight of iron in milli-grams	Percent of iron in ash
1	1.0100	.0386	3.821	1.282	3.321
2	1.0698	.0394	3.683	1.242	3.153
3	1.6500	.0674	4.084	2.2314	3.310
4	.6462	.0262	4.054	.8772	3.348

The flame test indicated sodium was present. To determine it quantitatively, a volumetric method as developed by Dobbins and Byrd[11] was used. This method is based upon the precipitation of sodium as sodium zinc uranyl acetate, and the subsequent titration of the uranium by standard sodium hydroxide.

The sodium salt was disolved from the ash by successive washings with hot water. The volume was then evaporated to three cubic centimeters

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[11] J. A. C. S. v. 53, no. 9, September 1931, pp. 3288-3291.

and the precipitation reagent added (one cubic centimeter for each milligram of sodium present--after the first trial one can tell how much to add) care being taken to keep the solution in an ice bath as the sodium zinc uranyl acetate is appreciably soluble above twenty degrees centigrade. After an hour the solution was filtered through a Gooch crucible, and the precipitate washed first with the mother liquor, then with alcohol saturated with the triple salt. The precipitate, dissolved in 100 c.c. of water was titrated with sodium hydroxide using phenolphthalein as indicator. The reaction equation is $NaZn(UO_2)_3(C_2H_3O_2)_9 + 10NaOH = Na_2U_2O_7 + 9NaC_2H_3O_2 + ZnSO_4 + 5H_2O$. Since the ratio of the base to the triple salt is 10:1 the possibility of error is greatly reduced. The ratio being 10:1, we divide the milli-equivalents of sodium hydroxide by ten to get the milli-equivalents of sodium. The four trials as shown in Table 5 gave an average of 4.739% sodium in the ash. The ash content was 4.462% of which 14.444% was soluble in hot water.

Table 5

Sodium Content of Ash

Weight of sample in grams	Weight of ash in grams	Percent ash	Weight of soluble ash in grams	Percent soluble ash	Weight of Sodium in grams	Percent Sodium in Ash
7.7802	.3496	4.493	.0491	14.044	.015966	4.566
6.8978	.3022	4.381	.0444	14.692	.0145	4.798
1.3398	.0602	4.495	.0088	14.618	.00290	4.817
3.0144	.1352	4.484	.0195	14.423	.00646	4.777
					Average	4.739

Silica

Scotts[12] method of determining silica was modified. The colloid was ashed in a platinum crucible; the weight of the ash determined; then it was transferred, by washing with hot water and twenty percent hydrochloric acid, to an ashless filter. After several washings the filter paper containing the ash was transferred to the crucible and ashed. The new weight gave the insoluble portion which was treated with one and one-half cubic centimeters hydrofluoric acid containing two drops of sulphuric acid. On evaporating to dryness the loss in weight was taken to represent silica. The two trials as shown in Table 6 gave an average silica content of 38.742% of the ash. The ash content was 4.502% and 27.924% of this ash is soluble in hot water and twenty percent hydrochloric acid. Since 14.444% of the ash was soluble in hot water, then 13.48% was soluble in the acid.

Table 6

Silica Content of Ash

Weight of sample in grams	Weight of ash in Grams	Percent ash	Weight of soluble ash in grams	Percent soluble ash	Weight of silica in grams	Percent silica
1.1543	.0519	4.496	.0145	27.938	.0201	38.728
3.3590	.1513	4.508	.0422	27.910	.0586	38.756

Average = 38.742%

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[12] Scott, W. W., loc. cit., v. 1, p. 446.

A qualitative test for calcium gave negative results. Ammonium oxalate added to a hot water solution of the ash gave no white precipitate which shows calcium was not present. Barium chloride added to a hot water solution of the ash gave a heavy white precipitate, which shows the presence of the sulphate group. The iron and sodium are possibly present as sulphates.

Preparation of a Colloidal Solution

The washed purified colloid does not disperse in water. To bring it into a colloidal solution it is necessary to peptize with sodium hydroxide. Peptization[13] is the transformation of a gel to a sol by the addition of a small quantity of dispersing agent, in this case sodium hydroxide. The peptizer should be capable of chemical reaction with the colloid so as to form a "soluble link" between molecules of the colloid and liquid medium.

