CHAPTER IV

4.1 Isotherm for adsorption of organic molecules

Adsorption isotherms are equations that describe the variation of experimentally obtained values of the substance that are adsorbed per unit area of metal surface with its activity in the bulk phase at constant temperature, pressure and the charge on the metal surface. The adsorption on the electrodes can be explained either in terms of the surface excess $\Gamma$ at a given potential and at a given activity of the adsorbed substance or by the fractional surface coverage $\theta$ ($\Gamma/\Gamma_{\text{max}} = \theta$) for a given potential and activity. While correlating the surface coverage, the constancy of charge density on the metal was chosen rather than the potential since it is independent of the reference electrode and represents an unique parameter comparable to the adsorbability of ions[1].

Normally the definition of $\theta$ implies two assumptions.

i) Monolayer formation and

ii) Constant area covered by a single molecule.

However these assumptions are not justifiable at high coverages.
4.2 Evaluation of interfacial parameters under ideally polarisable conditions

4.2.1 Charge on the metal

From Lippmann equation, it is known that

$$\frac{dY}{dE}_{\text{comp,T,P}} = -q^M$$ .... (4.1)

Hence it is computed by the graphical differentiation of the electrocapillary curve at different potentials. The accuracy of the values are ± 0.5 uC near PZC and ± 1 uC at extremes [2]. Also computerized graphical differentiation of a polynomial curve fit involving number of r, E values are also available. $q^M$ can also be obtained from differential capacity curves by graphical integration with the knowledge of the electrocapillary maxima. The values obtained by this method are accurate to ± 0.1 uC.

4.2.2 Surface excess

Capacity curves when twice integrated gives the interfacial tension, from which the surface excess can be calculated using the expression

$$\frac{dY}{d\mu_{\text{org}}} E \text{ or } q = \Gamma_{\text{org}}$$ .... (5.2)

Radio tracer methods have been developed [3,4] which give direct and clear information on the extent of adsorption subject to the condition that the electrosorbed molecule do not undergo any chemical change on the surface.
In this method [5-7], which assumes linearity between electrode charge and surface coverage at constant potential, in the case of aliphatic compounds the relation is given as

\[ q^M = q_{\theta=0} (1-\theta) + q_{\theta=1} \theta \]  \hspace{1cm} \text{.... (4.3)}

where \( \theta \) is the coverage of the electrode surface by the adsorbed organic molecule. \( q_{\theta=0} \) and \( q_{\theta=1} \) referred to the charge density on the metal when \( \theta = 0 \) and \( \theta = 1 \) respectively at the potential \( E_r \) of the ideally polarised electrode with reference to the point of zero charge in the absence of organic compounds in solution. The above equation in terms of capacity can be written as

\[ C = \frac{dq}{dE_r} = \theta C_{\theta=1} + (1-\theta) C_{\theta=0} \frac{d\theta}{dE_r} \]  \hspace{1cm} \text{.... (4.4)}

The quantity \( d\theta/dE_r \) is negligible in the vicinity of electrocapillary maximum. The measured interfacial capacity may be treated as the sum of two capacities one due to water dipoles and the other due to the organic compound, connected in parallel. Hence we can write

\[ C = \theta C_{\theta=1} + (1-\theta) C_{\theta=0} \]  \hspace{1cm} \text{.... (4.5)}

\( C_{\theta=1} \) is obtained by plotting \( 1/\text{minimum capacity} \) vs \( 1/\text{bulk concentration} \) and finding the capacity value at \( C \to \infty \) assuming
the curve to be linear. The minimum capacity is linear with concentration in dilute solutions and tends to become higher at higher concentrations. One can write the equations in the form

$$C = C_{0=0}(1-\theta) + C_{0=1.\theta} + \frac{(q_{0=0} + C_{0=1}(E_n-E_r))^2 h}{RT \Gamma_m} \ldots \ldots (4.6)$$

where

$$h = \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}$$

and $E_n$ is the shift of the potential of zero charge when the coverage changes from $\theta=0$ to $\theta=1$.

