

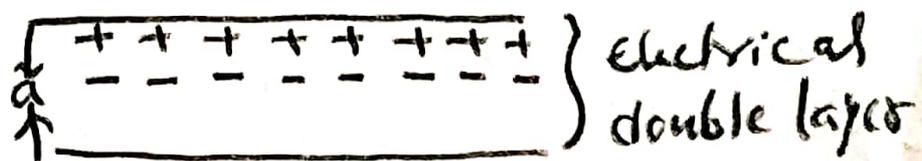
Electrical double layer

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It is formed due to set up potential when particles are moved in a resting layer means immovable layer. The opposite charged are produced because movement of colloidal particles. The effect is for the reasons

1. Electrophoresis
2. Electrokinetics or electro osmosis
3. Sedimentation
4. Streaming

When liquid especially colloidal particles are forced to move through a tube under pressure, there must develop a potential that tends to make double layer due to opposite charged. This is known as Zeta potential (ζ)



First, there is an immovable layer of ions that adhere tightly to the surface of the colloidal particles.
Second — The charged particles attract the opposite charged

and make inner and outer layers
an atmosphere which is called electrical
double layer.

The potential energy of double layer
having radius "a"

$$V_{\text{repulsion}} = + \frac{Aa^2 \psi^2}{R} e^{-s/R_d}$$

where $A \rightarrow$ constant

$a \rightarrow$ radius

$\psi \rightarrow$ potential

$s \rightarrow$ separation

between the layers

$R_d \rightarrow$ Thickness.

When double layer is thick i.e. ($a \gg R_d$)

$$V_{\text{rep}} = \frac{1}{2} A \psi^2 \ln(1 + e^{-s/R_d})$$

When attractionⁿ is developed the eqⁿ will
be somewhat different

$$V_{\text{attrac}} = - \frac{B}{s} \quad \text{where } B \rightarrow \text{another constant.}$$

$s \rightarrow$ separation

At high ionic strength the ionic atmos-
phere is dense and the potential tends
to minimum. This separation or effect is
called flocculation

Again when flocculation materials
are redispersed by agitation it is
known as coagulation.

Role of double layer —

The primary role of electrical double layer is to confer kinetic stability. Colliding colloidal particles break the double layer

The protective role of double layer is the reason ~~why~~ why it is important not to remove all the ions when a colloids are being purified by dialysis.

Surface Excess — Surface Active agents

For binary solution in terms of colloidal solution
Gibbs Duhem equation can be had as

$$n_1 d\mu_1 + n_2 d\mu_2 + A d\gamma = 0$$

When surface area is A we have

$$n_1 d\mu_1 + n_2 d\mu_2 + A d\gamma = 0 \quad \dots (1)$$

In standard binary solution \Rightarrow

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad \dots (2)$$

Multiplying eqⁿ (2) by $\frac{n_1}{n_1^0}$ so that

$$\frac{n_1}{n_1^0} \times n_1^0 d\mu_1 + \frac{n_1}{n_1^0} n_2^0 d\mu_2 = 0$$

$$\frac{n_1}{n_1^0} d\mu_1 + \frac{n_2^0}{n_1^0} n_1 d\mu_2 = 0 \quad \dots (3)$$

(1) - (3) \Rightarrow

$$n_2 d\mu_2 - \frac{n_2^0}{n_1^0} n_1 d\mu_2 + A d\gamma = 0$$

or

$$\left(n_2 - \frac{n_2^0}{n_1^0} n_1 \right) d\mu_2 + A d\gamma = 0$$

$$\left(n_2 - \frac{n_2^0}{n_1^0} n_1 \right) d\mu_2 = -A d\gamma$$

$$\text{or } \frac{\left(n_2 - \frac{n_2^0}{n_1^0} n_1 \right)}{A} = \frac{-d\gamma}{d\mu_2} \quad \dots (4)$$

or $\frac{-d\gamma}{d\mu_2} = \Gamma_2$

But $d\mu_2 = RT d \ln a_2$

$\therefore \Gamma_2 = - \frac{d\gamma}{RT d \ln a_2}$

or $\Gamma_2 = - \frac{d\gamma}{RT \frac{da_2}{a_2}} = - \frac{d\gamma}{da_2} \frac{a_2}{RT}$

$= - \frac{d\gamma}{dc} \times \frac{c}{RT}$

If a solute lowers the surface tension then $\frac{d\gamma}{dc}$ is negative so that Γ_2 is positive. It is called surface excess. The colloidal particles such as soap, detergent etc reduce surface tension, these are called surface active agents. If γ does not depend on c , $\Gamma_2 = 0$.
The quantity $-\frac{d\gamma}{dc}$ as $c \rightarrow 0$ is known as surface activity.