INFLUENCE OF HYDROGEN-ION CONCENTRATION ON THE ADSORPTION OF PLANT FOOD BY SOIL COLLOIDS

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INTRODUCTION

All know, according to Faraday's researches, that charges accumulate at the surface and, hence, at a boundary between two liquids, two solids, or liquid and solid, and that even between a gas and liquid we have a seat of electrical energy. Some believe that this seat has an electronic origin, while others believe that it is due to the Helmholtz's "double layer." In view of the latter, the charge on the surface of a solid or liquid would imply the existence of an equal and opposite charge on the other side of the interface, for a charge of a particular sign cannot exist without one of opposite sign in its proximity.

Perrin (6) has shown beyond the shadow of a doubt that the electrical charge on surfaces is in reality diminished, neutralized, or even reversed by ions of opposite charge. Acids and alkalies are very active in this power of conferring the electrical charges on surfaces. This is attributed to the fact that the H and OH ions are more readily absorbed than other ions, and, hence, the charge on an absorbent would depend on which of these ions is in excess.

Knud Estrup (4) has done some work along the line just mentioned. He showed that both the cation and anion were absorbed by charcoal in equivalent quantities when he worked with neutral salt solutions, and when the ions were not absorbed in equivalent quantities he attributed the difference to the presence of impurities in the form of acids and bases. In other work (3) with blood charcoal Estrup finds that the negative ion is positively absorbed in acid solutions, but on addition of a base the absorption of the negative ion disappears, giving place to the absorption of the positive ion.

It has been further shown that electrical charges tend to reduce surface tension. V. Boumat (1) finds that acids decrease surface tension and ascribes the fact to the accumulation of H-ions in the surface layer.

From the point of energetics, the following view of electrical adsorption has been formulated: Any process that will reduce the electrical energy at a surface will tend to take place, hence, in the case of a negatively charged surface, we will have positive charges collecting upon it in order to annul its charge, and vice versa. These bodies may be ions or colloidal aggregates.

A great many more or less obscure phenomena in the field of soil chemistry as well as in many other fields have been attributed to adsorption where it was not known whether they had physical adsorption, chemical reaction or an adsorption phenomena which might be attributed to charged aggregates where the adsorbing aggregate had a sign opposite to that of adsorbed substance.

Since it was known that OH and H ions were the most strongly adsorbed ions, and their adsorption should help to determine the charge on the colloid, it became of interest to determine the adsorption by single soil colloids under varying hydrogen-ion concentrations. It was hoped that such work might throw some definite light on how acidity or alkalinity of soil effects adsorption of plant foods, and also the availability of soil salts. A few of the results have already been published in a preliminary paper by Gordon and Starkey (5).

MATERIAL

The salts used were those prepared by the J. T. Baker Company and recommended by the National Research Council. They were the acid phosphates, sulfates and nitrates of potassium and calcium.

The hydrogels used were the hydrogels of silica and iron. The hydrogel of silica was obtained from the Davison Chemical Company. This hydrogel was washed free from all impurities before being used. The hydrogel of iron was prepared in our laboratory by precipitation from ferric chloride solution with ammonium hydroxide and washed free of ammonia and chlorides.

The apparatus used for determining the pH values of the solutions was of the Leeds, Northrup type. The Bailey hydrogen electrode was used in conjunction with a 1 *N* solution of KCl and the calomel electrode as described by Clarke (2). The mixtures of solutions and gels were shaken in 250-cc. ground-glass stoppered bottles with a mechanical shaker making about three oscillations per second.

TABLE 1
Adsorption of KH_2PO_4 by hydrogel of silica

NUMBER OF SOLUTION	REACTION	K ADSORBED PER GRAM GEL		PO ₄ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	9.501	9.63	9.99	-4.15	-0.57
2	7.692	6.56	7.40	-4.15	-0.57
3	6.086	1.74	2.18	-3.15	0.00
4	3.888	-0.68	0.71	-1.36	1.92

EXPERIMENTAL WORK

A series of four or five solutions of each of the salts used was made up. The pH values in each series were varied by adding the required amounts of NaOH or HCl (ranging from neutral to N/5) before the solutions were made up to the mark. The salt concentration was kept constant throughout. The concentration of each solution was determined by official methods.