This equation, though satisfactory for some compounds fails when applied to compounds like $n$-valeric acid in 0.1N perchloric acid [8,9] which assumed a variation of $'a'$ with $E$. Therefore the equation (4.6) will be written as

$$C = C_{0=0}(1-\theta) + C_{0=1.\theta} + \frac{[q_{0=0} + C_{0=1}(E^*_n-E_r)]^2 h}{2RT \Gamma_m \frac{da}{dE_r}} \ldots \ldots (4.7)$$

where $E^*_n = E_n$ if $da/dE_r = 0$.

The above equation can be used to obtain the value of $\theta$ in the case of aliphatic organic compounds. However in the case of
aromatic compounds it is not possible to calculate $\Theta$ from the above equation [10,11]. The above treatment suffers from the disadvantage that it offers no suitable explanation for the variation of $\alpha'$ from one substance to another and for the same substance in different supporting electrolytes. Also it fails to give any method of independently obtaining $\alpha'$ from molecular parameters.

(ii) Devanathan's model method

Devanathan's method [12,13] is based on a model of the electrical double layer wherein a Helmholtz plane $X_1$ of specifically adsorbed ions and Gouy plane $X_2$ of solvated cations and anions constitute the interface. The diffused layer terminates at $X_2$. $\phi_m$, $\phi_1$ and $\phi_2-s$ are the electrical potentials of the metal, Helmholtz and Gouy planes respectively. The potential due to the dipoles is assumed to be equal to

$$\phi_{org} = \frac{2\pi n d \Gamma_{org}}{\varepsilon} = \frac{\varepsilon_0 \Gamma_{org}}{K_{org}} \quad \ldots \quad (4.8)$$

Where there is no change in the dielectric constant of the compact layer. $K_{org}$ is the integral capacity of the organic species and the other terms have their usual significance. The measured capacity is given by
Thus it is possible to obtain $\Gamma_{\text{org}}$ from differential capacity curves and there is found to be good agreement with thermodynamic values for the adsorption of thiourea. For aliphatic organic molecules

$$\frac{1 - \alpha \theta}{C} = \frac{1}{C_B} - \frac{e_0}{K_{\text{org}}} \frac{\mathrm{d}\Gamma_{\text{org}}}{\mathrm{d}q^M} \quad \ldots \quad (4.10)$$

where $\alpha = \varepsilon_w - \varepsilon_0 / \varepsilon_w$

where $\varepsilon_0$ and $\varepsilon_w$ referred to the permittivity of organic molecules and water molecules respectively.

The above equation cannot be used to situations when the compact layer thickness increases to the distance equal to the length of the organic molecules from the metal due to the formation of water-free coherent film [14].

(iii) Parson's method

In this method surface excess is directly obtained from the differential capacity of the electrode [15-20] which is given as

$$\frac{1}{C} = \frac{1}{C_B} \frac{-RT}{\mathrm{d}q^M} \frac{\Gamma_2}{\mathrm{d}q^M} \frac{\mathrm{d}\ln \delta}{\mathrm{d}q^M} \quad \ldots \quad (4.11)$$
The above equation permits the calculation of parameters also from differential capacity data.

4.3 Isotherms for organic adsorption

To propose a suitable isotherm that describes the behaviour of organic molecules at the metal/solution interface one has to necessarily calculate the partial surface coverage. In the classical approach [21] \( \Gamma \) is directly determined from a plot of \( V_s \ln a \). Maximum value of \( \Gamma \) deduced from the above plot is the value of \( \Gamma_{\text{max}} \) corresponding to any concentration. Using Devanathan's approach [22], \( \Gamma_{\text{max}} \) can be evaluated from a plot of \( C/\Gamma \) against \( C \) for \( q^\text{M}=0 \). The gradient of the straight line gives \( 1/\Gamma_{\text{max}} \) from which \( \Gamma_{\text{max}} \) is calculated.

