

## Surface tension of electrolyte solution.

Surface tension of liquid may increase or decrease in addition of solid (electrolyte). Natural occurrence <sup>is due to</sup> decrease of surface tension by addition of surfactant. Surface tension of surfactant is low.

Gibb's energy of total system of sol<sup>n</sup>.

$$G_t = G_{\text{solvent}} + G_{\text{solute}} = n_1 \mu_1 + n_2 \mu_2$$

where  $n_1, n_2 \rightarrow$  no. of gm. moles of solvent & solute respectively.

$\mu_1, \mu_2 \rightarrow$  chemical pot. of solv. & solute

$$G_t = n_1 \mu_1 + n_2 \mu_2 + \gamma S$$

$\gamma =$  Surface tension  
 $S =$  area of interface  
 $\gamma S =$  surface energy

$$dG_t = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma ds + S d\gamma$$

①

In another way,

$$G_t = f(P, T, n_1, n_2, S)$$

$$dG_t = \left( \frac{\partial G_t}{\partial P} \right)_{T, n_1, n_2, S} dP + \left( \frac{\partial G_t}{\partial T} \right)_{P, n_1, n_2, S} dT + \left( \frac{\partial G_t}{\partial n_1} \right)_{P, T, n_2, S} dn_1 + \left( \frac{\partial G_t}{\partial n_2} \right)_{P, T, n_1, S} dn_2 + \left( \frac{\partial G_t}{\partial S} \right)_{P, T, n_1, n_2} dS$$

$$= V dP - S dT + \mu_1 dn_1 + \mu_2 dn_2 + \gamma dS$$

$$\text{or, } dG_{t, P, T} = \mu_1 dn_1 + \mu_2 dn_2 + \gamma dS \quad \text{---} \rightarrow \text{②}$$

Comparing eq<sup>n</sup> ① & ② at surface we get.

$$n_1 d\mu_1 + n_2 d\mu_2 + S d\gamma = 0 \quad \text{---} \rightarrow \text{③}$$

Similar equation at the bulk of solv. is given by Gibb's duhem eqn.

$$\sum n_i d\mu_i = 0$$

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad \text{--- (A)}$$

where  $n_1^0, n_2^0 \rightarrow$  no. of gm moles of solvent and solute present at the bulk of the solution

$n_2 > n_2^0$ , if there is accumulation at surface

Considering (3) & (4),

$n_1, n_1^0, n_2, n_2^0$  are different, but  $d\mu_1, d\mu_2$  are same because the chemical potential will be same at surface & bulk as system is in equilibrium.

$$\therefore \mu_1 \text{ at surface} = \mu_1 \text{ at bulk}$$

$$\mu_2 \text{ at surface} = \mu_2 \text{ at bulk}$$

$$d\mu_1 = d\mu_2$$

From (A)  $n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$

$$\text{or, } n_1^0 d\mu_1 = -n_2^0 d\mu_2$$

$$\text{or, } d\mu_1 = -\frac{n_2^0}{n_1^0} d\mu_2 \quad \text{--- (5)}$$

Putting (5) in (3)

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

$$\text{or, } -s dz = \left( n_2 - \frac{n_2^0 n_1}{n_1^0} \right) d\mu_2$$

$$\text{or, } \frac{dz}{d\mu_2} = -\frac{1}{s} \left( n_2 - \frac{n_2^0 n_1}{n_1^0} \right)$$

$$\left[ \frac{dz}{d\mu_2} = \Gamma_2 = \text{surface excess of solute} \right]$$

Significance

At bulk solution

The surface

$$\Gamma_2 = n_2 - \frac{n_2^0 n_1}{n_1^0}$$

Surface

It is the solute present over & above been existing as a layer depletion

$$\frac{dz}{d\mu_2}$$

We have

## Significance:

At bulk solution  $n_1^0$  moles of solvent associated with  $n_2^0$  moles of solute.

$$n_1 \quad n_2 \quad 1 \quad \dots \quad \frac{n_2^0}{n_1^0} \text{ moles solute}$$

$$n_1 \quad n_2 \quad 1 \quad \dots \quad \frac{n_2}{n_1}$$

∴ The surface excess of solute ( $\Gamma_2$ )

$$\Gamma_2 = \frac{1}{S} \left( n_2 - \frac{n_1 n_2^0}{n_1^0} \right)$$

$\left( n_2 - \frac{n_1 n_2^0}{n_1^0} \right)$  = excess no. of gm moles of solute present at the surface of the system.