In determining the adsorption of the various ions by hydrogel of silica, 200 cc. of each of the solutions of the salts was mixed with 50 gm. of the wet hydrogel of silica which had first been washed as free as possible of sulfates and which

contained 43.7 per cent moisture. These mixtures were placed in 250-cc. ground-glass stoppered bottles and shaken for 72 hours. At the end of this time it was found that equilibrium had been reached. The mixtures were then allowed to settle until clear or, if a hydrosol was produced which would not settle, a Pasteur filter was used. Aliquots were then pipetted from the clear, supernatant liquid or filtrate and analyzed by the same methods as before the hydrogel had been mixed. The pH value of each of the solutions was also determined.

In the case of the hydrogel of iron, the same procedure was followed with the exception that 25 gm. of the wet hydrogel containing 95.5 per cent moisture, was used.

EXPERIMENTAL RESULTS

In the following tables, adsorption is indicated in milligrams adsorbed per gram of dry hydrogel. The negative sign denotes negative adsorption. All others are positive.

TABLE 2
Adsorption of potassium by the hydrogel of silica

NUMBER OF SOLUTION	KNO ₃			K ₂ SO ₄		
	Reaction	K ADSORBED PER GRAM GEL		Reaction	K ADSORBED PER GRAM GEL	
		Dry	Wet		Dry	Wet
	pH	mgm.	mgm.	pH	mgm.	mgm.
1	9.873	11.2	11.45	9.890	10.06	10.38
2	8.554	9.86	10.22	8.706	9.93	10.19
3	6.830	2.60	3.68	7.337	4.70	5.37
4	6.390	-1.07	0.37	7.117	1.91	2.79
5	3.360	-1.332	0.114	5.275	1.16	2.36

Results shown in the "dry" column were calculated not on a volume of 200 cc. of the solution, but on 200 cc. plus the amount of moisture contained in the hydrogel at the time it was added. Results shown in the "wet" column were calculated on a basis of 200 cc., the amount of the salt solution added. It will be noted that the amount of the positive potassium ion adsorbed decreased with a decrease of pH or OH concentration, showing the greatest adsorption took place in an alkaline solution, while the negative phosphate ion was adsorbed to a greater extent at high hydrogen-ion concentrations. This may be seen more plainly by referring to the curves on figure 1 of the authors' previous paper (4).

The adsorption of the potassium varied with the hydrogen-ion concentration as in table 1 where potassium acid phosphate was used. The curves in the above mentioned figure show how similar the adsorption of the potassium with the three salts was. Near the neutral point a small change in the pH value made a marked change in the amount of potassium adsorbed.

FIG. 1. ADSORPTION OF K, NO_3 , PO_4 , SO_4

Table 3 gives the adsorption by hydrogel of silica in solutions of $\text{CaH}_4(\text{PO}_4)_2$.

In the case of calcium salts it was impossible to obtain a wide range of pH values due to the precipitation of $\text{Ca}(\text{OH})_2$ by NaOH . In table 3 it will be noted that solutions 2 and 3 had the same pH value. Solution 2 contained a small amount of NaOH and HCl in equal quantities, while solution 3 contained only the salt $\text{CaH}_4(\text{PO}_4)_2$.

The calcium ion was adsorbed in the same order as the potassium ion in the potassium salts, but the order of adsorption of the phosphate ion in this case was reversed over that in the potassium phosphate.

TABLE 3
Adsorption of $\text{CaH}_4(\text{PO}_4)_2$ by the hydrogel of silica

NUMBER OF SOLUTION	REACTION	Ca ADSORBED PER GRAM GEL		PO ₄ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	4.243	0.45	1.09	-0.64	2.56
2	4.193	0.41	1.05	-0.75	2.47
3	4.193	0.36	1.01	-1.00	1.87
4	4.142	0.18	0.85	-1.56	1.72
5	2.463	-0.89	-0.12	-2.62	0.77

TABLE 4
Adsorption of $\text{Ca}(\text{NO}_3)_2$ by the hydrogel of silica

NUMBER OF SOLUTION	REACTION	Ca ADSORBED PER GRAM GEL		NO ₃ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	6.695	0.61	1.25	-3.32	-0.88
2	6.120	-0.86	-0.07	-3.32	-0.88
3	6.086	-1.49	-0.64	-0.86	-1.33
4	6.052	-1.57	-0.71	-1.35	0.88
5	2.284	-2.86	-1.52	-1.35	0.88

The adsorption of calcium followed the same order as potassium, but the adsorption of the nitrate ion did not seem to be influenced to any great extent by the hydrogen-ion concentration though the general tendency was to decrease with a decrease in hydrogen-ion concentration. The maximum adsorption occurred in the solution which contained neither NaOH nor HCl . Solutions 1 and 2 contain .002 *N* and .0002 *N* NaOH , solution 3 contained only the salt, and solutions 4 and 5 contain .002 *N* and .0002 *N* HCl . It would appear that the presence of these compounds influenced the adsorption of the nitrate ion.