A determination was made to find the amount of sodium hydroxide required to peptize the colloid. To weighed portions of the dried colloid, sodium hydroxide (.1012 normal) was added; first in five cubic centimeter protions; then, when nearly all the colloid was brought into colloidal solution, in one cubic centimeter portions. Twenty cubic centimeters of water was also added to each sample. It took 26 c.c. to peptize .501 grams of dried colloid of 51.88 c.c. per gram, and 44 c.c. to peptize .8053 grams or 54.64 c.c. per gram. The average of this sample was 53.26 c.c. of sodium hydroxide to peptize one gram of colloid; or 215.6 milligrams sodium hydroxide per gram of colloid. A different sample required 17 c.c. to peptize .412 grams colloid or 41.26 c.c. per gram; this can be expressed as 167. milligrams of sodium hydroxide per gram of colloid; another sample required 30 c.c. to peptize .780 grams or 38.46 c.c. per gram, which also can be expressed as 155.6 milligrams per gram. The first sample must not have been washed free from hydrochloric acid, as it required 13.4 c.c. more than the average of the other

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[13] H. N. Holmes, Laboratory Manual of Colloid Chemistry.

two samples.

To obtain a sol it is not necessary to weigh the dried colloid and add the required volume of sodium hydroxide to peptize it; instead the jelly-like mass of flocculated colloid after washing, was treated with sodium hydroxide. On standing a few hours any unpeptized colloid would settle out, leaving a pure colloidal solution. The excess of sodium hydroxide was removed by dialysis.

The sol was purified by dialysing the collodion bags[14] of 200 c.c. capacity, for one month. By using a not too concentrated solution of collodion and draining the flasks rapidly, one gets quite thin bags which dialyze much faster, but which require care in handling. The water was changed every hour for the first two days, then for the next four days about every two hours; and after that about three times a day. Tap water was used for the first two days, as the concentration of electrolytes was quite high, then distilled water for the rest of the month. To start with the bags were only half filled with the sol; but by the next day due to so called osmotic pressure they were filled. They were half emptied and again they were filled the next day. This was repeated again, but when the bags filled up there was no more dilution. By leaving the bags filled up (the sol was now about ten times its original concentration) the height of the liquid balanced the so-called osmotic pressure and there was no more dilution. The electrolytes had become quite scarce now so the pressure was reduced. However, by keeping the bags only partly filled the sol would become nearly as

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[14] W. W. Taylor, The Chemistry of Colloids. p. 97.

dilute as water. This was due to increased pressure on the outside because of higher level of water.

During the first stages of dialysis the outer water was colored, the color becoming less as the dialysis proceeded. The finer particles of the sol diffused through the membrane, thereby forming a weak colloidal solution on the outside of the bag. This solution exhibited all the properties of a colloidal solution, but when viewed under the ultramicroscope the particles were barely visible. The conductivity of the outer solution (due to diffused electrolytes) was still noticible after a week of dialysis. Some of the bags appeared to have holes in them out of which little streamers of sol came. After a few days the streamers disappeared; the holes were probably filled with the larger particles of the colloid.

Pressure dialysis could have been arranged to prevent dilution, but a dilute sol was wanted for the various tests performed.

The analysis of the dried colloid was being made while the sol was dialyzing.

Precipitation Tests

This colloid is sensitive to the addition of small quantities of electrolytes, first becoming turbid and then precipitating. Preliminary tests showed that the colloid had a negative charge. It precipitated immediately when aluminum chloride and magnesium chloride were added, but not when sodium sulphate was added. We would also expect the sol to have a negative charge, since it was peptized with sodium hydroxide.

Various electrolytes of different concentrations were added to twenty-five cubic centimeter portions of the sol, and the time noted when precipitation began and when it was complete. Since precipitation depends on the concentration of the mixture, small volumes of salt solution were added to larger volumes of colloid. Also all the salt solutions were added at the same rate, since the rate of adding a precipitating reagent affects its power to precipitate. By adding the reagent slowly it may take twice as much to cause precipitation as when added rapidly.

The precipitating powers of the various electrolytes are shown in Table VII. It will be noticed that potassium sulphate and sodium sulphate do not precipitate unless the concentration of the electrolyte is very high. As this is a negative colloid the negative sulphate ions are absorbed and so tend to peptize. But when the concentration becomes too great precipitation takes place, due to the sodium ions.