\( \Gamma_{\text{max}} \) can also be calculated using molecular models manufactured by 'Catalin Products Ltd.', Waltham Abbey, Essex, which are so meticulously made that each square centimeter of the drawn curve over a graph sheet with the assembled model placed over the graph sheet in the planar position, corresponds to 1 square A* i.e., the models are exactly \( 10^8 \) times magnified from the actual microscopic size of the molecule. Thus knowing the area, one can calculate the surface excess maxima.
Experimental methods for the determination of the surface coverages may be classified into two groups.

i) Those in which coverage is directly determined experimentally as a function of potential.

ii) Those in which the capacity is measured directly and the coverage is obtained from it by integration with respect to potential.

The evaluation of $\theta$ is done using the equation

$$\theta = \frac{C - C_0}{C_0 - C_{-0}}$$

... (4.12)

This equation is applicable in the range where the variation of $\theta$ with potential is very little and requires a correct knowledge of the potential of zero charge and the value of interfacial tension at this potential. This method finds wide applications in the study of adsorption on solid electrodes.

Fast potential sweep transients and charging curve method are also used for the determination of $\theta$ on solid electrodes [23-26]. The charging curve method is sensitive to the mode of adsorption on the surface and measures approximately the number of sites occupied, independent of the nature of the species. However, the sweep method monitors the charge required to oxidise
the species on the surface. Hence the two methods do not yield the same results for a given system. The results by these methods may not be taken as wholly reliable, but can be used in combination with other methods such as radio tracer method [3,4].

Any electrochemical adsorption isotherm must show the variation of $\Gamma$ (or $\Theta$) with bulk activity and with the electrical state of the system i.e., $q^M$ or $E$. The conversion of an equation of state to the corresponding isotherm is made possible by making use of Gibb's isotherm. The generalised form of adsorption isotherm which expresses the activity in the adsorbed state as a function of bulk activity and the electrical state of the system is expressed as

$$a_A^a = \beta a_A^b$$

where $\beta = e^{-\Delta G^f/RT}$ and $\Delta G^f = a_{\mu A} - \mu^*{A}$.

where $a_{\mu A}$ is the standard electrochemical potential of the substance $A$ in the adsorbed state and $\mu^*{A}$ is the standard chemical potential of $A$. $a_A^a$ can be expressed in terms of either surface concentration $\Gamma_A$ or surface pressure $\Phi$. While formulating a particular adsorption isotherm it is always better to take into consideration the particle-metal interactions and the particle-particle interaction of the adsorbed particles in their state of
adsorption. For metal/solution interface the applicable isotherms are discussed.

4.3.1 Langmuir's adsorption isotherm and its modification[27]

The isotherm is subject to the following conditions:

1) fixed site of adsorption (immobility of adsorbate)
2) no lateral interaction or heterogeneity of the surface, i.e., the energy of adsorption to be independent of coverage \( \theta \).
3) equilibrium between interface and bulk for adsorption up to a mono layer (\( \theta = 1 \)).

The isotherm is given as

\[
\frac{\theta}{1-\theta} = KC
\]  \hspace{1cm} (4.14)

\( K \) is related to the standard free energy of adsorption and is given as

\[
K = \exp \left[ -\frac{\Delta G^o}{RT} \right]
\]

and \( C \) represents the bulk concentration.

At high coverages, surface activity coefficient has to be introduced to accommodate the deviations from ideality [28-31]. Under such conditions the isotherm reads as

\[
\ln \frac{\theta}{1-\theta} = 55.5 - \ln f_\theta = -\frac{\Delta G^o}{RT} \text{ C} \hspace{1cm} (4.15)
\]
Where $f_\theta$ is the surface activity coefficient at a coverage of $\theta$ and is a measure of non ideal free energy interaction of the adsorbate dipole. The isotherm can be rewritten as

$$\frac{C}{\theta} = C + C_w e^{-\Delta G^* / RT} \quad \text{..... (4.16)}$$

Where $C_w$ is the concentration of water and $\Delta G^*$ is the free energy of adsorption at zero charge. Hence a plot of $C/\theta$ against $C$ should yield a straight line of unit slope. This has been observed to be true at $q^M = 0$.

