[CONTRIBUTION FROM THE VIRGINIA TRUCK EXPERIMENT STATION]

Interrelation of Electrokinetic Behavior and Cation Exchange of Iron Phosphate

BY JACKSON B. HESTER

The fact that soil colloidal materials divide themselves electrokinetically into positive and negative colloids has brought forth some of the most interesting studies and fundamental results in soil research. Since the soil colloids consist principally of silica, humus, phosphates (electronegative material) and the sesquioxides of iron and aluminum (electropositive material), many studies[1] concerning the basic properties of these materials and their combinations have been most gratifying. It has been shown[2] that the seat of base exchange in colloidal material is in the uncombined or free valence of the electronegative materials. This being the case, a combination of materials in a reaction unfavorable for mutual precipitation of the positive and negative colloidal material should give a maximum base exchange capacity for a specific colloid. This paper is a presentation of data attempting to establish this point.

A series of seven precipitations of iron phosphate varying from the distinctly electropositive precipitate to the distinctly electronegative precipitate was made in the following manner. Five millimoles of iron chloride together with hydrochloric acid to produce the acid reaction were diluted to one liter; 10 millimoles of sodium hydrogen phosphate (dibasic) and the sodium hydroxide necessary to produce the alkaline reaction were diluted to one liter and added to 500 cc. of molar ammonium chloride; the two solutions were mixed together in large containers by pouring from one container to the other and back again in rapid succession several times and finally stoppering the mixture in a three-liter Erlenmeyer flask. The ammonium chloride was added to ensure complete precipitation of the colloid.

The above mixtures were allowed to stand overnight and the supernatant liquid was siphoned off. Then the total mass was thrown on a filter paper and the precipitate was allowed to become air dry for further analysis. The cation exchange capacity was determined by saturating the complex to *P*H 7.0 with calcium acetate and replacing the calcium with ammonium chloride.

The composition of each precipitate was determined by analysis and is reported in Table I as molecular formulas.

The water represented in the molecular formula was determined by igniting the material, dried at 108°, at a dull red heat until a constant weight was obtained. The M_2O represents the cation exchange capacity

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(1) Mattson, *J. Phys. Chem.*, **32**, 1532–1552 (1928); *Soil Sci.*, **30**, 459–495 (1930); **31**, 57–77 (1931).

(2) Mattson, *Soil Sci.*, **31**, 311–331 (1931); **32**, 343–365 (1931); **33**, 75–94 (1932).

TABLE I

MOLECULAR FORMULAS BY CHEMICAL ANALYSIS AND THE *P*H VALUE AT PRECIPITATION OF SEVEN IRON PHOSPHATE PRECIPITATES

5 Millimoles of $FeCl_3$, 10 millimoles of Na_2HPO_4, and 500 millimoles of NH_4Cl used in each case with the acid and alkali added to give a final volume of 2500 cc.

			Molecular formula			
No.	Millimoles of HCl and NaOH added	*P*H of medium	F_2O_3	P_2O_5	H_2O	M_2O
1	5	3.1[a]	1	0.946	3.845	0.917
2	2.5	3.7	1	.939	3.645	.864
3	0	4.4	1	.928	3.316	.838
4	5	6.8	1	.895	3.325	.956
5	10	7.5	1	.841	5.165	1.111
6	20	8.0	1	.780	2.803	0.964
7	40	8.7	1	.568	2.630	.734

[a] Determined colorimetrically.

of the colloid. The colloid was air dried before the cation exchange capacity was determined.

System Number 3[3] represents the isoelectric mixture; Numbers 1 and 2 are the most highly electropositively charged colloids. Numbers 4, 5, 6 and 7 are the electronegatively charged colloids.

The formulas in Table I show that there is a slight decrease in the phosphate content of the molecule as the *P*H value of the medium rises. There is, however, only a small change in the phosphate content of the first five precipitates, whereas there is a rather large decrease in the phosphate content of the last two precipitates.

The cation exchange capacity of the colloidal complex is influenced by the reaction of the medium in which it is precipitated. Thus, the isoelectric colloid has a lower cation exchange capacity than the electropositive colloid. The exchange capacity of the electronegative precipitates increases progressively until above reaction *P*H 7.5, after which it decreases, due no doubt to the decrease in phosphate content.

The slight increase of the phosphate ion in the colloid on the electropositive side of the isoelectric point hardly accounts for the increase in the exchange capacity, nor does the increase of phosphate account for the increase in the molecular held water. On the electronegative side of the isoelectric point the phosphate content of the colloidal complex continues to decrease slightly till a reaction of *P*H 7.5 is reached and above this point it decreases rapidly.

Figure 1 shows the relation of the charge on the colloidal particle and the base exchange capacity of the colloid. The cation exchange capacity is calculated on the basis of 5 millimoles of PO_4 and shown in curve C.