The effect[14] of the electrolyte is first of all to diminish the potential difference between the disperse phase and the medium, and precipitation only occurs when the potential difference has been brought sufficiently near to zero. Smaller amounts have practically no effect on the stability of the sol.

No precipitation occurred in three hours when ten cubic centimeters of magnesium chloride (twenty milli-equivalents per liter) were added to twenty-five cubic centimeters of sol, then on heating to boiling there was immediate precipitation. Another twenty-five cubic centimeter portion of sol to which ten cubic centimeters of magnesium chloride were

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W. W. Taylor. The Chemistry of Colloids, p. 97

Table VII
Results of Precipitation Tests

Electrolyte	c.c. of electrolyte added	Volume of sol in c.c.	Time of initial prec. in minutes	Time of complete prec. in minutes
$MgCl_2$	1	25	70	240
(400 milli-equiv.	3	25	14	165
per liter)	5	25	8	120
	8	25	7	105
	10	25	5	105
20 milli-equiv.	10	25	not in two days	
per liter	15	25	not in two days	
$AlCl_3$	1	20	immediately	60
(400 milli-equiv.	2	25	"	35
per liter)	5	25	"	40
	8	25	"	30
6 milli-equiv.	10	25	not in four hours (after boiling)	
per liter				
NaCl	5	25	not in two days	
(400 milli-equiv.	15	25	not in two days	
per liter				
K_2SO_4	5	25	not in two days	
(400 milli-equiv.	10	25	"	
per liter)	15	25	"	
	20	25	"	
Na_2SO_4	15	25	not in two days	
(400 milli-equiv.	20	25	13 "	180
per liter)	100	25		
Lead acetate	5	25	immediately	60
(400 milli-equiv.	10	25	"	45
per liter)				
$Al(NO_3)_3$	10	25	Not in four hours (after boiling)	
(1 milli-equiv.				
per liter)			40	200
	3	25	15	180
HCl .2050 N	8	25	15	160
(200 milli-equiv.	10	25	20	150
per liter)	15	25		

were added did not precipitate in two days. This shows that boiling causes rapid precipitation. Ten cubic centimeters of each of the following electrolytes: sodium, sulphate, potassium sulphate (each with a concentration of 400 milli-equivalents per liter), aluminum chloride (six milli-equivalents per liter), and aluminum nitrate (one milli-equivalent per liter), were added to twenty-five cubic centimeter portions of sol. After three hours they were all heated to boiling, but on cooling no precipitation had taken place. This shows that small amounts of electrolytes have practically no effect on the stability of this colloid.

Table VII shows that aluminum chloride had the greatest power to precipitate, then lead acetate, and least sodium chloride, sodium sulphate, and potassium sulphate. This is in agreement with the fact that trivalent ions have many times greater precipitating power than bivalent ions which again have much greater precipitating power than monovalent ions. In the case of aluminum chloride (400 milli-equivalents per liter) we see that one cubic centimeter added to twenty-five cubic centimeters of colloid causes complete precipitation in sixty minutes, while two and one-half cubic centimeters caused complete precipitation in thirty-five minutes. But when the quantity of electrolyte is increased still more the time for complete precipitation is also increased. It took about two and one-half times as long for complete precipitation when eight cubic centimeters of electrolyte were used as it did when two and one-half cubic centimeters were used. The iso-electric point which is the point of least stability, was probably reached when two and one-half cubic centimeters were used. The rapid addition of an excess of electrolyte probably carried the colloid past the iso-electric point and gave it an opposite charge which was somewhat more stable. We will see by the migration tests that the sign of the colloid does change when an excess of aluminum chloride is added.

The action of hydrochloric acid (209 milli-equivalents per liter) is similiar to that of aluminum chloride. The iso-electric point probably was reached when about eight cubic centimeters of acid were added to twenty-five cubic centimeters of colloid. In the case of magnesium chloride (400 milli-equivalents per liter) the iso-electric point was probably reached when ten cubic centimeters of electrolyte were added.

The solutions of aluminum nitrate (one milli-equivalent per liter) and aluminum chloride (six milli-equivalents per liter) were too weak to cause precipitation. Lead acetate shows the effect of a heavy metal in causing precipitation. It is bivalent but it has a much greater precipitating power than magnesium chloride of the same concentration. The acetate ion also somewhat decreases the precipitating power of the lead ion as organic ions are strongly absorbed. We see that hydrochloric acid has a much greater precipitating power than sodium chloride. As a rule H^+ and OH^- ions are very strongly absorbed[15] (ions that are most strongly absorbed have the greatest precipitating power); hence the precipitating power of acids and bases is not quite of the same order as that of salts in the same valence series.