The effective free energy $G_q$ at a charged interface is given by the equation

$$\frac{\theta}{1-\theta} = \frac{C}{C_w} e^{-\Delta G / RT} \quad \text{..... (4.17)}$$

and this equation is used to find out $\Delta G_q$. As mentioned earlier, this isotherm is valid when the surface of the electrode is completely homogeneous and lateral interactions as well as induced surface heterogeneity effect are completely negligible.

4.3.2 Frumkin's isotherm

The long range interaction between the adsorbed species is taken into account in this isotherm [5]. The equation for this adsorption isotherm is
BC = $\theta / (1 - \theta) \exp(-2a\theta)$ \hspace{1cm} \ldots (4.18)

Where 'a' is interaction parameter between adsorbed particles and 'B' is a constant determining the adsorption equilibrium at small coverages, i.e.,

$$B = \exp\left(-\frac{\Delta G^*}{RT}\right) \hspace{1cm} \ldots (4.19)$$

A positive value of the interaction parameter corresponds to attraction and a negative value to repulsion between adsorbed molecules. The isotherm is derived by assuming apparent linearity between the standard free energy of adsorption and coverages. If 'n' molecules of the solvent are displaced by 1 molecule of the solute during the adsorption process the above equation changes to a more general form [32].

$$\frac{\theta}{BC} = \left[ \frac{1 - \theta}{1 - \theta} \right] \exp(-2a\theta) \hspace{1cm} \ldots (4.20)$$

A plot of $\log C - \log \theta / (1 - \theta)$ against $\theta$ for various values of $q^H$ giving a family of parallel straight lines is taken as the test for applicability of the isotherm.

4.3.3 Temkin's isotherm

The adsorption isotherm [33] is for the adsorption of neutral species on the heterogeneous surface or for the adsorption on homogenous surfaces with lateral interaction
between adsorbed species. The isotherm is based on the assumption of a linear variation between \( H_{\text{ads}} \) and \( G_{\text{ads}} \) with coverage is

\[
\Delta G^*_{\text{ads}} = \Delta G^*_{\text{ads}} + r \theta 
\]  

Where \( \Delta G^*_{\text{ads}} \) is the apparent standard free energy of adsorption and \( \Delta G^*_{\text{ads}} \) is the standard free energy of adsorption at \( \theta \to 0 \) case. \( r \) represents the Temkin parameter which is often expressed as the units of \( RT (r = f RT) \). Here \( r' \) is assumed to be constant and independent of \( \theta \).

Temkin obtained the relation,

\[
\frac{1}{f} = \frac{\ln (1 + K_0 C)}{1 + K_0 C \exp(-f)} 
\]  

Here \( K_0 \) is the value of \( K \) in the Langmuir equation pertaining to the first micro adsorption patch, viz., when \( \theta = 0 \) and \( f \) is defined as the rate of change of the apparent standard free energy of adsorption with coverage, i.e.,

\[
\frac{1}{f} = \frac{d \Delta G^*}{\text{RT} \ d \theta} 
\]  

The following equation is represented as the logarithmic isotherm in a simplified form

\[
\frac{1}{f} = \frac{\ln (K_0 C)}{K_0 C} 
\]
This equation is applicable for intermediate values of the concentration and coverage. In cases where there is decrease in heat of adsorption due to lateral interaction effects or to the dipole potential generated by adsorbed species, the same isotherm can be used\[34\].

This model of "induced heterogeneity" by Boudart [35] has been applied by Conway and Gileadi [36,37] to electrochemical adsorption isotherm similar to Temkin's. The validity of Temkin's isotherm can be tested by a plot of $\theta$ Vs $\ln C$. The free energy of adsorption can be computed from the intercept of the plot. The adsorption behaviour of benzene-m-disulphonate on a mercury surface from aqueous solutions is reported to follow Temkin's isotherm[38].

