

ROLE OF SHORT RANGE INTERACTIONS IN THE CHARGE OF MAXIMUM ADSORPTION

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Adsorption of solvent or organic compounds at a metal/interface is characterized by a wide spectrum of interactions governing the phenomenon under effective fields of order $\approx 10^7$ V/cm. A generalized spin-1 Ising Hamiltonian was formulated by considering various interactions under molecular field approximation (MFA) to arrive at a three-state model of adsorption isotherm (i.e. the joint adsorption of two different organic compounds in the presence of solvent molecules). A general multi-state model was deduced heuristically and an expression for the charge (σ_{\max}^M) at which maximum adsorption (θ_{\max}) occurs derived explicitly for a three-state site parity model that incorporates short-range interaction energies, functional dependence of permanent and induced dipole moments of the organic adsorbate, and the solvent and substrate interactions.

Keywords: Electrosorption; short-range and coulombic interaction; dipolar; metal-electrolyte interface; field effect; surface thermodynamics.

1. Introduction

The phenomenon of adsorption is controlled by the various interactions among the constituents of the interface and the forms of adsorption isotherms hold the clue to the nature of interactions. The types of interactions are varied: electronic (chemisorptions like), long-range coulombic, Van der Waals, etc. An understanding of this phenomenon may be said to be complete only when parameters occurring in such expressions for isotherms are interpretable in terms of either molecular or electronic interactions. The method of expressing the parameters of isotherms through a microscopic modeling is a simple one. Such a task is particularly made difficult in case of charged interfaces.

Adsorption of organic compounds or solvent at a metal/electrolyte interface is characterized by the effective fields of order $\approx 10^7$ V/cm and with a wide spectrum of molecular interactions^{1–9} governing the phenomenon. Adsorption of neutral organic compounds at the electrochemical interfaces exhibits a maximum surface

Table 1. Values of σ_{\max}^M for various adsorbates.

Adsorbate	Interface	$\sigma_{\max}^M \mu\text{C}/\text{cm}^2$
Butane-1,4-diol	Hg/NaF	-2.5
<i>n</i> -Butanol	Hg/NaF	-2.0
2-Butyne-1,4-diol	Hg/NaF	-1.0
Diethyl ether	Hg/NaF	-4.5
Acetailide	Hg/NaF	0
Ethylene glycol	Hg/NaF	-3.5
Acetonitrilic	Hg/NaF	-3.5
5-Chloro-1-pentanol	Hg/NaF	-1.0
Ethyl bromide	Hg/KCl	-2.0 to 0
<i>n</i> -Propanol	Hg/NaF	-2.0
Butane-1,4-diol	Hg/NaF	-2.8 ($\theta \rightarrow 0$) to -3.7 ($\theta \rightarrow 1$)
Urea	Hg/KNO ₃	8
<i>n</i> -Butanol	Hg/NaCl	-2.8
Butyric acid	Hg/NaCl	-1.8
Butyramide	Hg/NaCl	-5.5
Butyl glycol	Hg/NaCl	-3.5
Succionitrile	Hg/NaF	-4.6
Butyronitrile	Hg/NaF	-4.0
<i>t</i> -Butanlo	Hg/NaF	-2.8
(2-Methylthio)ethanol	Hg/NaF	+1.0
<i>n</i> -propanol	Cd/KF	-3.9
Dimethylformamide	Hg/NaF	0
<i>n</i> -Butanol	Ag/KCl	-1.1
Ethylene glycol	Ag/KCl	-3.2
Polyvinyl alcohol	Ag/KCl	-2.1 \pm 0.2
Sucrose	Hg/NaF	0
Tetra methyl urea	Hg/NaF	-4.0
Ethylene glycol	Hg/KCl	-3.7
Ethylene glycol	Hg/KBr	-4.0
Ethylene glycol	Hg/KI	-5.0

Source: Ref. 12.

coverage, usually near the potential of zero charge (pzc). There are also instances when no maximum adsorption (as a function of charge or potential) is found, for example, thiourea,¹⁰ tetra methyl thiourea,¹¹ etc. Table 1 indicates¹² a partial list of organic adsorbate and the corresponding values of the charge (σ_{\max}^M) at which maximum adsorption (θ_{\max}) occurs.

The simplest description of the adsorption at charged interface is a two-state ($s = 1/2$) model wherein the adsorbate and the solvent is assumed to have one orientation each at the interface. A lattice site is to be occupied either by an organic molecule or by a solvent dipole. It has been shown¹³ that the analysis of such a simple model itself is nontrivial. There exist several reasons for the need of a higher state model ($s = 1, 3/2$, etc.).¹⁴ In the discrete lattice versions, the preliminary step is to label each site with the help of a spin variable viz. s_i . For the simple two-component model (adsorption of two different entities), s_i can assume -1 or $+1$

(spin-1/2 model). In the next higher version viz. a three-state (spin-1 model), the allowed values of s_i are +1, -1, and 0. Once occupancy of the lattice site is described using s_i , the next step is to express the various energetic contributions individually and formulate the total Hamiltonian characterizing the system. Solution of the Hamiltonian leads to the various equilibrium coverage, the relevant order parameter, the potential difference across the inner layer, etc.

A hierarchy of multistate models¹⁵⁻¹⁷ has been developed for describing the electrosorption of neutral organic compounds, and the functional dependence of the charge and potential of maximum adsorption on permanent and induced dipole moments of the organic adsorbate and the solvent, substrate interactions etc. has been derived. An issue hitherto not extensively analyzed, in this context, is the dependence of maximum adsorption parameters on the surface coverage.