Migration Tests

Since the colloid has a negative charge we would expect it to migrate

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[15] H. N. Holmes, Laboratory Manual of Colloid Chemistry, P. 53.

to the positive electrode, and it does. We also saw that when excess electrolytes were added to the colloid, a longer time was required for complete precipitation. It was thought that this was due to a reversal of charge. Migration tests were made to find the iso-electric point and see if the charge on the particle was reversed (if the charge was reversed the particle would migrate to the opposite electrode.). The concentration of the hydrochloric acid used throughout the migration tests was .1013 normal. The acid was added by half cubic centimeter portions to twenty cubic centimeters of colloid. That is, one-half cubic centimeter of acid was added to twenty cubic centimeters of sol and the direction of migration noted. Then one cubic centimeter was added to another twenty cubic centimeter portion, then one and one-half cubic centimeters, etc. When the colloid refuses to migrate to either the anode or to the cathode it is at the "Iso-electric point" or the point where it has no charge (the point of least stability).

A reversal of charge did take place, but it was not sharp. After one cubic centimeter of acid had been added, practically all the colloid still migrated to the negative electrode. Taylor[16] says that a charged particle may be attracted to an electrode of the same sign as the particle if the potential difference between them is sufficiently great. This may explain why some particles migrated to the negative electrode. One and one-half cubic centimeters of acid causes the colloid to migrate to

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[16] W. W. Taylor. loc. cit. p.78.

both electrodes, about the same amount to each electrode. Two cubic centimeters of added acid causes most of the colloid to migrate to the negative electorde; a small amount migrated to the oposite electrode. The charge had completely reversed (all the colloid migrated to the negative electrode) when three cubic centimeters of acid were added to twenty cubic centimeters of colloid. The coagulated colloid dropped from the electrodes when the charge was neutralized. This was not immediate and also some coagulated colloid remained at or near the electrode after an hour.

One and one-half cubic centimeters of acid were added to twenty cubic centimeters of the colloid and after two hours, when precipitation had started, a migration test was made. Now the precipitated colloid did not seem to migrate to either electrode.

The colloid precipitated by an excess of aluminum chloride or magnesium chloride migrated to the negative electrode, showing the sign of the charge had reversed.

pH Determinations

A pH determination was made to determine the iso-electric point. A modified hydrogen electrode apparatus was used: the sol being contained in a tube, of about 100 cubic centimeters capacity, to exclude air. Fifty cubic centimeters of sol were used for each determination; the concentration of the hydrochloric acid was .1012 normal. The acid was added from a burette in small quantities, readings being taken after each addition. The results of the three determinations are shown in Tables VIII, IX, and X. These results are plotted in Figure I. The precipi-

Table VIII
pH results of the pure sol

c.c. HCl added	Bridge readings	E – .3028	pH = $\frac{E-.3028}{.0591}$
0	65	.3472	5.874
.5	48	.1972	3.336
1.0	46	.1772	2.998
2.0	45	.1672	2.829
4.0	44	.1572	2.659
6.0	43.5	.1522	2.575
8.0	42.5	.1422	2.406
12.0	42	.1372	2.321
16.0	42	.1372	2.322
20.0	42	.1372	2.321
28.0	41.5	.1322	2.236

Table IX
pH results of the pure sol
Second Trial

c.c. HCl added	Bridge readings	E – .2828	pH = $\frac{E-.2828}{.0591}$
0	67	.3872	6.551
1.0	49	.2072	3.506
2.0	47.5	.1922	3.253
3.0	46.5	.1822	3.083
4.0	45.5	.1722	2.913
6.0	44.5	.1622	2.744
8.0	44	.1572	2.659
12.0	43.3	.1502	2.541
16.0	43	.1472	2.490
20.0	42.5	.1422	2.406
24.0	42.5	.1422	2.406
27.0	42.5	.1422	2.406