4.3.4 Parson's isotherm

To avoid the personal errors in the graphical method of evaluation of surface excess, Parson suggested the analysis of surface pressure data for the assignment of isotherms. The evaluation of surface pressure eliminated the differentiation of $\gamma$ Vs $\mu$ curves. He considered [15,18] several adsorption isotherms from the equation of state corresponding to the hot sphere model in the dimensions with or without interactions. It has been
shown that a virial equation of state provides the best fit with experimental data for the adsorption of thiourea at mercury/sodium fluoride interface. An empirical term $gr^2$ accounting for particle-particle interaction is incorporated in the virial equation. Instead of obtaining the free energies and interpreting them in terms of molecular parameters, Parsons has chosen the isotherm a priori, assumes a per-set dependence for the variation of the free energy with charge and then works back the shape of the capacitance curve. He has also pointed out [15] that equations of state may be used for understanding the adsorption behaviour at liquid metal/solution interface, as surface tension and its variation with potential can be measured accurately and directly. It has to be pointed out that the surface pressure is less sensitive to adsorption and Parson's method is not so useful as it appears to be.

4.3.5 Recent statistical models for the adsorption isotherm

Levine et al. [39,40] have made significant contributions to the modelling of the adsorption of molecules at charged interfaces. Earlier approaches of Frumkin [6], Hansen et al. [41], and Parsons [16] have led to some simple forms of relationship between the electrode charge and the interfacial potential difference. Damaskin, Damaskin et al. [42-44] have given an
empirical equation connecting the electrode charge and potential under a hypothesis termed 'Generalised Surface Layer Model'.

Sangaranarayanan and Rangarajan [45-48] have developed a hierarchy of models to describe the adsorption at an electrochemical interface that consider multicomponent, multisite and local polarisation effects besides coulombic and substrate interactions. They have provided three isotherms for three molecular descriptions. A brief description of these models is given below.

Model I

It is a two state model, one state each for the solvent and the adsorbate. Parity is assumed with regard to the size of the solvent and the adsorbate.

The adsorption isotherm as per the simple model is given as

\[
\theta = \frac{\theta_0 \exp\left(\frac{ab^2}{2\theta_0}\right)\left(\frac{q - q_{\text{max}}}{(a_1 + a_2\theta)^2}\right)^{\frac{1}{2}}}{1-\theta}
\]

where \( \theta_0 = \frac{\beta_0 \exp\left(-P^2/2\theta_0\right)}{55.5} \)

and \( \beta_0 = \exp\left(\frac{\mu^0_A - \mu^0_S + U_A - U_S}{\theta_0}\right) \)

Here \( \mu^0_A \) and \( \mu^0_S \) are the chemical potentials of the adsorbate and the solvent and \( U_A \) and \( U_S \) are the energies of interaction of various states with the adsorbate. \( P = P_A - P_S \)
where $P_A$ and $P_S$ represent the normal component of permanent dipole moment of the adsorbate and the solvent.

$$a = a_A - a_S,$$

where $a_A$ and $a_S$ represent polarisabilities of the adsorbate and the solvent.

$$a_1 = 1 + C_a a_S/d^3 \quad \text{and}$$

$$a_2 = C_e a/d^3$$

$$\theta = N_A/N_T (1-\theta) = N_S/N_T \quad \text{and} \quad b = 4\pi \quad \text{and} \quad C_e \quad \text{is the effective coordination number}.$$  

This model has certain limitations like

i) size disparity between the solvent and the adsorbate.

ii) restrictions imposed by limited number of sites included in analysis.

iii) constraints on the accessibilities of parameters like permanent dipole moment and polarisabilities and lack of quantitative prediction of the asymmetric $\Delta G^*$ dependence on $q^M$.