Again, in order to show further that the reaction at which the material

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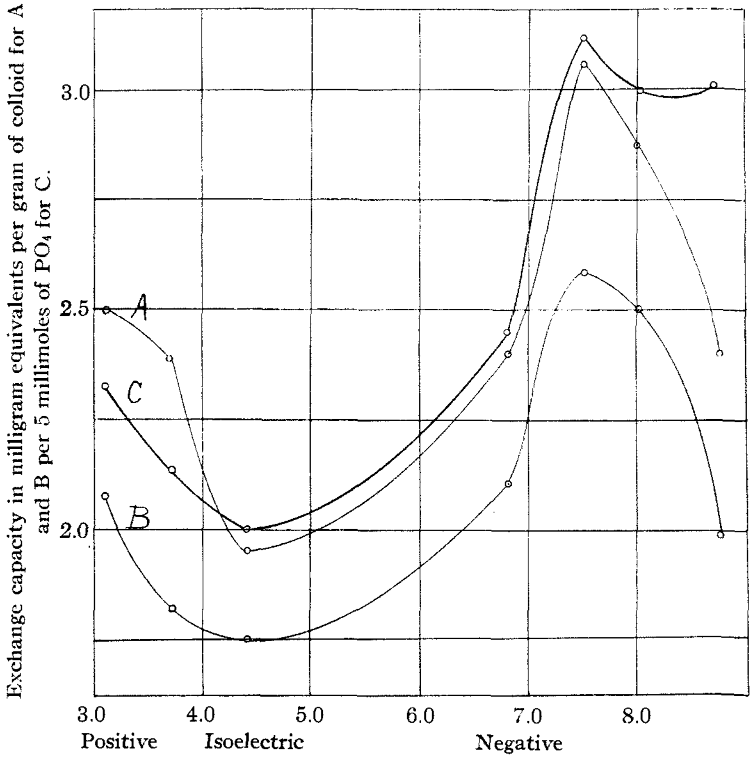
(3) The cataphoretic measurements of the particles were not actually made, but previous work by Dr. Sante Mattson [*Soil Sci.*, **30**, 459–495 (1930)] showed the particles to carry the charges mentioned. The author had the privilege of starting this work in Doctor Mattson's laboratory. The results were repeated and confirmed at the Virginia Truck Experiment Station.

was precipitated influenced the exchange capacity as ordinarily estimated, the calculations were made on the basis of one gram of air-dried material and material dried at 108°. The data are also presented in Fig. 1 as curves A and B.



P_H value at precipitation: A, based on material dried at 108°; B, based on material air dried; C, based on 5 millimoles of PO_4.

Fig. 1.—The cation exchange capacity of iron phosphate.

In connection with the molecularly held water (that water given off by ignition), it will be noted that the water content of the precipitate follows somewhat the same trend as the base exchange capacity. The two curves also show upon interpretation that the water lost from the air-dried material upon heating to 108° is greatest where the cation exchange capacity is the largest.

A survey of the data in Table I and the curves in Fig. 1 shows how the reaction of the medium in which a precipitation takes place alters the combination of the two oppositely charged colloidal materials. At the isoelectric point the two oppositely charged materials carry equal charges and a mutual precipitation takes place. This more complete union makes the isoelectric colloid the more stable colloid. Since the neutralization of the charged colloids is the most complete at the isoelectric point, the free valence is at a minimum, the seat of the base exchange capacity is then at a minimum, and the quantity of combined water is at a minimum for a given colloid.

Summary

The cation exchange capacity of seven iron phosphate precipitates varying from the electropositive to the electronegative combinations was investigated. The data presented indicate that high base exchange accompany high electrokinetic potential, whereas low base exchange is characterized by a low electrokinetic potential.

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The Atomic Weight of Lead from Bedford Cyrtolite

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The lead–uranium ratio in a specimen of cyrtolite from Bedford, N. Y., U. S. A., has recently been determined by Muench[1] to be 0.0513 (Pb 0.374, U 7.29, Th 0.0?). In estimating the age of this mineral it is important to discover by the determination of its atomic weight whether this lead was wholly derived from the disintegration of uranium. An added interest to this determination comes from the fact that the mineral is nearly if not quite free from thorium.

Since cyrtolite consists chiefly of zirconium silicate and is extremely refractory, the extraction of the lead was a matter of some difficulty. The method finally adopted after some exploration was that of treatment with hydrofluoric acid. About 1250 grams was available.

The lumps were first crushed in a previously cleaned jaw crusher. The material was then finely ground in a Quaker grinding mill which had been cleaned by grinding in it several hundred grams of marble. Prolonged digestion in 100-g. portions with hydrofluoric acid in a platinum dish followed. Removal of the hydrofluoric acid was effected by repeated evaporation with concentrated nitric acid. The portion soluble in hot dilute nitric acid was then separated from the very considerable residue of undissolved zirconium silicate.

The lead was next separated and purified by the following processes: (1) double precipitation as sulfide; (2) solution of the sulfide in nitric acid and precipitation of lead chromate in ammonium acetate solution; (3) solution of the chromate in nitric acid and precipitation of lead sulfate; (4) conversion of the sulfate to carbonate by boiling with sodium carbonate

(1) Muench, *Am. J. Sci.*, **21**, 356 (1931).