Table X
pH results of the pure sol
Third Trial

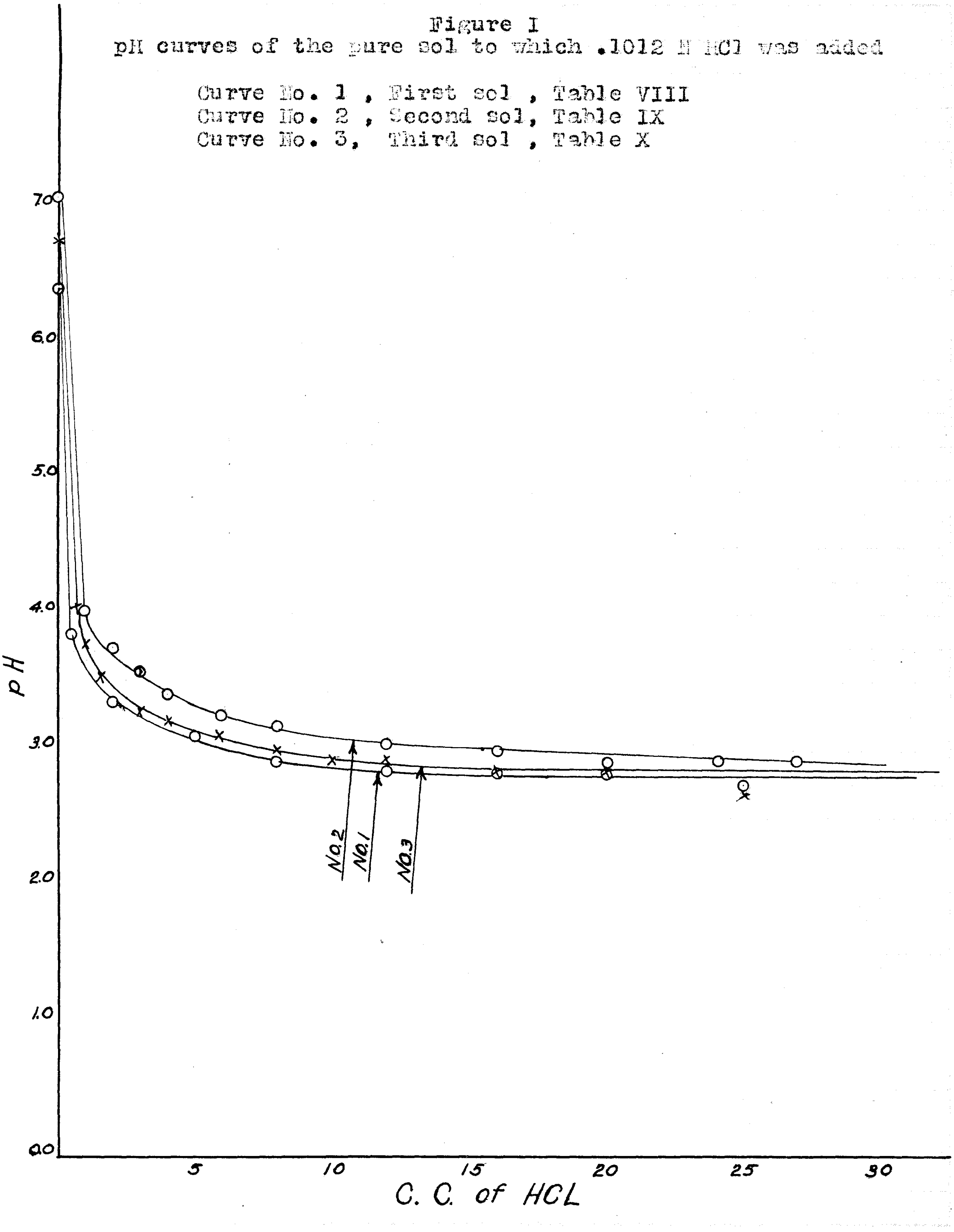
C.C. HCl added	Bridge readings	E - .2828	$pH = \frac{E-.2828}{.0591}$
0	59	.3072	5.198
.5	49	.2072	3.506
1.0	47.5	.1922	3.252
1.5	46.5	.1822	3.083
2.0	45.5	.1722	2.914
3.0	44.5	.1622	2.744
4.0	44.0	.1572	2.660
6.0	43.5	.1522	2.575
8.0	43	.1472	2.491
10.0	42.5	.1422	2.406
15.0	42.5	.1422	2/406
20.0	42	.1372	2.321
25.0	41.5	.1322	2.237
30.0	41	.1272	2.152
35.0	40.5	.1222	2.067