The purpose of the present analysis is to derive a spin-1 isotherm and deduce heuristically a general ($N_s + 1$) state model (where N_s denotes the number of orientational state of the solvent dipoles) and to derive an expression for the charge (σ_{\max}^M) at which maximum adsorption (θ_{\max}) occurs explicitly for a three-state site parity model that incorporates short-range interaction energies, functional dependence of permanent and induced dipole moments (of the organic adsorbate and the solvent), and substrate interactions. The essential ingredients of the model and the methodology of deriving the equilibrium relations have been discussed in the next section.

2. Generalized Spin-1 Ising Model

A generalized spin-1 Ising Hamiltonian¹⁶ is formulated taking into account various interactions, and is resolved under molecular field approximation (MFA). The first step in the analysis of spin-1 model is to associate with each lattice site a spin variable s_i , which can take the values +1, -1, or 0 and then an auxiliary variable s_i^2 , which has the value 1 or 0. For this model, $s_i = +1$ indicates the presence of the neutral adsorbate (I) at the lattice site i and $s_i = -1$ is a sign for the occupancy of neutral adsorbate (II) at site i . When the lattice site i is occupied by the solvent species, $s_i = 0$. Using the spin variables, various interactions are then added appropriately in formalism.

Once such a physical picture for describing adsorbate(s) in terms of their site occupancy is presumed, the rest of the analysis concerns the formulation of the Hamiltonian. In the case of adsorption of neutral dipoles at the electrochemical interface, the multi-components, multi-site, and multi-configurational characteristics of the species are dealt. The organic adsorbate and solvent molecules can have different dipolar orientational states (i.e. configurations) at the interface.

2.1. Substrate interaction energies

The effective binding energies (specific interaction with substrate) of the two adsorbates and of the solvent with electrode surface are ΔU_{A1} , ΔU_{A2} and ΔU_w . Then,

the contribution to the total Hamiltonian (H_{ne}) is

$$H_{ne} = \sum \frac{s_i(s_i + 1)}{2} \Delta U_{A1} + \sum \frac{s_i(s_i - 1)}{2} \Delta U_{A2} + \sum (1 - s_i^2) \Delta U_w, \quad (1)$$

$$H_{ne} = -H_1 \sum s_i - D_1 \sum s_i^2 + \text{constants}, \quad (2)$$

$$\text{where } H_1 = -(\Delta U_{A1} - \Delta U_{A2})/2, \quad (3a)$$

$$D_1 = -(\Delta U_{A1} + \Delta U_{A2} - 2\Delta U_w)/2. \quad (3b)$$

$$\text{Further, } D_1 + H_1 = -(\Delta U_{A1} - \Delta U_w)/2 = -\Delta U_1, \quad (4)$$

$$D_1 - H_1 = -(\Delta U_{A2} - \Delta U_w)/2 = -\Delta U_2. \quad (5)$$

The purpose of writing Eqs. (4) and (5) is to identify the energetic contributions of each adsorbate with respect to the solvent, the reference frame. From the literature it was noted that this *modus operandi* was hitherto not adopted. However, this was implemented in the entire paper to indicate the energetic contribution of each species.

2.2. Coulombic interactions

The field at a given site is composed of the external field $4\pi\sigma^M$ due to electrode charge density σ^M and the reaction field arising from the dipole-dipole interaction. The coulombic interaction energy between a pair of dipoles depends on their mutual orientations, and the state of a dipole at a given lattice site will be influenced due to the occupancy of the neighboring site by other dipoles. The local field ξ_i at lattice site i can be written as

$$\begin{aligned} \xi_i = & 4\pi\sigma^M + \sum \frac{f_{ij}s_j(s_j + 1)}{2} (p_{A1} - \alpha_{A1}\xi_j) + \sum \frac{f_{ij}s_j(s_j - 1)}{2} (p_{A2} - \alpha_{A2}\xi_j) \\ & + \sum f_{ij}(1 - s_j^2)(p_w - \alpha_w\xi_j), \end{aligned} \quad (6)$$

where ξ_j is the field at the dipole site j , f_{ij} is the potential due to a pair of (unit) dipoles at sites i and j , σ^M is the charge density on the electrode surface, p_{A1} , p_{A2} , p_w are (the normal components of) permanent dipole moments pertaining to the two adsorbates and the solvent, respectively, and α_{A1} , α_{A2} , α_w are the polarizabilities of the adsorbate and the solvent, respectively.

The above equation represents many center effects contained in the ξ_i term. Under MFA, Eq. (6) can be rewritten as

$$\langle \xi \rangle = \frac{4\pi\sigma^M + p_{A1} \sum \frac{f_{ij}s_j(s_j+1)}{2} + p_{A2} \sum \frac{f_{ij}s_j(s_j-1)}{2} + p_w \sum f_{ij}s_j(1 - s_j^2)}{1 + \alpha_{A1} \sum \frac{f_{ij}s_j(s_j+1)}{2} + \alpha_{A2} \sum \frac{f_{ij}s_j(s_j-1)}{2} + \alpha_w \sum f_{ij}s_j(1 - s_j^2)}. \quad (7)$$

