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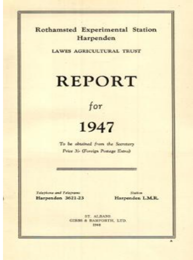

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THE ELECTRIC CHARGE ON SOIL PARTICLES

By R. K. Schofield

Experimenting both in his laboratory and in his garden near Moscow in 1808, Reuss found that water in contact with soil carries a positive electric charge in consequence of which it is transported towards a cathode. In this way he discovered the phenomenon now known as electro-osmosis. Nearly half a century later, Thompson and Way discovered the phenomenon of base exchange in soil. For many years these two phenomena were separately investigated: the first by physicists, and the second by chemists. The artificial division between these investigations retarded progress, and the realisation that both phenomena have the same root cause is a comparatively recent development. One object of the physico-chemical studies conducted in the Physics Department has been to establish the nature of the electric separation in soil. For while electro-osmosis and base exchange provide the clearest evidence for electric separation it influences both the physical and the chemical behaviour of soil in other ways.

The fact that clay soils shrink when dried, and swell again when rewetted, leads to the conclusion that the particles are not in solid contact but are separated by water films. It is now clear that the exchangeable cations play a dominant part in maintaining these water films and regulating their thickness. In this phenomenon the chemical nature of the exchangeable ions profoundly influences the physical effects they produce.

In connection with the availability of exchangeable cations as plant nutrients the fact that they are held by electrostatic attraction to negatively charged soil particles is of great significance, and it is not surprising that investigations with a purely chemical outlook, which take no account of the powerful electric fields close to soil particles, have achieved only a limited success.

It has become increasingly clear that as far as possible all the consequences of electric separation must be considered in relation to one another, and that the artificial distinction between physics and chemistry must be completely broken down. The undertaking is formidable, and much groundwork is needed before results can be obtained that bear directly on the very complex conditions actually existing in field soil.

MEASUREMENT OF THE ELECTRIC CHARGES ON SOIL PARTICLES

Ionic exchange provides the only reliable method for measuring the net electric charge carried by a particular sample of soil. Since the charge depends to some extent upon the nature and concentrations of the ions in the solution surrounding the soil particles these must be controlled or determined at the same time. Hitherto most methods used for determining exchangeable cations have been designed for the routine examination of large numbers of soil samples, and have been considered satisfactory so long as they were reasonably rapid and furnished reproducible results. For precise measurement of net charge no existing method was found to be entirely satisfactory. Control of aluminium ions has been the main problem.

A technique has now been worked out which effectively prevents disturbance from aluminium ions from pH 2·5 to pH 8 (1). The belief generally held that clays lose their negative charge when in contact with solutions of low pH is ill-founded. The methods usually employed fail to detect the presence of exchangeable aluminium. When sufficient washings are given to remove the exchangeable aluminium it is found that the negative charge falls off much less with fall in pH than earlier work had indicated. For example, a sample of Rothamsted subsoil clay, which has a net negative charge of 27 milliequivalents per 100 g. when in equilibrium with a N/5 ammonium chloride solution at pH 7, has a net negative charge of 22 milliequivalents when the pH of the solution is reduced to 2·5.

By simultaneously measuring the retention of ammonium and chloride ions it has been found that only ammonium ions are concentrated close to the surfaces of the clay particles in the solution at pH 7. Chloride ions are actually repelled from the surfaces, which indicates that all the electric charges on the clay particles are of negative sign. In the solution of pH 2·5, however, chloride ions are slightly attracted. Compared with the condition at pH 7 about 2 milliequivalents of chloride ions are attracted to the surfaces of the particles. It thus appears that the 22 milliequivalents of *net* negative charge is made up of 24 milliequivalents of negative and 2 milliequivalents of positive charge.

An independent test fully supports this conclusion. It has been found that if the clay is repeatedly washed with acid ammonium oxalate in sunlight a photo-chemical action occurs resulting in the solution of iron and aluminium amounting to about 7 per cent. of the original weight. The residue is nearly white, and has a charge at pH 2·5 of close on 24 milliequivalents computed on the original weight. There can be no doubt that the positive charges present on the original clay when in the solution of pH 2·5 were on the hydrous oxides of iron and aluminium (which the oxalate washing removed), leaving the negative charges carried on the clay mineral proper. It was also observed that the residue repels chloride ions in the solution of pH 2·5, thus confirming that only negative charges are present.