Model II

It is also a two state model. But there is no site parity between the solvent and adsorbate in this case. Adsorbates occupy $n$-sites and solvent one site. This model takes into account
(i) dipole-dipole interactions (permanent and induced)
(ii) discreteness of charge and imaging and
(iii) specific interactions with the substrate at a molecular level. Here organic adsorbate is assumed to occupy `n' lattice sites at the interface as compared to one by the solvent.

The isotherm can be represented as

\[
\epsilon = \frac{\beta_1^* c_a \exp\left(-\frac{n b^2}{2 K T \beta}\right)}{\left(1 - \frac{q}{n}\right)^{c(n-q)/2} (q/n)^{q_c/2}}
\]

\[
= \frac{\beta_1^* c_a \exp\left(-\frac{n b^2}{2 K T \beta}\right)}{\left(1 - \frac{q}{n}\right)^{c(n-q)/2} (q/n)^{q_c/2}} \left[ B (\alpha_B - \alpha_B/n) + \alpha^2 \right]
\]

\[
= \frac{\beta_1^* c_a \exp\left(-\frac{n b^2}{2 K T \beta}\right)}{\left(1 - \frac{q}{n}\right)^{c(n-q)/2} (q/n)^{q_c/2}} \left[ B (\alpha_B - \alpha_B/n) + \alpha^2 \right]
\]

\[
\text{where} \quad \beta_1^* = \beta_0 \exp\left\{ -\frac{n}{2 K T \beta} \right\} \left[ p^2 - b^2 (q_{max})^2 (\beta a_B - \alpha_B/n + \alpha^2) \right]
\]

and A and B are defined as

\[
A = \left( \frac{d^3}{c_e} + \alpha_B \right)
\]

\[
B = \left( \frac{d^3}{c_e} \right) (q/n - 1) + (\alpha_B a_B^2/n^2 - \alpha_B)
\]

The isotherm is found to be more general than the earlier multi-site versions of Bockris and Swinkles, Mohilner et al., and Bennes[49-51], as far as the entropy considerations are concerned.
The role of electrostatic forces is explicitly reflected in the adsorption isotherm via Gibbs energy of adsorption term.

The limitation of the model is the restriction on the number of orientational states allowed (one only) for the solvent and the adsorbate.

Model III

This is a three state model. Two types of models are proposed. Two configurations are permitted for the solvent and only one for the adsorbate at the first instance.

\[
\frac{\theta}{1 - \theta} = \left(\frac{C_A}{C_S}\right) \exp\left[\frac{-\Delta G^o}{KT}\right] \hspace{1cm} \ldots (4.27)
\]

where

\[
\Delta G^o/\text{KT} = f(\zeta)
\]

\[
= (\Delta \mu^* + \{ U_A - S_1 \}) - \alpha \zeta^2/2 + \frac{P\zeta}{\text{KT}} \\
+ \ln[1 + \exp(\Delta U_{S1} - \Delta U_{S2} + 2P\zeta)/\text{KT}] \hspace{1cm} \ldots (4.28)
\]

In the above equation \( \zeta \) represents the total average field experienced by the dipoles and is a function of \( q^M \) and coverage \( \theta \) of the adsorbate. The other parameters occurring on the right hand side of equation (4.27) are molecular constants. The equation satisfied by the variable \( \zeta \) is
\[(a_1 + a_2 \theta)\zeta = \left(\frac{C_0}{d^3}\right)(P_S R + P_A \theta) + 4\pi q^M \quad \ldots \quad (4.29)\]

\[= \left(\frac{C_0}{d^3}\right)[P_A \theta - P_S(1-\theta) \tanh(\Delta U_{S1} - \Delta U_{S2} + 2P_S\zeta)/2KT] \]
\[+ 4\pi q^M \quad \ldots \quad (4.30)\]

The above equation gives \(\zeta\) as a function of \(\theta\) and \(q^M\). The isotherm is a straightforward relationship containing all the effects due to dipole potentials and external fields. Parity is assumed with regard to site. In the case of aromatic hydrocarbon, the adsorbate has been assigned two configurations and the solvent only one configuration.

