

## Module 8: "Stability of Colloids"

### Lecture 38: ""

The Lecture Contains:

- ☰ Calculation for CCC ( $n_c$ )
- ☰ Relation between surface charge and electrostatic potential
- ☰ Extensions to DLVO theory

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Calculation for CCC ( $n_c$ )

In this section we will calculate the Critical Coagulation Concentration (CCC) which is concentration of the solute in the electrolyte at which coagulation is favorable. Spontaneous coagulation means that no activation energy is required for coagulation.

Graphical representation for CCC is shown in Graph-4 in Figure 10.4. From graph we can see that following conditions must be satisfied at point P (for CCC):

$$G^{TOTAL} = 0 \quad \text{i.e. barrier height is 0, and,} \quad (10.2)$$

$$\frac{dG^{TOTAL}}{dD} = 0 \quad \text{i.e. the maxima lies at the point} \quad (10.3)$$

If we solve the above equations then we would get the required critical concentration. Applying these in equation (10.1) we get

$$-\frac{A_{121}}{12\pi D_m^2} + B \exp(-\kappa D_m) = 0 \quad (10.4)$$

and

$$\frac{A_{121}}{6\pi D_m^3} - \kappa B \exp(-\kappa D_m) = 0 \quad (10.5)$$

where  $D_m$  is the distance at which equations (10.2) and (10.3) satisfy and

$$B = \frac{64n_0 kT \gamma_0^2}{\kappa}$$

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Comparing equation (10.4) and (10.5) we get,

$$\kappa D_m = 2$$

or

$$D_m = 2\kappa^{-1}$$

Substituting this back in equation (10.4) or (10.5) and putting the value of B we get

$$-\frac{\kappa^2 A_{121}}{48\pi} + \frac{64n_0 kT \gamma_0^2}{\kappa} \exp(-2) = 0$$

$$\frac{\kappa^2 A_{121}}{48\pi} = \frac{64n_0 kT \gamma_0^2}{\kappa} \exp(-2)$$

Solving for  $n_0$ , (or the CCC) and substituting for  $\kappa$  we get-

$$n_0 = \frac{512(48\pi)^2 \varepsilon^3 (kT)^5 \gamma_0^4}{A^2 (Ze)^6} \exp(-4) \quad (10.6)$$

where,

$$\gamma_0 = \tanh\left(\frac{Ze\psi_0}{4kT}\right)$$

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Now, let us consider two limits of the surface potential in order to get a few simplifications,

Case – 1: potential is very large  $\psi_0 > 100 \text{ mV}$

In this regime,

$$\gamma_0 = \tanh\left(\frac{Ze\psi_0}{4kT}\right) \rightarrow 1$$

Under this condition, from Eq -10.6

$$n_0 \propto \frac{1}{Z^6} \quad (10.7)$$

This relation is called as the Schultz-Hardy rule.

This dependence of CCC on valence of the counter-ions is very strong, and just doubling the charge on ions ( $Z' = 2Z$ ), reduces the CCC by a factor of 64. ( $n_0' = n_0/64$ )

Case – 2: potential is very small

Under this approximation,  $\tanh$  could be approximated by

$$\gamma_0 = \tanh\left(\frac{Ze\psi_0}{4kT}\right) \approx \frac{Ze\psi_0}{4kT}$$

$$\text{or, } \gamma_0 \propto Z\psi_0$$

Thus,  $n_0 \propto \frac{\psi_0^4}{Z^2}$  which suggests that  $n_0$  has weaker dependence on  $z$ .

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Now, the surface potential (or more precisely the zeta potential,  $\psi_0$ ) varies inversely with the valence of ion due to the irreversibly adsorbed counter-ions at the surface (also known as Stern layer).

Note that Boltzmann’s distribution for potential holds for free charge in the solution (diffused region). In case of adsorption of ions on the surface, we would have to define a new value of  $\psi_d$  outside the surface of the bound charges as shown in the figure.

Thus, again

$$n_0 \propto \frac{1}{Z^6}$$

which implies that Schultz-Hardy rule is valid for small potentials as well.

Let’s look at some experimental values in this regard:

Table 10.1: Some typical values for CCC for common metal ions

Valence of ion	Example	CCC (mmol/L)
1	Li, Na, K	50
2	Mg, Zn	0.7
3	Al, Ce	0.09

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## Example: Potential Determining Ions

Till now we have looked at indifferent ions which do not change potential on surface. But when the surface consists of mobile ions (like  $H^+$  or  $OH^-$ -ions) which can go from surface to solution, the surface acquires excess charge due to the movement of mobile ions into the solution.