## Surface excess ( $\Gamma$ )

It is defined as excess no. of gm. moles of solute present per unit area of the interface over & above the value that could have been existed as there been no double layer i.e. no accumulation or depletion of solute.

$$\boxed{\frac{d\gamma}{d\mu_2} = -\Gamma_2} \rightarrow \text{Gibb's adsorption equation.}$$

We have

$$\mu_2 = \mu_2^0 + RT \ln a_2$$

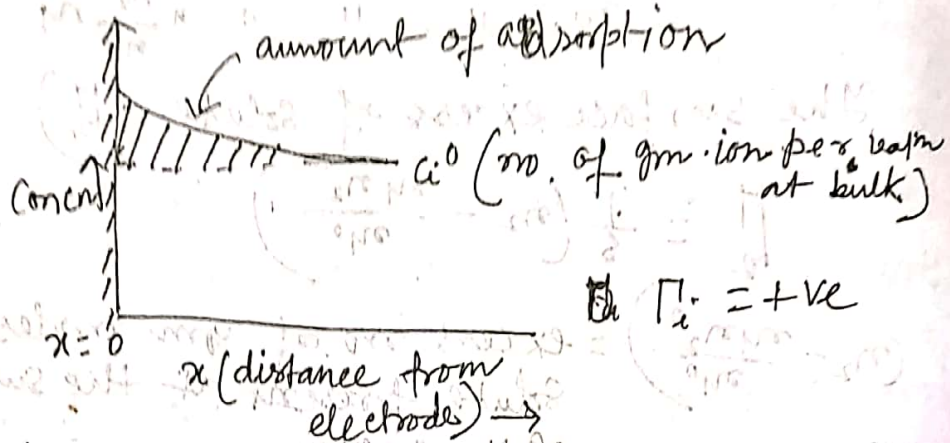
$$d\mu_2 = RT d \ln a_2$$

$\mu_2^0$  = Standard chemical potential

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

$$\sigma_i = \frac{d^2}{RTdA} = -\frac{\Pi_i}{2}$$

= Due to application of external field to the electrode ions at the surface are accumulated or depleted.



$$c_i'(x) - c_i^0 = c_i(x) \rightarrow \text{perturbation in conc}^n \text{ or excess in conc}^n$$

$$\begin{aligned} \Pi_i &= \int_0^\infty c_i(x) dx = \frac{1}{A} \int_0^\infty c_i(x) A dx \\ &= \frac{1}{A} \int_0^\infty [c_i'(x) - c_i^0] dx \\ &= \frac{1}{A} [n_i - n_i^0] \\ &= \frac{n_i}{A} - \frac{n_i^0}{A} \end{aligned} \quad [\because dv = A dx]$$

Surface excess is defined as  $\rightarrow$  excess no. of gm moles present per unit area of interface over and above that value that would have been existed as there been no double layers

$\frac{n_i}{A}$  = amount of absorption per unit area with double layer

$$\Pi_i \neq \frac{n_i}{A}$$

If very dilute solution  $n_i \rightarrow 0$ ; in that case  $\Pi_i = \frac{n_i}{A}$

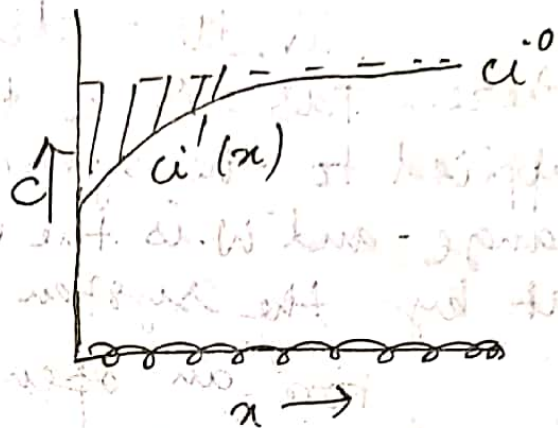
$\Pi_i$  may be (+)ve or (-)ve

If  $\Pi_i = (+)ve$ ,  $n_2 > \frac{n_1 n_2^0}{n_i^0}$ , then

accumulation occurs

$$\frac{d\gamma}{d\mu_2} = (-)ve$$

i.e.  $\gamma$  decreases with  $a_2$  or  $c_2$



For dilute solution,

$$\frac{d\gamma}{RT d\ln c_2} = -\Pi_2$$

Increase in conc<sup>n</sup> of surfactant surface ~~tension~~ tension decreases.

If  $\Pi_2 = (-)ve$ ,  $\gamma$  increases with  $a_2$  or  $c_2$  then, depletion of solute occurs.

Solute - Solvent interaction is less than the solvent - solvent interaction.