Consequently, the coulombic contribution to the total Hamiltonian becomes

$$H_C = \sum \frac{s_j(s_j + 1)}{2} \left(p_{A1} \langle \xi \rangle - \frac{\alpha_{A1} \langle \xi \rangle^2}{2} \right) + \sum \frac{s_j(s_j - 1)}{2} \left(p_{A2} \langle \xi \rangle - \frac{\alpha_{A2} \langle \xi \rangle^2}{2} \right) + \sum (1 - s_j^2) \left(p_W \langle \xi \rangle - \frac{\alpha_W \langle \xi \rangle^2}{2} \right) \tag{8}$$

$$H_C = -H_2 \Sigma s_j - D_2 \Sigma s_j^2, \tag{9}$$

$$\text{where } H_2 = -\frac{1}{2} \left[(p_{A1} - p_{A2}) \langle \xi \rangle - (\alpha_{A1} - \alpha_{A2}) \frac{\langle \xi \rangle^2}{2} \right] \tag{10a}$$

$$D_2 = -\frac{1}{2} \left[(p_{A1} + p_{A2} - 2p_W) \langle \xi \rangle - (\alpha_{A1} + \alpha_{A2} - 2\alpha_W) \frac{\langle \xi \rangle^2}{2} \right]. \tag{10b}$$

$$\text{Then } D_2 + H_2 = - \left(\Delta p_1 \langle \xi \rangle - \Delta \alpha_1 \frac{\langle \xi \rangle^2}{2} \right), \tag{11}$$

$$D_2 - H_2 = - \left(\Delta p_2 \langle \xi \rangle - \Delta \alpha_2 \frac{\langle \xi \rangle^2}{2} \right), \tag{12}$$

where

$$\Delta p_1 = p_{A1} - p_W \quad \Delta p_2 = p_{A2} - p_W, \tag{13a}$$

$$\Delta \alpha_1 = \alpha_{A1} - \alpha_W \quad \Delta \alpha_2 = \alpha_{A2} - \alpha_W. \tag{13b}$$

2.3. Short-range interactions

The total short-range or nearest neighbor interaction between two particles at the location sites i and j is J_{ij} . Defining P_i^1 , P_i^2 , and P_i^3 as

$$P_i^1 = \frac{s_i(s_i + 1)}{2}, \tag{14a}$$

$$P_i^2 = \frac{s_i(s_i - 1)}{2}, \tag{14b}$$

$$P_i^3 = (1 - s_i^2). \tag{14c}$$

The short-range interaction between similar species is J_{11} or J_{22} , or J_{33} , and dissimilar species is J_{12} or J_{23} or J_{31} . Hence, particle-particle interaction¹⁸⁻²² can be written as

$$H_S = \sum_{\langle ij \rangle} [(J_{11} P_i^1 P_j^1 + J_{22} P_i^2 P_j^2 + J_{33} P_i^3 P_j^3) + J_{12} (P_i^1 P_j^2 + P_i^2 P_j^1) + J_{23} (P_i^2 P_j^3 + P_i^3 P_j^2) + J_{31} (P_i^1 P_j^3 + P_i^3 P_j^1)]. \tag{15}$$

The above Hamiltonian can be rewritten as shown below to point out how they can be characterized by three interaction energies: K, L, J , and the two other fields D'_3

and H'_3 . Equation (15) becomes

$$H_S = -K \sum_{\langle ij \rangle} s_i^2 s_j^2 - L \sum_{\langle ij \rangle} (s_i s_j^2 + s_i^2 s_j) - J \sum_{\langle ij \rangle} s_i s_j - D'_3 \sum_i s_i^2 - H'_3 \sum_i s_i, \quad (16)$$

$$\text{where } K = \frac{(J_{11} + J_{22} + J_{33})}{4} + (J_{33} - J_{31} - J_{32}), \quad (17a)$$

$$L = \frac{(J_{11} - J_{22})}{4} + \frac{(J_{32} - J_{31})}{2}, \quad (17b)$$

$$J = \frac{J_{11} + J_{22} - 2J_{12}}{4}, \quad (17c)$$

$$D'_3 = (J_{31} + J_{32} - 2J_{33}), \quad (17d)$$

$$H'_3 = (J_{31} - J_{32}). \quad (17e)$$

$$\text{Then, } D'_3 + H'_3 = 2(J_{31} - J_{33}), \quad (18)$$

$$D'_3 - H'_3 = 2(J_{32} - J_{33}). \quad (19)$$

2.4. Spin-1 Ising Hamiltonian

If the energetic involvement due to the chemical potential included in the short-range interaction of the two fields D'_3 and H'_3 then turn out to be D_3 and H_3 . Hence,

$$D_3 = (J_{31} + J_{32} - 2J_{33}) + \frac{(\mu_{31} + \mu_{32} - 2\mu_{33})}{2}, \quad (20a)$$

$$H_3 = (J_{31} - J_{32}) + \frac{(\mu_{31} - \mu_{32})}{2}. \quad (20b)$$

$$\text{Then, } D_3 + H_3 = 2(J_{31} - J_{33}) + \Delta\mu_1^\circ + kT \ln \left(\frac{c_{A1}}{c_W} \right), \quad (21)$$

$$D_3 - H_3 = 2(J_{32} - J_{33}) + \Delta\mu_2^\circ + kT \ln \left(\frac{c_{A2}}{c_W} \right), \quad (22)$$

$$\text{where } \mu_{A1} = \mu_{A1}^\circ + kT \ln c_{A1}, \quad (23a)$$

$$\mu_{A2} = \mu_{A2}^\circ + kT \ln c_{A2}, \quad (23b)$$

$$\mu_W = \mu_W^\circ + kT \ln c_W, \quad (23c)$$

$$\Delta\mu_1^\circ = \mu_{A1}^\circ - \mu_W^\circ, \quad (23d)$$

$$\Delta\mu_2^\circ = \mu_{A2}^\circ - \mu_W^\circ. \quad (23e)$$

c_{A1} and c_{A2} are the concentrations of the adsorbate. Consequently,

$$D = D_1 + D_2 + D_3, \quad (24a)$$

$$H = H_1 + H_2 + H_3. \quad (24b)$$

The total Hamiltonian^{16,18–20} with all terms including the energetic contribution due to chemical potential can be written as

$$H_T = -K \sum_{\langle ij \rangle} s_i^2 s_j^2 - L \sum_{\langle ij \rangle} (s_i s_j^2 + s_i^2 s_j) - J \sum_{\langle ij \rangle} s_i s_j - D \sum_i s_i^2 - H \sum_i s_i, \quad (25)$$