Tables 5, 6, 7, 8, and 9 give the adsorption of salts by the hydrogel of ferric hydroxide. The pH values in the case of this gel were made much higher than

the corresponding pH values for the silica gel, in order to avoid a chemical solution with the hydrogel.

Table 5 shows that the negative phosphate ion is adsorbed to the greatest extent in the lower hydroxyl-ion concentration and decreases as the hydroxyl-ion concentration increases. But the positive potassium-ion does not follow the general rule of the positive ion. This is the only case found so far where the positive ion adsorption increases with the decrease of pH values throughout.

TABLE 5
Adsorption of KH_2PO_4 by the hydrogel of ferric hydroxide

NUMBER OF SOLUTION	REACTION	K ADSORBED PER GRAM GEL		PO ₄ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	12.730	-65.2	-16.3	9.3	97.2
2	11.868	-14.3	29.2	51.2	135.0
3	7.439	63.0	99.0	216.0	324.1
4	6.695	77.7	111.2	320.9	378.1
5	6.627	80.9	114.1	329.9	386.2

TABLE 6
Adsorption of KNO_3 by the hydrogel of ferric hydroxide

NUMBER OF SOLUTION	REACTION	K ADSORBED PER GRAM GEL		NO ₃ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	13.389	-0.5	39.9	34.4	97.8
2	12.612	11.0	50.2	34.4	97.8
3	11.868	48.9	84.0	34.4	97.8
4	9.417	0.2	40.4	34.4	97.8
5	9.281	-4.9	36.2	34.4	97.8

From table 6 it is seen that the adsorption of the anion was not affected by a change of pH values but that its adsorption rate was independent of other ions present. The cation seemed to present a maximum adsorption in this case around a pH value of 11.868. The same will be noticed in table 7 which shows a minimum adsorption of the sulfate ion at the same pH value. Curves in figure 1 make this more plain.

The maximum adsorption of the potassium ion at a pH value of 11.530, and the minimum adsorption of the sulfate ion at the same hydrogen-ion concentration is worthy of note. This is better shown by the curves in figure 1.

In table 8 we find the greatest adsorption throughout that has been noticed so far. While the change of pH values seems to have had but little effect on the adsorption of the phosphate ion, it has a tendency to present a minimum

adsorption as was noted in table 7. The cation here followed the general order of cation adsorption with a change of pH value.

It will be seen in table 9 that there was slightly greater adsorption in solution 5 than in solution 4, which breaks the order of the cation adsorption. This is accounted for by the fact that solution 5 suffered such a high peptiza-

TABLE 7
Adsorption of K_2SO_4 by the hydrogel of ferric hydroxide

NUMBER OF SOLUTION	REACTION	K ADSORBED PER GRAM GEL		SO ₄ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	12.645	-60.8	-14.5	44.2	91.1
2	12.578	-01.0	38.9	21.2	70.5
3	11.530	21.7	59.2	10.1	60.7
4	8.182	-02.4	37.7	19.1	68.9
5	7.624	-07.8	32.8	19.1	68.9

TABLE 8
Adsorption of $CaH_4(PO_4)_2$ by the hydrogel of ferric hydroxide

NUMBER OF SOLUTION	REACTION	Ca ADSORBED PER GRAM GEL		PO ₄ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	5.156	109.5	118.6	554.8	589.0
2	5.156	104.5	114.1	536.8	572.8
3	5.038	101.9	111.8	536.8	572.8
4	5.021	101.9	111.8	581.7	613.3
5	4.446	56.4	71.2	587.7	618.7

TABLE 9
Adsorption of $Ca(NO_3)_2$ by the hydrogel of ferric hydroxide

NUMBER OF SOLUTION	REACTION	Ca ADSORBED PER GRAM GEL		NO ₃ ADSORBED PER GRAM GEL	
		Dry	Wet	Dry	Wet
	pH	mgm.	mgm.	mgm.	mgm.
1	6.036	29.3	47.6	-12.0	62.0
2	5.241	-03.6	18.3	-12.0	62.0
3	5.122	-39.1	-13.3	-12.0	62.0
4	5.038	-46.4	-20.0	-12.0	62.0
5	4.432	-31.5	-06.5	-12.0	62.0

tion, that the accurate determination of the adsorption became very difficult. Here again we notice the general tendency of the nitrate ion not to be affected by the pH value.

