A qualitative derivation of the diffuse double layer

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ABSTRACT

The diffuse double layer (DDL) of ions surrounding colloidal and soil clay particles accounts for much soil and colloidal behavior. The DDL is a problem for teachers of soil chemistry, however, because the mathematical derivation of the DDL is difficult, does not illustrate the physical mechanisms that give rise to the DDL, and does not explain the role of anion repulsion. A series of simple hypothetical steps illustrates these parts of DDL by describing electrostatic attraction/repulsion vs. ion diffusion, the two opposing major phenomena causing the DDL.

Additional index words: Colloid chemistry, Surface chemistry, Interfacial phenomena.

IONS and molecules at the interface between two phases are in a different chemical environment than the ions and molecules in the interior of the phases. This difference perturbs the ions and molecules, and, in fluid phases, rearranges them into what is called a double layer. The ions and molecules in the fluid phase double layer are somewhat free to move, making the limits of the double layer diffuse and difficult to define. This diffuse double layer (DDL) has a significant effect on the behavior of particles in an aqueous system when the particles are colloidal and less than about 1 μm in size.

In addition to purely interface phenomena, unsatisfied charges within clay mineral lattices and at crystal edges greatly increase the magnitude of the DDL. The ions neutralizing these charges are part of the DDL.

The mathematical derivation of the DDL is an excellent exercise but may be beyond the ability of many beginning soil chemistry students. A qualitative derivation, based on several imaginary steps which can be clearly illustrated, may be helpful to students and can usefully supplement a quantitative derivation. The steps emphasize two main counter-acting phenomena responsible for the DDL—ion attraction and repulsion at the interface vs. ion diffusion in solution. The steps point out the role of anion repulsion in neutralizing the charge of the clay.

DESCRIPTION

Initially, the clay particle is assumed to be dry, salt-free, and contains only those ions which neutralize or counter the particle's charge. For soil clays which are typically negatively charged, the counter ions would be cations. The counter ions are on the surface of the dry colloid and near each charged site (Fig. 1). This layer of negative charges in the solid and the layer of counter ions on the surface is called a Helmholtz, or rigid, double layer.

If pure water is added to the clay, the counter ions can diffuse to some extent from the charged surface (Fig. 2). Diffusion tries to equalize cation concentrations throughout the aqueous phase but is counteracted by electrostatic attraction of cations to the charged surface. At equilibrium, the concentration of counter ions is high near the colloid surface and diminishes with distance from the surface. Only half of the DDL is diffuse; the charge layer in the clay lattice remains rigid. The shaded area represents the amount of ions in the ion cloud which balances the clay's charge, i.e., it represents the soil's cation exchange capacity.

The cation concentration decreases rapidly but asymptotically with distance, so the DDL theoretically extends to infinity. The so-called double layer "thickness" estimates the volume of solution significantly affected by the colloid's charge but is uncertain. The influence of the charged surface on water molecules in the DDL, for example, apparently varies from 1 to 20 nm, depending on the measurement technique.

The thickness of the DDL ion swarm surrounding the colloid particle depends on the salt concentration in solution. In Fig. 3, salt has been added to the suspension to give an equilibrium concentration Cl. The distribu-

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Fig. 1. The Helmholtz double layer on the surface of a dry clay particle. Each + sign denotes a monovalent cation.

Fig. 2. The DDL of cations formed when pure water is added to a salt-free clay. Shaded area corresponds to cation excess over concentration in bulk solution.
tion of Fig. 2 is shown as a dashed line. In Fig. 3, the anions are assumed to be unaffected by the colloid's charge or by the cation concentration so the anion concentration is the same throughout the suspension. Although the DDL of cations still extends to infinity in theory, the added salt reduces the cation diffusion gradient away from the charged surface and shrinks the effective thickness of the DDL. At distance $B_0$, the cation concentration has become essentially equal to that of the bulk solution.

In Fig. 4, by contrast, the anions are assumed to respond to the negative surface charge, and cations do not respond to the surface charge or anion concentration. The negative charge of the colloid is then neutralized by anion repulsion or exclusion. Near the colloid, anion repulsion creates a cation-rich solution which neutralizes the colloid charge. At the same time, anion repulsion increases the salt concentration in the bulk solution. For example, if a dry clay were mixed with 1.00 M NaCl, the solution outside the DDL might contain perhaps 1.05 M NaCl, because the solution immediately surrounding the clay particles is depleted of Cl$^-$. Adding more salt to concentration $C_1$ increases the gradient and driving force for anion diffusion toward the surface and therefore shrinks the thickness of the DDL (Fig. 5). As in Fig. 3, added salt shrinks the DDL, and also the distance to the cross-over point $B_1$.

Adding Fig. 3 and 5, and removing the restrictive assumptions, yields the actual DDL (Fig. 6). The final shape of the DDL is the sum of cation attraction, anion repulsion, and cation and anion diffusion. Cations are attracted to, and diffuse away from, the surface. Anions are repelled from, and diffuse toward, the negatively charged surface, yielding a salt concentration $C_0$ in the bulk solution. $C_1$ is the salt concentration if no anion repulsion had occurred.