where J, K, L, D , and H are the composite parameters composed of the molecular constants, like permanent dipole moments, lattice spacing, etc. and those characterizing the various interactions among the configurations in the electrostatic field. They will assume different forms depending upon the model chosen. The (i, j) refers to the sites spanning the basic lattice picture. The parameters D and H are averaged field-dependent terms containing certain chemical potential. Then,

$$\begin{aligned} D + H &= (D_1 + H_1) + (D_2 + H_2) + (D_3 + H_3) \\ &= -\Delta U_1 - \left(\Delta p_1 \langle \xi \rangle - \Delta \alpha_1 \frac{\langle \xi \rangle^2}{2} \right) + 2(J_{31} - J_{33}) + \Delta \mu_1^0 + kT \ln \left(\frac{c_{A1}}{c_W} \right), \end{aligned} \quad (26)$$

$$\begin{aligned} D - H &= (D_1 - H_1) + (D_2 - H_2) + (D_3 - H_3) \\ &= -\Delta U_2 - \left(\Delta p_2 \langle \xi \rangle - \Delta \alpha_2 \frac{\langle \xi \rangle^2}{2} \right) + 2(J_{32} - J_{33}) + \Delta \mu_2^0 + kT \ln \left(\frac{c_{A2}}{c_W} \right). \end{aligned} \quad (27)$$

For brevity, the terms correspond to the medium effects not included in the Hamiltonian. Equation (25) represents a general Hamiltonian for a three-state description. The fields D and H contain $\langle \xi \rangle$, which is a function of spin variables, $\langle s_i \rangle$ and $\langle s_i^2 \rangle$. However, the spin variable itself is simply related to equilibrium coverage θ_1 and θ_2 through

$$\frac{\langle s_i \rangle \langle \langle s_i \rangle + 1 \rangle}{2} = \theta_1, \quad (28a)$$

$$\frac{\langle s_i \rangle \langle \langle s_i \rangle - 1 \rangle}{2} = \theta_2, \quad (28b)$$

$$1 - \langle s_i^2 \rangle = 1 - \theta_1 - \theta_2. \quad (28c)$$

Hence, the isotherm can be obtained.

2.5. Derivation of isotherm

The MFA solution of the Hamiltonian^{16,18–20} represented by the equation leads to two implicit equations (29) and (30) containing $\langle s_i \rangle$ and $\langle s_i^2 \rangle$:

$$\frac{\langle s_i \rangle}{\langle s_i^2 \rangle} = \tanh\{\beta(H + 2J\langle s_i \rangle + 2L\langle s_i^2 \rangle)\}, \quad (29)$$

$$\frac{1 - \langle s_i^2 \rangle}{\langle s_i \rangle} = \frac{\exp\{\beta(D + H + 2[J + L]\langle s_i \rangle + 2[K + L]\langle s_i^2 \rangle)\}}{1 + \exp\{-2\beta(H + 2L\langle s_i^2 \rangle + 2J\langle s_i \rangle)\}}, \quad (30)$$

where $\beta = 1/kT$.

Then, after manipulation, to be familiar with the energetic contributions of various interactions, the following equation can be written in terms of spin variables to each of the adsorbates appropriately, as shown below:

$$\frac{\langle s_i \rangle (\langle s_i \rangle + 1) / 2}{1 - \langle s_i^2 \rangle} = \exp\{\beta(\tilde{D} + \tilde{H})\} \quad (31)$$

$$\frac{\langle s_i \rangle (\langle s_i \rangle - 1) / 2}{1 - \langle s_i^2 \rangle} = \exp\{\beta(\tilde{D} - \tilde{H})\} \quad (32)$$

$$\tilde{H} = H + 2J\langle s_i \rangle + 2L\langle s_i^2 \rangle \quad (33a)$$

$$\tilde{D} = D + 2L\langle s_i \rangle + 2K\langle s_i^2 \rangle. \quad (33b)$$

In addition, as stated above, spin variables can be identified in terms of surface coverage as given below:

$$\frac{\theta_1}{1 - \theta_1 - \theta_2} = \exp\{\beta(\tilde{D} + \tilde{H})\} \quad (34)$$

$$\frac{\theta_2}{1 - \theta_1 - \theta_2} = \exp\{\beta(\tilde{D} - \tilde{H})\} \quad (35)$$

$$\begin{aligned} \tilde{D} + \tilde{H} &= D + H + (2J + 4L + 2K)\theta_1 + (2K - 2J)\theta_2 \\ &= D + H + 2a_{11}\theta_1 + 2a_{12}\theta_2 \end{aligned} \quad (36)$$

and

$$\begin{aligned} \tilde{D} - \tilde{H} &= D - H + (2K - 2J)\theta_1 + (2J + 4L + 2K)\theta_2 \\ &= D - H + 2a_{21}\theta_1 + 2a_{22}\theta_2, \end{aligned} \quad (37)$$

$$\text{where } 2a_{11} = \beta(2J + 4L + 2K), \quad (38a)$$

$$2a_{22} = \beta(2J - 4L + 2K), \quad (38b)$$

$$2a_{12} = 2a_{21} = \beta(2K - 2J), \quad (38c)$$

and a_{11} , a_{22} , and a_{12} or a_{21} are the short-range interaction constants composed of J_{AA} , J_{SS} , J_{AS} etc. as defined above in Eqs. (38a)–(38c) all the way through (17a)–(17c). After substituting for $D + H$ and $D - H$ from Eqs. (26) and (27), the isotherms are obtained as

$$\frac{\theta_1 \exp\{-2a_{11}\theta_1 - 2a_{12}\theta_2\}}{1 - \theta_1 - \theta_2} = \exp[\beta(D_1 + H_1)] \exp[\beta(D_2 + H_2)] \exp[\beta(D_3 + H_3)] \quad (39)$$

$$\frac{\theta_2 \exp\{-2a_{21}\theta_1 - 2a_{22}\theta_2\}}{1 - \theta_1 - \theta_2} = \exp[\beta(D_1 - H_1)] \exp[\beta(D_2 - H_2)] \exp[\beta(D_3 - H_3)]. \quad (40)$$

So far isotherms are expressed in terms of fields D and H . Hereafter, they will be expressed in terms of molecular parameters.