Inasmuch as it seems to be the general tendency for an acid reaction to fasten the negative ion and an alkali reaction to fasten the positive ion, we believed

that by reversing the charge on the gel we should get a release of the ions which were adsorbed the most strongly. That is to say, by washing a gel which had adsorbed a negative ion strongly with an alkali, the ion should be released or washed out. So we proceeded in the following manner.

The silica gels from solutions 1, 2, 4 and 5 of table 1 (Absorption of KH_2PO_4 by hydrogel of silica) were used. Solutions 1 and 2 contained or had absorbed a relatively large amount of the potassium while solutions 4 and 5 had absorbed the phosphate ion. All the samples were then placed in filter papers in separate funnels and washed with water to remove that portion of solution mechanically held. Analysis of these portions were made as shown in the results. After the analysis showed only a small quantity of potassium and phosphate ions in the wash water, the acid and alkali washings were begun. For this, 0.1N HCl or NaOH were added in 50-cc portions. The filtrates were collected in separate beakers. To gel 1, 1 N HCl was added; to gel 2, 0.1N NaOH; to gel 4, 0.1N HCl and to gel 5, 1.0N NaOH. Three successive samples of washings were collected from each of the gels, then a fourth portion was added to each and allowed to stand over night. This was run off the next morning and analyzed along with the others. Table 10 gives the results obtained from the analyses of the HCl and corresponding previous water washings.

TABLE 10
Analysis of HCl washings of hydrogel of silica

WASHING	GEL NO. 1 K RELEASED	GEL NO. 4 PO_4 RELEASED
	mgm.	mgm.
1st 50 cc. H_2O	15.52	85.31
3rd 50 cc. H_2O	0.83	7.33
1st 50 cc. HCl	22.91	5.19
2nd 50 cc. HCl	21.96	2.70
3rd 50 cc. HCl	19.84	1.63
Over night HCl	24.37	8.69

TABLE 11
Analysis of NaOH washings of hydrogel of silica

WASHING	GEL NO. 2 K RELEASED	GEL NO. 5 PO_4 RELEASED
	mgm.	mgm.
1st 50 cc. H_2O	20.67	95.65
3rd 50 cc. H_2O	1.66	1.09
1st 50 cc. NaOH	2.94	2.70
2nd 50 cc. NaOH	3.65	1.35
3rd 50 cc. NaOH	2.59	1.09
Over night NaOH	14.77	7.88

Table 11 gives the results obtained from the analyses of the NaOH and corresponding water washings.

It will be seen from table 10 that the HCl washing caused a marked release of the potassium ion, whereas no increase was noticed in the phosphate ion until the HCl was left overnight in contact with the gel.

In table 11 it will be noticed that the NaOH caused a slight increase in the liberation or movement of the phosphate ion. The small increase was probably due to the small amount present to begin with. We also obtained a

slightly increased movement of the potassium ion. This is accounted for by a replacement of the potassium by the sodium ion until a state of equilibrium is reached. The explanation becomes even more plausible when the results for the overnight washings are observed.

DISCUSSION

We had expected when starting the work that an increase in the concentration of the hydroxyl ions would increase the adsorption of cations by soil colloids. These results were very generally found as seen in the preceding tables. This was anticipated in accordance with Helmholtz's electrical double-layer theory which assumes that one ion may become more closely associated with the colloidal particle than the other ion. This most closely associated ion would impart its charge to the colloidal particle, but this charged colloid and ion will attract ions of opposite charge and in our case, if it is the OH ion that is giving the charge to the colloid, it should attract the metal ions which have the opposite sign. Hence, the solution should become poorer in metallic ions. This was what was found, but this is only one explanation of the general behavior of the metallic ions. The negative ions showed many specific cases, and work is now in progress to explain the entire phenomenon in terms of chemical reactions which are governed by difference of solubility or hydrogen-ion concentration.

SUMMARY

1. The adsorption of the cation as a rule increased with increased hydroxyl ion concentration, or with increased pH value.
2. The adsorption of the phosphate ion increased with decreased pH value in some cases.
3. Adsorption of the nitrate and sulfate ions was not consistently influenced by the reaction of the solutions.
4. Anions seem to be adsorbed in the order of phosphate, sulfate and nitrate with phosphate well in the lead.
5. Adsorption by ferric hydroxide gel is greater than by silicic acid gel.
6. There is a large change in adsorption of potassium ions for very slight change in the hydrogen-ion concentration around the neutral point.

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