These and parallel results with several other clays compel us to abandon the view hitherto widely held that between pH 3 and pH 7 clays greatly increase their negative charge by dissociation of hydrogen ions. No clay mineral so far examined has been observed to dissociate any hydrogen ions between pH 2·5 and pH 5 in N/5 ammonium chloride solutions. From pH 5 and pH 6 dissociation is just detectable, and it becomes progressively greater to pH 8—the limit of the present measurements.

The crystallographic study of the clay minerals has led to the view that isomorphous replacement should give rise to negative charges that are permanent in the sense that they cannot be increased and decreased reversibly by altering the pH, but can only be changed by processes that disturb the atomic arrangement within the crystals. Below pH 2·5 the charge diminishes but is not restored again on raising the pH. There is other evidence that the clay mineral has suffered destructive attack.

It is entirely reasonable to suppose that the constant charge found between pH 2·5 and pH 5 is the "permanent" charge due to isomorphous replacement. It would be very desirable to check this conclusion by direct chemical analyses, but until the process for freeing clay minerals from contamination has been further refined this cannot be done.

It is also reasonable to attribute the progressive rise in the negative charge above pH 6 mainly to the dissociation of hydrions from hydroxyls attached to silicon atoms. Such hydroxyl groups occur round the edges of the silicon-oxygen sheets of the clay minerals and on the free silica. There is some evidence that the iron oxide removed by acid ammonium oxalate, besides carrying positive charges at low pH, may carry a few negative charges above pH 7; but this matter requires further study.

NEGATIVE ADSORPTION AND SURFACE AREAS

Parallel with measurements of the electric charges on soil and clay, investigations have been made to elucidate the way in which electric separation influences soil properties. Mention has already been made of the repulsion exerted by the negative charges on the soil particles upon the free negative ions in the soil solution. By extending Gouy's theory of the diffuse electric double layer the relationship

$$\frac{\Gamma_-}{n} = \frac{q}{\sqrt{\nu\beta n}} - \frac{4}{\nu\beta\Gamma}$$

has been obtained (2). Here Γ_- is the "negative adsorption" of the repelled ion, n is the normality of the solution and Γ_-/n is a distance that conveniently expresses the extent of the repulsion. q is a factor depending on the valency ratio, ν is the valency of the repelled ion, β is a constant depending on the temperature and dielectric constant of the solvent, and Γ is the electric charge on the surface expressed in milliequivalents per square centimetre. This simple equation is valid so long as Γ is large enough for the first term to be several times the second, otherwise a more complex expression must be used.

This equation was first applied to existing data of Mattson for the negative adsorption of the chloride, nitrate, sulphate, and ferrocyanide ions by sodium bentonite. Dividing the negative adsorption per 100 g. of bentonite by the normality, and plotting this quotient against $q\sqrt{\nu\beta n}$, the points fall very well on a single straight line from the slope of which an area of 450 square metres per gram is obtained. From crystallographic data we find that pure montmorillonite completely dispersed into its constituent sheets would expose an area of 800 m.^{2} per gram. Measurements of negative adsorption were, therefore, made using a very fine fraction of bentonite separated with the aid of the supercentifruge. As it is difficult to handle this material except in a flocculated state, calcium chloride was used. Even so, the material could not be concentrated by centrifuging to more than 2 per cent. compared with 10 per cent. used by Mattson. The measurement of negative adsorption in these circumstances requires high precision in the chloride determinations, and it was considered very satisfactory that none of the points deviated from a line for 800 m.^{2} per gram by more than the possible experimental error.

Measurements were also made of negative adsorption by jute (3) in solutions of lithium, sodium, potassium and calcium chlorides. With this material a small negative adsorption was found even in N/20 hydrochloric acid, in which case there would be scarcely any negatively charged carboxyl groups. It appears that about 11 per cent. of water is taken up by the solid matter, the chloride ions being too large to be admitted. In neutral solutions a large additional negative adsorption is found which clearly must be due to the repulsive action of the negative charges resulting from the dissociation of hydrions from the carboxyl groups.

Values ranging from 6 to 22 milliequivalents per 100 g., by means of cation exchange, were obtained for the carboxyl content of different samples of jute. It was found that the negative adsorption observed in the sample of lowest carboxyl content scarcely differed from the amount calculated by the use of Donnan's equation for the membrane equilibrium. Examination of the theory showed that this result is to be expected when the surface density of charge is low in relation to the distances separating opposing surfaces.

The sample with the greatest carboxyl content gave values considerably below the value given by the Donnan equation. The results obtained for solutions above N/20 indicated that in this jute the charges were spread over an area of 160 m.^{2} per gram. This is roughly a thousand times the external area of the fibres. At the same time an extrapolation of the values obtained in more dilute solutions shows that, in the limit, the chloride ions are completely expelled from 70 c.c. per 100 g. of jute. This is evidently the volume of internal passages within the jute fibres. The area of the walls of the passages being 160 m.^{2}, it follows that the average width of the passages is of the order of 100 Angstrom units.