2.6. Isotherms with short-range effects

Substituting for appropriate fields

$$\frac{\theta_1 \exp\{-2a_{11}\theta_1 - 2a_{12}\theta_2\}}{1 - \theta_1 - \theta_2} = \beta_1 \left(\frac{c_{A1}}{c_W}\right) \exp\left[-\beta \left(\Delta p_1 \langle \xi \rangle - \Delta \alpha_1 \frac{\langle \xi \rangle^2}{2}\right)\right] \quad (41)$$

$$\frac{\theta_2 \exp\{-2a_{21}\theta_1 - 2a_{22}\theta_2\}}{1 - \theta_1 - \theta_2} = \beta_2 \left(\frac{c_{A2}}{c_W}\right) \exp\left[-\beta \left(\Delta p_2 \langle \xi \rangle - \Delta \alpha_2 \frac{\langle \xi \rangle^2}{2}\right)\right], \quad (42)$$

where

$$\beta_1 = \exp \beta[2(J_{31} - J_{33}) + \Delta \mu_1^0] \exp(-\beta \Delta U_1) \quad (43a)$$

$$\beta_2 = \exp \beta[2(J_{32} - J_{33}) + \Delta \mu_2^0] \exp(-\beta \Delta U_2). \quad (43b)$$

Then,

$$\langle \xi \rangle = \frac{4\pi\sigma^M + \frac{c_e}{d^3}[p_{A1}\theta_1 + p_{A2}\theta_2 + p_W(1 - \theta_1 - \theta_2)]}{1 + \frac{c_e}{d^3}[\alpha_{A1}\theta_1 + \alpha_{A2}\theta_2 + \alpha_W(1 - \theta_1 - \theta_2)]} \quad (44a)$$

or

$$\langle \xi \rangle = \frac{4\pi\sigma^M + \frac{c_e}{d^3}p_W + \frac{c_e}{d^3}[\Delta p_{A1}\theta_1 + \Delta p_{A2}\theta_2]}{1 + \frac{c_e}{d^3}\alpha_W + \frac{c_e}{d^3}[\Delta \alpha_{A1}\theta_1 + \Delta \alpha_{A2}\theta_2]}. \quad (44b)$$

After substituting for f_{ij} , the dipole-dipole interaction term, c_e/d^3 , where c_e is the effective coordination number, the two equations (41) and (42) have to be solved for θ_1 and θ_2 to know the joint adsorption as $\theta = \theta_1 + \theta_2$. This is the two-component version of the Frumkin isotherm. However, this derivation has not yet been demonstrated.

2.7. Absence of short-range interactions

In this analysis when short-range interactions are neglected, there is much simplification in the algebraic analysis. The isotherm can be represented as

$$\frac{\Sigma \theta_i}{(1 - \Sigma \theta_i)} = \sum B_i c_{Ai} \exp\left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2}\right)\right] \quad (45)$$

or

$$\frac{\theta}{(1 - \theta)} = \sum B_i c_{Ai} \exp\left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2}\right)\right], \quad (46)$$

where

$$\theta = \Sigma \theta_i \quad (47a)$$

$$B_i = \beta'_i \exp(-\beta \Delta U_i) / c_w \quad (47b)$$

$$\beta'_i = \exp \beta[2(J_{3i} - J_{33}) + \Delta \mu_i^0] \quad (47c)$$

$$\langle \xi \rangle = \frac{\Sigma[4\pi\sigma^M + (c_e/d^3)p_k]f_k}{\Sigma[1 + (c_e/d^3)\alpha_k]f_k}, \quad k_w = 1, 2, \text{ and } f_w = 1 \quad (47d)$$

$$f_i = \frac{\theta_i}{(1 - \Sigma\theta_i)} = B_i c_{Ai} \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2} \right) \right], \quad i = 1, 2. \quad (47e)$$

It should be noted that Δp_i and $\Delta \alpha_i$ are defined with the solvent as the “reference frame” and therefore $\Delta p_w = 0$ and $\Delta \alpha_w = 0$, and consequently k_w is zero.

3. Generalized N -State Model

Generalizing the procedure for an N -state model, heuristically the isotherm for multi-component adsorption can be rewritten as

$$\frac{\theta}{1 - \theta} = \sum_i B_i c_{Ai} \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2} \right) \right] \exp \left(2 \sum_j a_{ij} \theta_j \right), \quad (48a)$$

where $i = 1, 2, \dots, N$ and $j = 1, 2, \dots, N$ for N different adsorbates and one solvent. The parameters, $\theta = \Sigma\theta_i$ is the total surface coverage of all the organic adsorbates, c_{Ai} is the concentration of i th species, $\Delta p_i = p_{Ai} - p_w$, $\Delta \alpha_i = \alpha_{Ai} - \alpha_w$, $\Delta U_i = U_{Ai} - U_w$, $\Delta \mu_i^o = \mu_{Ai}^o - \mu_w^o$, and $B_i = \exp\{-\beta[\Delta \mu_i + 2(J_{iw} - J_{ww})] \exp(-\beta \Delta U_i)/c_w$ and

$$\langle \xi \rangle = \frac{[4\pi\sigma^M + (c_e/d^3)p_w] + (c_e/d^3)\Sigma \Delta p_i \theta_i}{[1 + (c_e/d^3)\alpha_w] + (c_e/d^3)\Delta \alpha_i \theta_i}, \quad (48b)$$

where

$$\frac{\theta_i}{1 - \theta_i} = B_i c_{Ai} \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2} \right) \right] \exp \left(2 \sum_j a_{ij} \theta_j \right), \quad (48c)$$

and a_{ij} is the short-range interaction constant.

