Clay in Water: The Electrical Double Layer

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One observes that a chunk of dried clay swells more when immersed in tap water than in salty water. We aim to explain why.

Clays are made of platelets whose surface bears a negative electric charge and whose edge bears a positive electric charge (see Fig. 1a). In this exercise we focus on the interactions between neighboring platelets immersed in an electrolyte (see Fig. 1b).

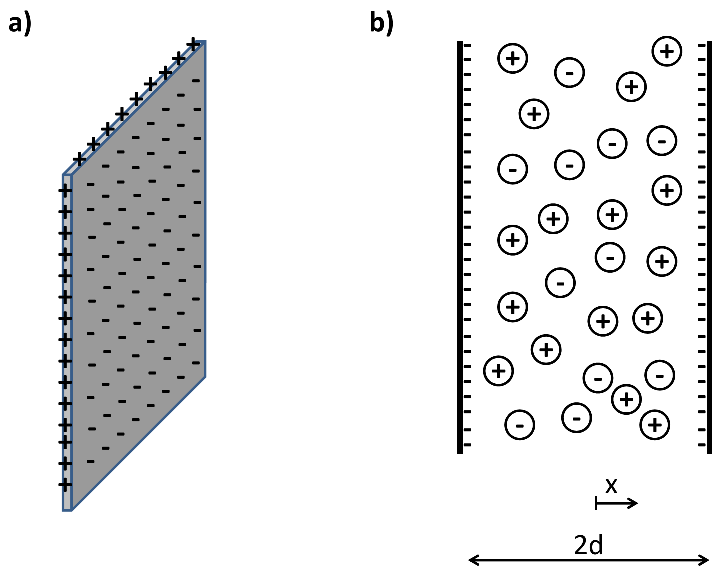

Figure 1: a) Clay platelet and b) two clay platelets immersed in an electrolyte.

1 - We consider two clay platelets parallel to each other and separated by a distance $2d$ (see Fig. 1b). The surface (wall) of the platelets bears a negative electric charge (charge q per unit surface). The platelets are immersed in a 1:1 electrolyte. The molar concentrations of cations and anions in-between the two platelets are noted $c_+(x)$ and $c_-(x)$, respectively. Let F be the Faraday constant ($F = 9.65\text{x}10^4$ C.mol^{-1}), i.e., the charge of one mole of protons. Can we find a relation between $c_+(x)$, $c_-(x)$, and q by expressing the overall electroneutrality of the system?

2 - What is the electrostatic contribution p_{el} to the pressure that is applied on a wall of the platelets (hint: two very large plates separated by a distance l and bearing a charge per unit surface q_1 and q_2, respectively, exert a pressure $q_1 q_2 / 2\epsilon_r \epsilon_0$ on each other, where ϵ_0 is the vacuum permittivity and ϵ_r is the relative permittivity)? Does this contribution correspond to an attraction or a repulsion?

3 - Considering now the osmotic contribution of the electrolyte, what is the *total* pressure p_{total} that is applied on a wall, in excess of the osmotic pressure $2RTc_\infty$ that prevails in the bulk solution?

4 - Considering the fluid to be an ideal mixture, the molar chemical potentials $\mu_+(x)$ for the cations and $\mu_-(x)$ for the anions that form the electrolyte are given by:

$$\mu_+(x) = f_+(T) + RT\ln c_+(x) + F\psi(x) \tag{1}$$
$$\mu_-(x) = f_-(T) + RT\ln c_-(x) - F\psi(x) \tag{2}$$

where ψ is the electrostatic potential. Far from the platelets the molar concentrations of cations and anions are c_∞. How do the concentrations $c_+(x)$ and $c_-(x)$ at equilibrium relate to the electrostatic potential? Find a relation that links $c_+(x)$, $c_-(x)$, and c_∞ at equilibrium.

5 - Starting from Poisson's equation ($\Delta\psi = -\rho/\epsilon_0\epsilon_r$, where ρ is the free charge density), one can derive the following two relations:

$$\left.\frac{d\psi}{dx}\right|_{x=d} = \frac{q}{\epsilon_0\epsilon_r} \tag{3}$$
$$\frac{1}{2}\epsilon_0\epsilon_r\left(\frac{d\psi}{dx}\right)^2 = RT[c_+(x) + c_-(x) - c_+(0) - c_-(0)] \tag{4}$$

Find an expression for the pressure p_{total} between clay platelets in which only the molar concentrations $c_+(0)$ and $c_-(0)$ at the mid-plane intervene. Conclude on whether this pressure between clay platelets is attractive or repulsive.

6 - Starting from Poisson's equation, find out a differential equation that governs the electric potential between the platelets. Find an expression for the characteristic distance between clay platelets. Is it now possible to explain the experimental observation described in the abstract?