Table XI
pH results of pure water

C.C. HCl added	Bridge readings	E - .2828	$pH = \frac{E-.2828}{.0591}$
0	71	.4272	7.228
.5	49	.2072	3.506
1.0	46.5	.1822	3.083
1.5	45.5	.1722	2.914
2.5	44.5	.1622	2.744
4.0	43.5	.1522	2.575
7.0	43.0	.1472	2.491
10.0	42.5	.1422	2.406
17.0	42	.1372	2.321
22.0	42	.1372	2.321
27.0	41.5	.1322	2.237

Figure I
pH curves of the pure sol to which .1012 N HCl was added

Curve No. 1 , First sol , Table VIII
Curve No. 2 , Second sol, Table IX
Curve No. 3, Third sol , Table X



An attempt was made to determine the particle size by counting the number of particles in a measured volume with the aid of the ultramicroscope. A slit-ultramicroscope was first used (the source of light being a carbon arc), but the particles could not be distinguished very easily. The diffraction rings representing the different particles were of different intensity (some being barely visible). This indicates that the particles were of different size. A paraboloid condenser was tried, so as to use sunlight. The difficulty encountered was that many of the particles precipitated on the glass slide and cover glass. The remaining particles seemed to vary in size. The Brownian movement of the particles was plainly visible in both cases.

Dispersion in Alcohol

The dry colloid was dispersed in alcohol by grinding in a mortor. A thick paste was first formed, which was then gradually thinned by adding alcohol till an alcohol sol was formed. The coarser particles had settled out by the next day leaving the finely dispersed colloid which gave the alcohol sol a rich brown color.

Other organic liquids as benzene, linseed oil, glycerol, carbon tetrachloride, and chloroform were tried as the dispersing medium. The dispersion in benzene and chloroform separates out clear, while a brownish color is left in the linseed oil, carbon tetrachloride, and glycerol. If the colloid is in the alkaline form it will not disperse in any of the liquids but will separate out immediately.

Migration and Precipitation Tests on Alcoholic Dispersion

The dispersed colloid migrated to the anode; the sign of the charge had not changed. Precipitation tests showed that the dispersion was not very sensitive to the addition of electrolytes. All the electrolytes seemed to have about the same effect.

Discussion

The object of this research as stated was to ascertain the chemical composition and some of the colloidal properties of the colloid obtained from weathered lignite.

From the analysis of the dried colloid which gave:

Carbon - 61.949%

Hydrogen - 2.804%

Oxygen - 29.582%

Nitrogen - 1.539%

Ash - 4.050%

we calculated the formula $C_{41}H_{28}O_{18}N$, assuming of course that it was a single compound; probably more likely to be of a multiple ring structure.

The substance was found to contain no hydroxy phenyl or phenyl group as such, and no simple aliphatic proteins. Negative sugar tests showed no sugars to be present. We shall also see that the sodium relation shows these structures to be absent. It was assumed that the hydrolysis would break up any complex protein structure to simple proteins and amino acids, and any polysaccharides to mono saccharides.

The percentage composition of a large number of proteins was found to fall with in the following rather narrow limits.[17]

Carbon - 50-55%
Hydrogen - 6-7%
Oxygen - 19-24%
Nitrogen - 15-19%

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[17] Hawk and Bergeim, loc. cit. p. 83.

The percentage composition of the colloid under study does not compare with the above analysis for proteins, especially in regard to the amount of nitrogen. This would indicate that the colloid is not of protein nature. However, it would be possible to have a protein group hooked up with a complex ring structure. By having a few protein structures in a large molecule would reduce the percent of nitrogen to quite a low value. The protein structures would also have to be so linked that they would not easily be liberated by hydrolysis (protein tests were negative) and the nitrogen would have to be bound so as not to react with nitrous acid (Van Slyke's test was negative).

We found by analysis that the colloid contained 0.21% of sodium. This indicates there are no free carboxyl (COOH) or hydroxyl (OH) groups present as they would react with sodium (the sodium replacing the hydrogen). The percentage of sodium would then be greater. If only one sodium atom was present in the colloid the percentage would be 2.39, but less than ten times this amount was present. So we can assume there are no free carboxyl or hydroxyl groups present.

We also see that the substance was saturated since bromine did not react with the substance when it was treated with bromine water. If the substance had been unsaturated it would have taken up bromine and the bromine water solution would have become less intense in color.