Thus, by applying physical reasoning to chemical measurements, a new way has been opened up for the exploration of minute structures which are not regular enough to be investigated by X-ray diffraction, and could not be preserved in the high vacuum conditions needed for examination by the electron microscope. It can only be applied when the surface area is very large and when it carries a sufficient density of electric charge, but even with these limitations it should have a wide scope.

FILM THICKNESS

The same basic theory that yielded the equation for negative adsorption has been used to obtain the equation (4)

$$X = \frac{\pi}{\nu\sqrt{\beta c_0}} - \frac{4}{\nu\beta\Gamma}$$

for the thickness, X, of the water film on a surface carrying a surface charge Γ balanced by exchangeable ions of valency ν, which have a concentration c_0 at the outer surface of the film.

The theory shows that for equilibrium between the film and water in bulk there must be a pressure difference given by the Van t'Hoff equation

$$p_0 = RTc_0.$$

Deryaguin and Kussakov's determinations by optical interference of the thickness of water films between hydrogen bubbles and surfaces of mica and glass are in excellent agreement with the relationship to be expected between X and p_0. There is no adjustable constant in the theory so the test is a searching one. The results of their experiments with solutions of sodium chloride are not in satisfactory agreement with the theory. This is puzzling since over the same range of concentration the equation for negative adsorption seems to be entirely reliable. New optical measurements are being carried out with the help of Prof. L. C. Martin.

The theory indicates that p_0 is the repulsive pressure between two parallel opposing surfaces separated by a water film of thickness $2X$. We have here a basic concept upon which to build the theory of swelling and shrinking of clay. By itself the concept is too simple because it does not explain flocculation. In its simple form it may, however, be expected to give a fairly good account of the swelling of bentonite containing only monovalent cations.

IONIC EQUILIBRIA

When a dilute solution is in equilibrium with a soil having sufficiently high density of surface charge, theory leads us to expect that the following "ratio law" will be obeyed (5):—

> When cations in a dilute solution are in equilibrium with a larger number of exchangeable cations, a change in the concentration of the solution will not disturb the equilibrium if the concentrations of all the monovalent cations are changed in one ratio, those of all the divalent cations in the square of that ratio, and those of all the trivalent cations in the cube of that ratio.

This ratio law has been tested for a number of ion combinations. Using soil from Park Grass Plot 7, that has received dressings of potassium and magnesium salts, a solution containing the chlorides of potassium, magnesium and calcium at a total concentration of N/100 was found, by trial, that would percolate unchanged through the soil. Another solution containing half the concentration of potassium and one quarter the concentrations of magnesium and calcium was then made up, and it was verified that this solution also would percolate unchanged through the same soil sample. The concentrations in these experiments were measured spectrographically in the Chemistry Department. In the majority of soils, calcium is the most abundant ion in the soil solution. These experiments and the theory they support indicate that the potash "status" of the soil should be judged by the ratio of the potassium ion concentration to the square root of the calcium ion concentration in a solution in equilibrium with it.

A further support to the "ratio law" was obtained in experiments with soil from Plot 9 (unlimed), which has become very acid after repeated application of ammonium sulphate. It was found that appreciable concentrations of aluminium ions and hydrogen ions must be present in the solutions in equilibrium with this soil.

Moreover, the aluminium behaved in the way expected of a trivalent ion, while the hydrogen behaved as a monovalent ion.

The behaviour of hydrogen ions has been the subject of special study. Experiments with soil from the unmanured Plot 3 (unlimed) show a nearly constant ratio of hydrogen ion concentration to the square root, the calcium ion concentrations ranging from 40 millinormal to 0·1 millinormal. In the course of these experiments several factors that disturb pH measurements on soil and similar materials have been recognised and brought under control.

When a sufficient degree of control can be secured it will be possible to determine the concentration at which the ratio law begins to fail. This should be higher the higher the density of electric charges on the soil. We already have general evidence to support this expectation, but more work is needed to establish the matter beyond doubt.

Conclusion

The presence of electric charges on soil particles could be inferred from the early observations mentioned at the beginning of this review. Yet it was only through the work recently carried out in this laboratory that the net amount of charge on soil particles has been measured with reasonable precision over an extended range of pH. The study of the effects produced by these charges has been facilitated by an extension of Gouy's theory which has been checked experimentally in several ways. In this way a number of new lines of investigation have been opened up.

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