For example, let's consider a surface consisting of AH type of molecules in an electrolyte. Now the AH molecule can dissociate into  $A^-$  and  $H^+$  ions.



Further, if this AH molecule is part of another large molecule embedded in the underlying surface (like-COOH group at the end of a protein molecule), the  $H^+$  ions could move into the solution, leaving the surface with an excess negative charge at the  $[A^-]$  ions sites.

If K is the equilibrium constant then,

$$K = \frac{[A^-][H^+]_{\text{soln}}}{[AH]}$$

where,

$[AH]$  is the concentration of those sites which have not dissociated,

$[A^-]$  is the concentration of ions on the surface and,

$[H^+]$  is the concentration of hydride ions in the solution near the surface.

If  $[n_0]$  is the total number of sites/dissociable molecules at the surface then,

Total no. of sites = no. of non-dissociated sites + no. of ions on the surface

$$[n_0] = [AH] + [A^-] \quad (10.8)$$

Combining equations (10.7) and (10.8), to eliminate  $[AH]$  we have

$$[A^-] = \frac{K [n_0]}{K + [H^+]_{\text{soln}}}$$

Since the surface consists of single valence  $[A^-]$  ions, the charge density could be written as:

$$\sigma = -e[A^-] \quad (10.9)$$

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This charge density depends upon the association/dissociation equilibrium of the  $[H^+]$  ions, which in turn depends upon their concentration near the surface. Higher  $[H^+]$  near the surface indicates larger number of associated ions.

If we have HCl in bulk then there will be a bulk concentration of  $[H^+]$



Boltzmann distribution of these ions in solution is given by:

$$[H^+]_s = [H^+]_b \exp\left(-\frac{e\psi}{kT}\right)$$

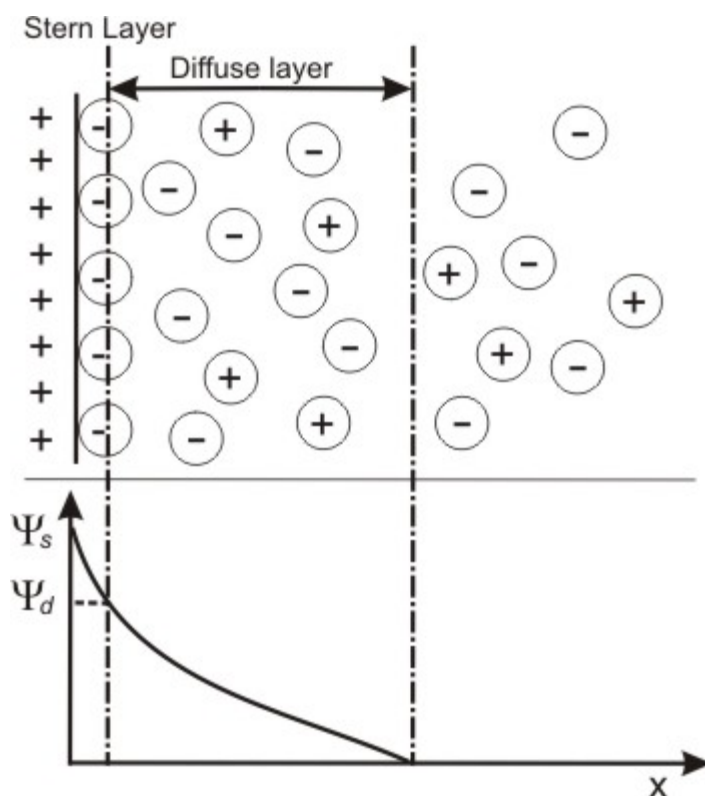
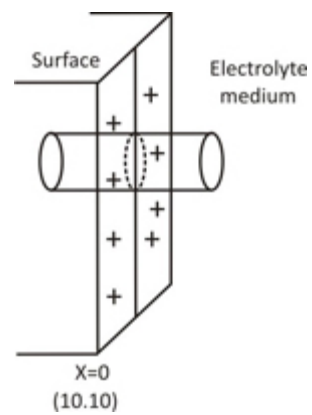


Fig. 10.5: Change in effective surface potential due to adsorption of ions on the surface

(Valence in this case is 1)

At the surface,  $\psi = \psi_0$ . Therefore

$$[H^+]_s = [H^+]_b \exp\left(-\frac{e\psi_0}{kT}\right) \quad (10.10)$$



Hydrogen ion is the counter ion in this case.

We can change  $[H^+]$ SOLN to change  $[A^-]$

Now the question is that how do we determine  $\psi_0$ .

