The negative charge of the particles in soil and clay suspensions leads to a deficit in the anion concentration close to the particle surface in comparison to the concentration in the intermicellar liquid. This has been measured in various ways (5, 6, 8).

This negative adsorption of anions affects the ionic concentrations on dilution of these suspensions. If, for example, a field soil containing \( V_1 \) cm\(^2\) of water per g of soil were diluted with distilled water to a suspension containing \( V_2 \) cm\(^2\) of water per g, the ionic concentration of the intermicellar liquid would be changed by a factor \( (V_1 - A^-/c_2) : (V_2 - A^-/c_2) \), in which \( A^- \) indicates the negative adsorption of anions per g of soil, and \( c \) is the concentration in the intermicellar liquid.

Negative adsorption is also the cause of the observed decrease in the concentration of successive portions of the pressure filtrate of a soil (9). The determination of positive adsorption of certain anions by soils, as e.g. phosphate adsorption, is also complicated by the simultaneously occurring negative adsorption. Any measurement would give the combined result of the positive and negative adsorption, and the separation of the two phenomena would require either special techniques or a theoretical estimate of one of the two.

For materials such as cation exchange resins, negative adsorption of anions could be accounted for satisfactorily, except in dilute solutions, on the basis of the Donnan equilibrium equations (1). For systems with non-homogeneous potential distributions such as clay suspensions, the Donnan equation was found to be unsatisfactory (2, 11). For these systems Schofield (10) has calculated the negative adsorption using the Gouy theory of the diffuse double layer.

This author derived an approximate equation, applicable to dilute clay suspensions, relating the negative adsorption to the product of the electrolyte concentration and the surface area of the clay. Measurements with a kaolinite, and recalculation of the values published by Mattson for a bentonite suspension, gave values for the surface area of the clays in reasonable agreement with those determined by other methods, thus confirming the equations for the calculation of negative adsorption (12). Examination of these calculations indicates that indeed reliable information should be obtained in this manner, since the errors caused by the approximations inherent in the Gouy theory affect only the description of the area immediately adjacent to the clay surface, which area is quantitatively unimportant for the evaluation of negative adsorption.

In view of possible interest in negative adsorption of anions in concentrated soil and clay systems, a brief derivation of a complete equation for its calculation in such systems is presented below, using symbols and procedure similar to those introduced by Schofield. In the experimental part of the paper, measurements of the negative adsorption of Cl by montmorillonite suspensions over a wide range of electrolyte concentration are presented.
Theoretical

Figure 1 indicates the ionic distribution close to a negatively charged surface in contact with a water layer of thickness \((D - \delta)\), and in equilibrium with a salt solution containing \(c_0\) moles/liter of a symmetric salt. The distance \(\delta\) indicates the point where the extrapolated concentration-distance function of the anions would reach zero. This “complete” concentration-function corresponds to the distribution function for a charged surface with infinitely high charge density (cf. 7). The negative adsorption of anions, indicated by the cross-hatched area, is equal to:

\[
\Gamma^- = z c_0 \left( \frac{D}{\delta} - \frac{1}{\delta} \right) \int_0^{\delta} \frac{u^{-z} du}{u^z} \]

[1]

in which \(\Gamma^-\) is the negative adsorption per unit area of clay surface, \(z\) is the valence of the anion, \(c_0\) is the concentration in the equilibrium dialyzate of the system, and \(u^{-z} = e^{-z}/c_0\). It follows from the standard theory of the diffuse double layer (7), since \(u = e^{-e\psi/kT}\) (with \(e =\) electronic charge, \(\psi =\) electric potential, \(k =\) Boltzmann constant, \(T =\) absolute temperature), that:

\[
\frac{d \ln u}{dx} = \sqrt{\beta} \cdot \sqrt{\Sigma_i c_i - \Sigma_i c_{ei}} \]

[2]

in which \(\Sigma_i c_i\) indicates the sum of the ionic concentrations, \(\Sigma_i c_{ei}\) is the sum of the ionic concentrations at the outer surface of the water layer, and \(\beta = \frac{2 \pi F^2}{1000 \epsilon RT}\) (with \(\epsilon =\) dielectric constant).

If only one symmetric electrolyte is present in the system this equation becomes:

\[
\frac{d \ln u^z}{dx} = z \sqrt{\beta c_0} \cdot \sqrt{u^z + u^{-z} - u_{-z}^z - u_{-z}^{-z}} \]

[2a]

Substitution of (2a) in (1) gives:

\[
\Gamma^- = z c_0 \left[ \left( \frac{D}{\delta} - \frac{1}{\delta} \right) \int \frac{u^z du}{u} \right] \int \frac{u^{-z} du}{u^z} \left[ \sqrt{\beta c_0} \cdot \sqrt{u^z + u^{-z} - u_{-z}^z - u_{-z}^{-z}} \right] \]

[3]

in which \(u_s\) indicates the value of \(u\) at the surface of the clay particle. This equation can be expressed in elliptic integrals, which for all practical purposes can be approximated by complete elliptic integrals, according to:

\[
\Gamma^- = z c_0 \left[ \left( \frac{D}{\delta} - \frac{2}{\sqrt{\beta c_0}} \left\{ F(x, \pi/2) - E(x, \pi/2) \right\} \right) \right] \]

[4]

in which \(F(x, \pi/2)\) and \(E(x, \pi/2)\) represent complete elliptic integrals of the first and second kind, respectively, with \(x = \arcsin (u_{-z}^{-z})\).

It can be easily proven that for \(u_c \rightarrow 1\) this equation simplifies to:

\[
\frac{\Gamma^-}{z c_0} \approx \frac{2}{z \sqrt{\beta c_0}} \delta \]

[4a]

which is the approximation derived by Schofield (10), valid for values of \(u_c\) close to unity. As was shown by Schofield, the distance \(\delta\) is a function of the surface density of charge of the clay, and can be approximated quite well by the relation:

\[
\frac{\Gamma^-}{z c_0} \approx \frac{4}{\sqrt{\pi}} \times \frac{1}{\delta} \]

[5]

in which \(\Gamma\) is the exchange capacity of the clay in me/cm² of surface area.

For practical purposes equation (4) can be approximated very well over the entire range of \(u_c\) by the equation:

\[
\frac{\Gamma^-}{z c_0} \approx \frac{2}{z \sqrt{\beta c_0}} \left( K_c - 1 - \frac{1}{u_c} \right) \]

[4b]

in which \(K_c = z \sqrt{\beta c_0} \left( u_{-z}^{-z} + 1/u_c \right)\) is Debye’s ionic parameter corresponding to the composition at the outer surface of the water layer. With increasing thickness of the liquid layer the composition at the surface approaches that of the dialyzate or intermicellar liquid, \(K_c\) becomes identical with \(K_0\) (the ionic parameter of the dialyzate) and equation (4b) becomes equal to equation (4a).

As was shown by Schofield (10) equation (4a) can be generalized for systems containing non-symmetric salts, and then takes the form:

\[
\frac{\Gamma^-}{z c_0} \approx \frac{q}{z \sqrt{\beta c_0}} \delta \]

[6]

in which \(q\) is a constant determined by the ratio of the valencies of cation and anion in