To account for the behaviour of organic adsorbates having appreciable \(\pi\)-electron interactions, at flat and vertical orientations of the surface, a three state multisite model of three parallel condensers has been proposed by Sangaranarayanan and Rangarajan[48].

The isotherm can be represented as

\[\theta = \frac{(C_A/C_S) \exp[-\Delta G^*/KT]}{(1 - \theta)} \quad \ldots \quad (4.31)\]

\[G^*/KT = f(\zeta_A)\]

\[= \left[ \mu^* + (\Delta U_S - \Delta U_{A1}) - \alpha \zeta_A^2/2 - P\zeta_A \right]/KT\]
\[- \ln \left[1 + \exp(\Delta U_{A1} - \Delta U_{A2} + 2PA \zeta_A)/KT \right] \quad \ldots \quad (4.32)\]
where
\[ \zeta_A = \left( C_0/d^3 \right) \int P_a R_A + P_S (1-\theta) + 4\pi q_m \]
and
\[ R_A = -\theta \tanh(\Delta U_{A1}-\Delta U_{A2}) + 2P_A \zeta_A/2KT \] .... (4.33)
and \( \theta = \theta_1 + \theta_2 \) corresponding to the surface coverages and the appropriate orientational states.

This model differs from other models in that the solvent and the adsorbate configurations are of different sites. Solvent is considered as a cluster occupying 'n' lattice sites. The adsorbate occupies only one site as before. Solvent site is always a cluster and is larger in size than adsorbate.

The two state multisite statistical mechanical model put forward by Nikitas [521] takes into account short range particle-particle interactions and field effects on adsorbed molecules. It is also applicable to any kind of adsorbate and solvent molecules of any size or shape occupying one or more lattice sites. The validity of this isotherm tested for the adsorption of 2-butanol at mercury/solution interface is quite encouraging for low values of the size ratio parameter.

Nikitas has recently [531] put forth a simple two state solvent model to describe the adsorption of rigid rods at polarisable interface.
Three models for metal electrode/electrolyte, semi conductor electrode/ electrolyte and insulator/electrolyte interface were proposed [54]. The difference between these three models was examined.

Using classical equilibrium statistical mechanics, the electrical double layer as a solvable model was proposed [55]. A charged hard wall (primitive electrode), a polarisable interface, an ideal conductor electrode and a semi permeable membrane are studied. The density profiles and correlation functions are computed. The differential capacity and the surface tension are also obtained.

4.4 Selection of electrode potential or charge in describing the adsorption process

In determining the form of isotherm Stern [56] has chosen the potential as the electrical variable at the site where an ion is adsorbed. As the potential $E$ included the electrostatic interactions of the adsorbed particles with its neighbours as well as the interaction with the electrode, this model was later changed by Grahame [57]. A similar proposal was made by Frumkin for the adsorption of neutral molecules at constant metal/solution potential difference.
Parsons suggested [15] that the adsorption should be considered under constant electrode charge. Under such conditions the electrode-particle interactions should be approximately constant so that the interaction parameters derived from the isotherm will be a true reflection of particle-particle interactions. Further it has been pointed out that the potential difference at the interface is a complex quantity deriving contributions from ions in the inner layer, oriented dipoles and the diffused layer and does not give a clear picture of their physical situation with regard to the interactions in the electrical double layer. This view of Parsons was supported by Bockris et al. [58,59], Devanathan [12], Devanathan and Tilak [60], Dutkiewicz et al. [61] and Battisti and Trasatti [62].

Damaskin [63,64], however preferred to hold the potential of the electrode constant, when dealing with adsorption of neutral molecules. His views are totally against that of Parsons.

Damaskin et al. [65] and Frumkin et al. [66] are of the view that the choice of the electrical variable $E$ or $q^M$ is not of fundamental importance as $F_{org}$ for neutral substances is thermodynamically derived from Gibb's equation. Thus according to them the choice is only of convenience.
REFERENCES