In the case of an organic adsorbate with one orientational state in the presence of a solvent in N -orientations, Eq. (48a) leads to

$$\frac{(1 - \theta)C_A}{\theta} = \sum_i^{N_S} B_i \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta \alpha_i \frac{\langle \xi \rangle^2}{2} \right) \right] \exp \left(2 \sum_j a_{ij} \theta_j \right) \\ (i = 1, 2, \dots, N_S; \quad j = 1, 2, \dots, N_S), \quad (49a)$$

where

$$\Delta p_i = p_{wi} - p_A, \Delta \alpha = \alpha_w - \alpha_A, \Delta \mu_i^o = \mu_w^o - \mu_A^o, \Delta U_i = U_{wi} - U_A \quad (49b)$$

$$B_i = c_w \exp[\beta\{\Delta \mu_i^o + 2(J_{Awi} - J_{AA})\}] \exp(-\beta \Delta U_i)$$

c_A is the concentration of the adsorbate,

$$\langle \xi \rangle = \frac{[4\pi\sigma^M + (c_e/d^3)[p_A \theta + \Sigma p_{wi} \theta_i]}{1 + (c_e/d^3)[\alpha_A \theta + (c_e/d^3)\alpha_w \Sigma \theta_i]}, \quad (49c)$$

and

$$\frac{\theta_i}{1 - \Sigma\theta_i} = B_i(c_w/c_A) \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta\alpha \frac{\langle \xi \rangle^2}{2} \right) \right] \exp \left(2 \sum_i a_{ij} \theta_j \right), \quad (49d)$$

θ_i is the surface coverage of the solvent dipoles in the i th orientation, $\theta = 1 - \Sigma\theta_i$ is the surface coverage of the organic adsorbate, and a_{ij} is the short-range interaction constant.

Although one would be tempted to regard the analysis of $(N_s + 1)$ state models as algebraically tedious and non-transparent, it is demonstrated here that the general equation can be written in a straightforward manner.

4. Analysis of $(N_s + 1)$ State Models with Coulombic Interactions

The essential ingredients of the model and the methodology of deriving the equilibrium relations have already been discussed. In the general case of $(N_s + 1)$ state model, where N_s denotes the number of orientational states of the solvent dipoles, the adsorption isotherm can be written as

$$\frac{\Sigma\theta_i}{1 - \Sigma\theta_i} = \frac{1}{(c_A/c_s)} \sum_1^{N_s} \exp[-\beta(\Delta U_{si} - \Delta U_A)] \exp \left[-\beta \left(\Delta p_i \langle \xi \rangle - \Delta\alpha \frac{\langle \xi \rangle^2}{2} \right) \right], \quad (50a)$$

$$\text{where } \Sigma\theta_i = 1 - \theta, \Delta p_i = p_{si} - p_A, \Delta\alpha = \alpha_s - \alpha_A, \quad \text{and} \quad (50b)$$

θ_i is the surface coverage of the solvent dipoles in the i th orientational state. Equation (50a) can also be written in a more familiar form as

$$\frac{\theta}{1 - \theta} = \frac{\beta_o c_A \exp \left\{ -\beta \left[(p_A - p_{s1}) \langle \xi \rangle + (\alpha_A - \alpha_s) \frac{\langle \xi \rangle^2}{2} \right] \right\}}{1 + \sum_2^{N_s} \exp \{ -\beta [(\Delta U_{si} - \Delta U_{s1}) + (p_{si} - p_{s1}) \langle \xi \rangle] \}}, \quad (51)$$

where $\beta_o = \exp\{\beta(\Delta U_{s1} - \Delta U_A)\}$ apart from the standard chemical potentials, and c_A is the bulk concentration of the organic adsorbate, relative to that of water, and the other symbols have their usual significance. The polarizability is assumed to be equal in each orientational state of the solvent and the short-range chemical interactions between the adsorbate(s) have been deliberately ignored; $\langle \xi \rangle$ is given by

$$\langle \xi \rangle = \frac{[4\pi\sigma^M + (c_e/d^3)p_A] + (c_e/d^3)\Sigma p_i \theta_i}{[1 + (c_e/d^3)\alpha_A] + (c_e/d^3)\alpha_s \Sigma \theta_i}. \quad (52a)$$

From the adsorption isotherm equation (50a), the following equation can be obtained:

$$4\pi\sigma_{\max}^M = \left(1 + \frac{c_e}{d^3} \alpha_A \right) \langle \xi_{\max} \rangle - \frac{c_e}{d^3} p_A, \quad (52b)$$

where $\langle \xi_{\max} \rangle$ is the solution of the implicit equation given by

$$\begin{aligned} \langle \xi_{\max} \rangle &= \frac{\Sigma \Delta p_{si} \theta_i}{\Delta \alpha \Sigma \theta_i} = \frac{\sum_i^{N_s} \Delta p_{si} \exp[-\beta\{(\Delta U_{si} - \Delta U_A) + \Delta p_{si} \langle \xi_{\max} \rangle\}]}{\Delta \alpha \sum_i^{N_s} \exp[-\beta\{(\Delta U_{si} - \Delta U_A) + \Delta p_{si} \langle \xi_{\max} \rangle\}]} \\ &= \frac{\sum_{i=1}^{N_s} (p_{si} - p_A) \exp[-\beta\{\Delta U_{si}\} \exp[-\beta p_{si} \langle \xi_{\max} \rangle]]}{\alpha \sum_{i=1}^{N_s} \exp[-\beta \Delta U_{si}] \exp[-\beta p_{si} \langle \xi_{\max} \rangle]}, \end{aligned} \quad (53)$$