It was previously mentioned that the colloid was not a single compound but probably a complex ring structure of related compounds. The fact that the substance is saturated would point to a ring structure.

One can see that the approximate formula could not exist as a straight chain compound and still be saturated.

The fact that the substance is in colloidal solution indicates either that the molecules are so large that even when dispersed in molecular solution they have properties of size and surface that characterize colloidal particles or else some force is present which makes them form aggregates of colloidal size. With the aid of the ultramicroscope we saw that the particles appeared to be of different sizes, which would suggest molecular aggregates.

The colloid was found to contain 4.23% ash; 13.48% of the ash being soluble in twenty percent hydrochloric acid, 14.444% soluble in hot water, and the remaining 72.076% insoluble. The water soluble portion was possibly chiefly sodium salts, while the acid soluble portion was probably composed of iron salts (possibly some silicates). The insoluble portion was assumed to be chiefly silicates.

In purifying the sol, collodion bags were used for dialysis. It was stated that these bags were only partly filled with the sol at the start of the dialysis, but had to be partly emptied several times or else they would overflow. It would seem that this tendency to dilute was due to osmotic action, but we also saw that this tendency to dilute decreased as dialysis progressed. We see the explanation in the fact that electrolytes although capable of passing through a membrane nevertheless encounter a considerable resistance as compared with water; hence the inflow of water exceeds the total outflow of water and electrolytes and we have dilution. But as dialysis proceeds the concentration of electrolytes becomes less and the tendency to dilute therefore decreases. (It has been shown by numerous experiments that colloids exert very little if any osmotic pressure.)

Precipitation tests show that the colloid carried a negative charge. The great precipitation effect of tri-valent ions and heavy metal ions is well illustrated. The effect of the lead ion in causing precipitation was nearly as great as that of the tri-valent aluminum ion. The acetate ion probably decreased the precipitating power of the lead ion as organic ions are strongly absorbed. And the strong absorption of a negative ion would tend to peptize. The peptizing tendency of the negative sulphate group is shown by the fact that a large quantity of sodium sulphate was required to cause precipitation.

Migration tests showed that the charge on the particle was reversible. The charge was first reduced to zero, which was the iso-electric point, then an added amount of electrolyte caused the particle to become oppositely charged. When the sign of the charge was reversed the colloid was slightly more stable than at the iso-electric point as it required a longer time for precipitation.to take place.

By using the results of the migration tests the pH of the iso-electric point was found from the pH curves of the colloid. The pH of the sol was found to be between 5.874 and 6.551; slightly acid but neutral to litmus. We found previously that the sign of the particle was negative; which is in agreement with the fact that a particle whether neutral or acid in character is negatively charged.

It was previously stated that the tendency to dilute decreased as dialysis progressed, but by testing the concentration of the sol dialyzed for one month and the sol dialyzed for two weeks it was found that the sol dialyzed for two weeks was a little more concentrated. This may have been due to using a more concentrated sol at the beginning of the dialysis. An attempt was made, however, to have each initial concentration about the same by peptizing like quantities of the jelly-like flocculated colloid in equal volumes of water.

Time did not permit the finding of the average particle size by a counting method with the aid of the ultramicroscope. The slit-ultramicroscope was first tried but the light was not strong enough, and the equipment was not available to use the sun as a source of light. The paraboloid condenser did not work very well either. Time was not available to try to remedy these difficulties.

It was found that the colloid dispersed in organic liquids; alcohol being the best medium of dispersion. It was noted that the sign of the charge was the same as when dispersed in water. Sometimes the medium of dispersion causes a change in the sign of the charge. On the whole the dispersions in organic liquids were not very satisfactory.

Summary

1. The dried colloid had the following percentage composition.

Carbon	61.349%
Hydrogen	3.024%
Oxygen	29.302%
Nitrogen	1.538%
Ash	4.836%

2. The hydrolyzed portion of the colloid was found to contain no simple protein or sugar structures.

3. Tests indicated that the substance probably had a complex ring structure or is a series of related ring structures.

4. The substance did not have any free carboxyl or hydroxyl.groups.

5. The charge on the particle was negative.

6. Various electrolytes cause the charge to reverse.

7. The pH of the pure sol was between 6.974 and 6.881.

8. The iso-electric point was found to be between pH 2.6 and pH 2.9.

9. Dispersions in organic liquids were not very satisfactory.

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