A slight additional complication is that the cation excess in the DDL attracts some anions and therefore somewhat decreases anion repulsion. Similarly, the anions in the DDL are accompanied by an equal charge of cations.

**DISCUSSION**

This simple derivation and many mathematical treatments of the DDL do not allow for differences between cations and between anions, except that the mathematical treatments account for ion charge. Differences of DDL behavior between Na$^+$ and K$^+$, however, and between Ca$^{2+}$ and Mg$^{2+}$ are well known. Shainberg and Kemper (1966) explained such differences by the amount of ion dehydration at the colloid surface. A fraction of the ions are in a more stable state if they lose some waters of hydration and thereby move closer to the colloid's charged surface. The greater energy of attraction between ion and clay partially overcomes the energy of hydration. Generally the larger the ion, the lower its energy of hydration, and the more easily it can be partially dehydrated. These partially dehydrated cations are held more rigidly in a Stern layer on the surface, similar to the Helmholtz layer of Fig. 1. The large cations K$^+$, NH$_4^+$, Cs$^+$, and Rb$^+$ also fit readily into cavities on the surfaces of 2:1 layer silicates, which compels even further dehydration. Shainberg and Kemper...
suggested that the concentrations in this Stern layer on clay surfaces are about 1.6 $M$ for $K^+$, 1.2 $M$ for $Na^+$, and 0.5 $M$ for $Li^+$. This follows the order of their dehydrated ion radii: 133, 95, and 60 pm, and the inverse order of their hydration energies: 314, 397, and 506 kJ/mol, respectively.

**Thickness of the Double Layer**

The thickness of the DDL is rather arbitrary and can be described in several ways. The B point in the figures are reference points rather than DDL thicknesses. One view of DDL thickness is to imagine the charged surface as one plate of an electrical capacitor. The other plate is then a parallel plane of counter ions at a distance such that the capacitance of these charged planes is equal to that of the DDL. The distance between these imaginary plates is then termed the thickness of the DDL. van Olphen (1977) calculated several such distances (Table 1). Increasing salt concentration or increasing cation valence collapses or shrinks the DDL. For a soil having 0.2 m²/kg surface area and a 0.01 $M$ soil solution of divalent cations, the values in Table 1 indicate that the double layer occupies 0.1 mL of solution per gram of soil.

A second expression of DDL thickness, a consequence of the mathematical derivation, is the center of gravity of the counter ion cloud or swarm. This is $1/x$, the weighted average thickness of the DDL, or the product of ion concentration at each incremental distance from the surface and this distance, divided by the total concentration. For a surface electrical potential of $\Phi_s$, $\Phi$ and the counter ion concentration decrease exponentially with distance away from the surface according to the equation

$$\frac{\Phi}{\Phi_0} = e^{-xX}$$

where $X$ is the distance from the surface in meters and $x$ has units of m⁻¹. The distance $1/x$ and the thickness of the DDL calculated as a capacitor, as in Table 1, should be similar.

A third expression of DDL thickness, a graphical method, is to consider the DDL thickness as the distance at which the anion concentration is one half that of the bulk solution. This is point D in Fig. 6, remembering that the log plot distorts ion concentrations.

**Table 1. Approximate “thickness” of the diffuse double layer surrounding colloidal particles.†**

<table>
<thead>
<tr>
<th>Counter ion concentration, mol/L</th>
<th>Thickness of the diffuse double layer</th>
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<tbody>
<tr>
<td>$10^{-4}$</td>
<td>100 nm</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>10</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>1</td>
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</tbody>
</table>

† van Olphen, 1977.

**Implications of the DDL on Cation Exchange Capacity Measurements**

Electroneutrality requires equal positive and negative charges of ion in the aqueous phase and the clay. For a suspension of a negatively charged clay or colloid:

$$\Sigma \text{cations} = \Sigma \text{anions} + \text{charge of clay}$$

An unequivocal measure of the clay’s cation exchange capacity (CEC) would be to subtract the sum of soluble anions from the sum of cations, as Okazaki et al. (1963) proposed. Since this requires at least two measurements, the CEC is usually measured as the amount of cations in the suspension. This shortcut is only approximate, in that it ignores anion repulsion. Simple cation displacement measures only the cation excess above $C_0$ in Fig. 6, whereas the actual CEC is the cation excess above $C_1$.

The relative contribution of anion repulsion to charge neutralization, (the relative difference between $C_0$ and $C_1$) increases with salt concentration. At a monovalent salt concentration of 1 $M$, as much as 25% of the CEC may be satisfied by anion repulsion. Measuring the small difference between two large $C_0$ and $C_1$ concentrations is prone to experimental error. The correction for anion repulsion is usually negligible when $C_0$ and $C_1$ are about 0.01 $M$ or less.

**LITERATURE CITED**