and p_{si} denotes the normal component of the permanent dipole moment of the solvent in the i th orientational state. Equation (53) can be further simplified and written elegantly as

$$\begin{aligned} \langle \xi_{\max} \rangle &= \frac{1}{\Delta \alpha} \left[\frac{\sum_i^{N_s} p_{si} \exp[-\beta \Delta U_{si}] \exp[-\beta p_{si} \langle \xi_{\max} \rangle]}{\sum_i^{N_s} \exp[-\beta \Delta U_{si}] \exp[-\beta p_{si} \langle \xi_{\max} \rangle]} - p_A \right] \\ &= \frac{\bar{p}_s - p_A}{\Delta \alpha}, \end{aligned} \quad (54a)$$

where

$$\bar{p}_s = \frac{\Sigma p_{si} \exp[-\beta(\Delta U_{si})] \exp[-\beta p_{si} \langle \xi_{\max} \rangle]}{\Sigma \exp[-\beta(\Delta U_{si})] \exp[-\beta p_{si} \langle \xi_{\max} \rangle]}. \quad (54b)$$

It is of interest to note that Eqs. (52a) and (52b) are of general validity, and particular cases for several site parity models can be recovered by assigning appropriate values for N_s . In the two-state site parity model, discussed in Ref. 12, $N_s = 1$, $\langle \xi_{\max} \rangle \rightarrow \Delta p / \Delta \alpha$, and we recover Eq. (1) of Ref. 12. For the three-state site parity model, $\langle \xi_{\max} \rangle$ is to be obtained from the solution of the transcendental equation (53) or Eq. (54a) with $N_s = 2$ and this is to be used in Eq. (52b) to obtain σ_{\max}^M . These results are in accordance with Eqs. (40) and (47) of Ref. 12.

5. Models with Short-Range (Chemical) Interactions Between the Adsorbates

In the models discussed in Ref. 12 and now in Sec. 4, the short-range interaction energies were not taken into account. Therefore, it is of interest to confirm the effect of the short-range interactions constant on the θ -dependent charge of maximum adsorption. For this, the general $(N_s + 1)$ -state model of the adsorption isotherm with short-range interaction was taken for maximization.

$$\begin{aligned} &\frac{\Sigma \theta_i}{1 - \Sigma \theta_i} \exp \left[-2 \sum_j a_{ij} \theta_j \right] \\ &= \frac{1}{(c_A/c_s)} \Sigma \exp \left\{ -\beta \left[(\Delta U_{si} - \Delta U_A) + \Delta p_i \langle \xi \rangle - \Delta \alpha \frac{\langle \xi \rangle^2}{2} \right] \right\}, \end{aligned} \quad (55)$$

where θ_i denotes the surface coverage of the solvent dipoles in the i th orientational state; the surface coverage of adsorbate is $\theta = 1 - \Sigma \theta_i$ and a_{ij} is the short-range

interaction constant composed of J_{AA} , J_{ss} , J_{As} etc. as defined above in Eqs. (38a)–(38c) all the way through (17a)–(17c). Using the criterion $(\frac{\partial \theta}{\partial \sigma^M})_{c_A} = 0$ at σ_{\max}^M , a general model for $\langle \xi_{\max} \rangle$ is given below and hence σ_{\max}^M :

$$\langle \xi_{\max} \rangle = \frac{\sum_i \left(\frac{\Delta p_i}{[(1/\theta_i) - 2a_{ii} + 2 \sum_{i \neq j} a_{ij}]} \right)}{\sum_i \left(\frac{\Delta \alpha}{[(1/\theta_i) - 2a_{ii} + 2 \sum_{i \neq j} a_{ij}]} \right)}. \quad (56)$$

For the case of the three-state site parity model, $i = 1, 2$, and $j = 1, 2$, are to be substituted in Eqs. (55) and (56) and hence two nonlinear algebraic equations have to be solved simultaneously to get $\langle \xi_{\max} \rangle$ (see Appendix). The numerical evaluation is rendered more difficult to estimate σ_{\max}^M when orientational states (N_s) increase. It can be noted further from Eq. (56) that the two-state site parity model with short-range interactions do not show θ -dependence of σ_{\max}^M , and the simplest model in the hierarchy showing the coverage-dependent σ_{\max}^M is the three-state site parity model albeit under molecular field approximation.

The functional dependence of $\langle \xi_{\max} \rangle$ on θ_{\max} , however for the three-state site parity model if $p_{s1} = p_{s2} = -p_s$ can be written as

$$\langle \xi_{\max} \rangle = \frac{1}{\Delta \alpha} \left[p_s \frac{(\theta_1 - \theta_2) + 2(a_{11} - a_{22})\theta_1\theta_2}{(\theta_1 + \theta_2) - [2(a_{11} + a_{22}) - 4a_{12}]\theta_1\theta_2} - p_A \right] \quad (57a)$$

or

$$\langle \xi_{\max} \rangle = \frac{1}{\Delta \alpha} \left[p_s \frac{(\theta_1 - \theta_2) + 8\beta L \theta_1 \theta_2}{(\theta_1 + \theta_2) - 8\beta J \theta_1 \theta_2} - p_A \right]. \quad (57b)$$

When $J = 0$ and $L = 0$ and if θ_1 and θ_2 are substituted from Eq. (50a), then equation (57b) yields

$$\langle \xi_{\max} \rangle = \frac{1}{\Delta \alpha} \left[p_s \frac{[\exp(-\beta \Delta U_{s1}) - \exp(-\beta \Delta U_{s2}) \exp(2\beta p_s \langle \xi_{\max} \rangle)]}{[\exp(-\beta \Delta U_{s1}) + \exp(-\beta \Delta U_{s2}) \exp(2\beta p_s \langle \xi_{\max} \rangle)]} - p_A \right]. \quad (58)$$

An interesting feature emerging from the above analysis is that an $(N_s + 1)$ state model with $N_s > 2$ incorporating only short-range chemical interactions and excluding all dipole–dipole interactions, (in MFA) leads to a coverage-dependent charge of maximum adsorption. The converse however is not true.

