B.Sc. (Honours) Part-III
Paper-VA
Topic: Gibbs Adsorption Isotherm
UG
Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)

GIBB'S ADSORPTION ISOTHERM

This isotherm normally considers the case when adsorbents are liquids and adsorbates are soluble or partially soluble in it e.g., surfactants / water or organic liquid / water system.

Considering a system having a plane interface between them, the Gibb's free energy of a system containing two components could be written as follows:

$$G = n_1\mu_1 + n_2\mu_2$$

Where n_1 and n_2 are the number of moles and μ_1 and μ_2 are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on the surface of another, an additional term of surface energy has to be introduced, and hence, equation modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma$$

where γ is the surface energy per unit area and σ is the surface area. It is now clear that first equation is for bulk while second equation will be applicable for the surface of the absorbent liquid. The complete differential of second equation may be written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma$$

We find that the total free energy G of the whole system depends on independent variables , namely , T,P,n_1,$n_2$and σ. Thus,

$$G = f(T, P, n_1, n_2, \sigma)$$

and complete differential of G will be,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} d\sigma$$

or
$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$$

At constant temperature and pressure, above equation reduces to,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$$

Comparing the equations, we get

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

A corresponding equation for the bulk of the system may be,

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$$

Where n_1^0 and n_2^0 are the number of moles of adsorbent liquid and solute in the bulk.

Hence, we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma}$$

Here, the term $\dfrac{(n_2 - n_1 n / n_1^0)}{\sigma}$ represents the corresponding excess moles of solute per

unit area on the surface of the adsorbent and now be represented by Γ_2

$$\therefore \quad -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute $\mu_2 = \mu_2^0 + RT \ln a_2$

or $d\mu_2 = RTd \ln a_2$

When solution is very dilute, the activity a_2 of solute could be replaced by its concentration.

$$\therefore \quad \Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{\partial c_2}\right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial\gamma}{\partial c}\right)_T$$

In the above equation γ is essentially surface energy per unit area, which may easily be

replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends

to accumulate at the interface its surface excess is positive, and so $\dfrac{d\gamma}{dc}$ is negative. This means

surface tension decreases when a solute accumulates at the surface.

3