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## Relation between surface charge and electrostatic potential

Consider a small pill box through the surface, one end of which is in the inner side of particle, where there is no charge, and the other end lies into the solution.

If the particle and the solution, as a whole are electrically neutral, then:

$$\sigma + \int_0^{\infty} \rho_e dx = 0 \quad (10.11)$$

now, using Poisson's equation:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\epsilon} \quad (10.12)$$

we get :

$$\begin{aligned} \sigma &= \epsilon \int_0^{\infty} \frac{d^2\psi}{dx^2} dx = \epsilon \left[ \frac{d\psi}{dx} \right]_0^{\infty} \\ \sigma &= -\epsilon \left[ \frac{d\psi}{dx} \right]_{x=0} \end{aligned} \quad (10.13)$$

Assuming the potential to be low, we can use the Debye-Hückel Model for the potential,

$$\psi = \psi_0 \exp(-\kappa x)$$

Therefore,

$$\sigma = \epsilon \kappa \psi_0 = \left( \frac{2\epsilon e^2 [H^+]_B}{kT} \right)^{\frac{1}{2}} \quad (10.14)$$

but if potential is high then we will have to use Chapman's equation as in this case DH approximation will not be valid.

Also,

$$[A^-] = \frac{K [n_0]}{K + [H^+]_B \exp\left(\frac{-e\psi_0}{kT}\right)}$$

Therefore, the surface charge density becomes,

$$\sigma = -e[A^-] = \frac{-eK [n_0]}{K + [H^+]_B \exp\left(\frac{-e\psi_0}{kT}\right)} \quad (10.15)$$

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Equating these 2 values of  $s$  we can solve for  $\psi_0$  as a function of  $[H^+]_B$ .

Let us look at some typical values:  $K = 10^{-4}M, [n] = 5 \times 10^{17}/m^2$

Table 2: Effect of  $H^+$  ion concentration on zeta-potential

$[H^+]_B$	$\psi_0(mV)$
10-4	-163
10-3	-91
10-2	-31

So we see that  $|\psi_0|$  decreases when  $[H^+]_B$  increases.

What will be the effect if more salt is added?

$$\kappa^2 = \frac{e^2}{\epsilon k T} ([H^+]_B + [Na^+]_B [Cl^-]_B)$$

(10.16)

In that case, value of  $\kappa$  will not be affected by  $[H^+]_B$ . Then the above done derivation does not hold.

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## Extensions to DLVO theory

The classical DLVO theory has limitations in that it has good validity for the particles that are neither Hydrophilic nor Hydrophobic. The recent developments in the experimental methods and instruments (such as AFM) have revealed that these non-DLVO forces play an important role in coagulation and dispersion of particles.

Thus, by adding these forces in the classical DLVO theory, an extended model could be developed.

$$G^{TOTAL} = G^{LW} + G^{EL} + G^{AB}$$

For spherical particles,  $G^{AB}$  could be written as

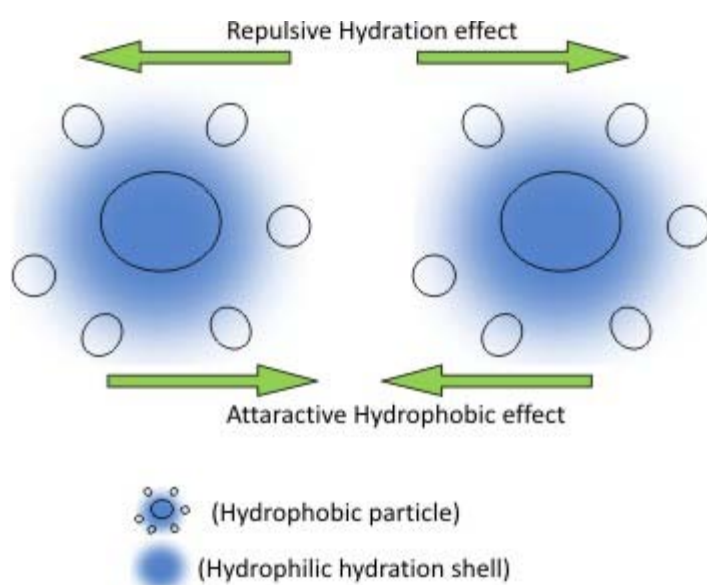


Fig. 10.6: Repulsive hydration effect

$$G^{AB} = G_0^{AB} \exp [(d_0 - d)/\lambda]$$

with,

$$G_0^{AB} = \gamma_{12}^{AB} - \gamma_{13}^{AB} - \gamma_{23}^{AB}$$

This extended version has applications in a large number of practical applications which involves polar molecules including biological, membrane-colloid interactions etc.