Although for the sake of clarity, results for a specific three-state site parity model (with short-range interaction energies) are reported here, in particular, the investigation is on the conditions under which σ_{\max}^M dependence is the key issue. The size variation between the organic adsorbate and the solvent is the outcome for the θ_{\max} dependence of (σ_{\max}^M) as discussed in Refs. 17 and 22, and the short constants ought to be functions of adsorbate size (or site), but it is yet to be analyzed. It is to be noted that these equations are derived assuming the point dipoles.

Since phenomenological models may sometimes mask the reality of the phenomenon and the conclusions drawn from them may not be wholly reliable, the analysis is restricted to molecular models here. For this reason, the analysis of Ref. 23

generalized surface layer (GSL) empirical equation of Damaskin *et al.*^{21,24,25} and the new empirical equations of Shuhmann,²⁶ which predict a θ -dependent charge of maximum adsorption, were not explored.

An elementary analysis of the two-state multisite model of Ref. 12, however leads to a θ -invariant σ_{\max}^M . This is further confirmed by the fact that adsorbates, which show a coverage-dependent σ_{\max}^M obey site parity adsorption isotherms.

6. Conclusions

It follows from the above analysis that incorporation of short-range chemical interactions has a dominant role in influencing the surface coverage dependence of σ_{\max}^M . The dependence of the charge of maximum (σ_{\max}^M) on the surface charge (θ_{\max}) sometimes experimentally observed, can be accounted for, by the inclusion of short-range (chemical) interaction energies. It is shown that a three-state site parity model with short-range interaction energies (under MFA) is the lowest in the hierarchy of multistate models that exhibit a coverage-dependent σ_{\max}^M .

Appendix A: General Numerical Procedure

A general procedure is illustrated with the help of Eqs. (60) and (61) to obtain θ and σ_{\max}^M .

With the known values of relevant input molecular parameters ($\Delta p_1, \Delta p_2, \Delta\alpha, \beta_1, \beta_1, \theta_1^k$ and θ_2^k are assumed initially. For the given value of short-range constants ($a_{11}, a_{22}, a_{12} = a_{21}$), with this guess value θ_1^k and θ_2^k , $\langle \xi_{\max}^k \rangle$ is evaluated using the following equation:

$$\langle \xi_{\max}^k \rangle = \frac{\left(\frac{\Delta p_1}{[(1/\theta_1^k) - 2a_{11} + 2a_{12}]} + \frac{\Delta p_2}{[(1/\theta_2^k) - 2a_{22} + 2a_{21}]} \right)}{\left(\frac{\Delta\alpha}{[(1/\theta_1^k) - 2a_{11} + 2a_{12}]} + \frac{\Delta\alpha}{[(1/\theta_2^k) - 2a_{22} + 2a_{21}]} \right)}, \quad (\text{A.1})$$

where θ_i^k denotes the surface coverage of the solvent dipoles in the i th orientational state, the superscript k denotes the iteration counter. Using the values of $\langle \xi_{\max}^k \rangle, \theta_1^k$, and θ_2^k the next values θ_1^{k+1} and θ_2^{k+1} are evaluated for any given value of θ from the following equations:

$$\theta_1^{k+1} = \beta_1 \exp \left\{ -\beta \left[\Delta p_1 \langle \xi_{\max}^k \rangle - \Delta\alpha \frac{\langle \xi_{\max}^k \rangle^2}{2} \right] \right\} \exp[2a_{11}\theta_1^k + 2a_{12}\theta_2^k](1 - \theta), \quad (\text{A.2})$$

$$\theta_2^{k+1} = \beta_2 \exp \left\{ -\beta \left[\Delta p_2 \langle \xi_{\max}^k \rangle - \Delta\alpha \frac{\langle \xi_{\max}^k \rangle^2}{2} \right] \right\} \exp[2a_{21}\theta_1^k + 2a_{22}\theta_2^k](1 - \theta), \quad (\text{A.3})$$

where the surface coverage of the adsorbate is $\theta = 1 - \Sigma\theta_i$ and a_{ij} is the short-range interaction constant composed of J_{AA}, J_{SS}, J_{AS} etc. as defined in Eqs. (38a)–(38c)

all the way through (17a)–(17c). The iteration is repeated until self-consistency is reached. That is, $\theta_i^k - \theta_i^{k+1} \approx 0$. For the given value of θ and $\langle \xi_{\max} \rangle$, the value of σ_{\max}^M can be computed from the following equation:

$$\langle \xi_{\max} \rangle = \frac{4\pi\sigma_{\max}^M + \frac{c_e}{d^3}p_A + \frac{c_e}{d^3}[\Delta p_1\theta_1 + \Delta p_2\theta_2]}{1 + \frac{c_e}{d^3}\alpha_A + \frac{c_e}{d^3}[\Delta\alpha\theta_1 + \Delta\alpha\theta_2]}. \quad (\text{A.4})$$

The entire process is repeated for different values of surface coverage of the adsorbate.

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