

Adsorption of Ions on Small Spheres at Low Ionic Strengths

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The adsorption isotherm of ions on small spherical particles at low ionic strength is evaluated by assuming that the reactions between ions and particles are reversible. The electrostatic repulsion between adsorbed ions is taken into account by using the Born equation. The evaluated expression is applicable to systems showing properties different to those of ideally reversible electrodes.

INTRODUCTION

One of the fundamental problems in the study of colloid stability of lyophobic colloid systems is the adsorption of potential determining ions (p. d. i.) on colloid particles¹. This problem was studied extensively by several authors²⁻⁷. The adsorption isotherm which corresponds to the dependence of the surface charge density on p. d. i. activity was evaluated by double layer equilibrium treatment. The distribution of ions in the double layer was always related to the surface potential and calculated on the basis of Debye-Hückel, Gouy-Chapman and Stern theories, which were refined and adapted to the colloids by Verwey and Overbeek², Levine³ and Mackor^{4,5}. All the above treatments involve an independent and nonmeasurable quantity — the surface potential (ψ) which can be taken for some systems as proportional to the logarithm of p. d. i. activity (a). The following relation²

$$\frac{d\Psi}{d(\ln a)} = \frac{RT}{zF} \quad (1)$$

can be applied for systems showing properties similar to the ideally reversible electrodes. This relation evaluated from thermodynamics does not give information on the »reference point« *i. e.* about the absolute value of the surface potential. It is assumed² that the absolute value of Ψ can be determined by using an experimental quantity — activity of p. d. i. at the point of zero charge ($a_{p.z.c.}$), so that

$$\Psi = \frac{RT}{zF} \ln(a/a_{p.z.c.}) \quad (2)$$

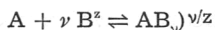
The real systems show more or less differences in relation to the model system used in theoretical treatments. In the case of equations (1) and (2) problems can be expected at high surface coverage and for some systems in the p. z. c. region. The charging process of the particles takes place *via* an adsorption or dissociation mechanism. The dissociation of certain groups on

the particle surface can be treated in a similar way as the adsorption of ions. If there are two kinds of dissociative groups on the surface, one resulting in a positive charge (*e. g.* $-\text{NH}_2$) and the other resulting in a negative charge (*e. g.* $-\text{COOH}$), equations (1) and (2) are suitable only if association-dissociation constants of these groups are in appropriate correlation with another equilibrium constant representing the relation between activities of p. d. ions (*e. g.* dissociation constant of water). There exist no reason that this correlation occurs generally. For another type of charging process *i. e.* the adsorption of constituent ions on inorganic salts, it is reasonable to expect that the solubility and the adsorption-desorption equilibrium of constituent ions are in such relations that equations (1) and (2) can be applied. For systems which can be charged only in one sense (positive or negative) the point of zero charge has no physical meaning, and the surface potential asymptotically reaches the zero value, so that equations (1) and (2) become invalid.

The aim of this study is to evaluate such an adsorption isotherm of potential determining ions for colloid systems to which equation (2) cannot be applied. In the first step of evaluation (which is presented here) the limiting conditions of zero ionic strength are considered.

THEORETICAL

The derivation of the adsorption isotherm described here is applicable to a system with a sufficiently large number of sufficiently small particles for which the rate of all other changes is negligibly small compared to the rate of approach of the adsorption-desorption equilibrium. The treatment involves the adsorption process of only one ionic species, and the adsorption process is treated as a reversible chemical reaction between the colloid particles (A) and ions B^z of charge number z .



where $(AB_\nu)^{\nu z}$ represents the colloid particles with ν adsorbed ions B^z *i. e.* with total charge $\nu z e$. Reaction (3) can be divided into ν steps, where the first step is represented by



The standard increase of the Gibbs energy of reaction (3), ΔG_v^0 can be taken as a sum of chemical ($\Delta G_{\text{ch},\nu}^0$) and electrical ($\Delta G_{\text{el},\nu}^0$) contributions. The electrical part of standard increase of the Gibbs energy for a single step increases with ν because of increasing repulsion between the adsorbed ions. It corresponds to the charging process of colloid particles. For spherical particles at low ionic strength (where there is no change in activity of colloid particles in the charging process and no compensating electrostatic effect of counter-ions in the double layer) $\Delta G_{\text{el},\nu}^0$ can be calculated from the Born equation⁸. At low equilibrium surface coverage where the distances between the adsorbed ions are large, when a relatively large free surface area exists, the chemical part of the standard increase of the Gibbs energy for each step can be taken to be the same, so that

$$\Delta G_v^0 = \nu \cdot \Delta G_{\text{ch},1}^0 + \frac{\nu^2 z^2 e^2 L}{8 \pi \epsilon r} \quad (5)$$

where L is the Avogadro constant, ϵ the permittivity of the effective space, and r the radius of particles. The ratio of the number of particles with ν adsorbed ions (N_ν) to the number of uncharged particles (N_0) is a function of the activity of p. d. i. (a) according to the distribution function

$$-\Delta G_\nu^\ominus = R T \ln (N_\nu / N_0 a^\nu) \tag{6}$$

From eqs. (5) and (6) the relation

$$N_\nu = N_0 \cdot \exp \left[\left(\ln a - \frac{\Delta G_{ch,1}^\ominus}{R T} \right) \nu - \frac{z^2 e^2 L}{8 \pi \epsilon r R T} \nu^2 \right] \tag{7}$$

can be derived. This enables one to calculate the average number of adsorbed ions per particle ($\bar{\nu}$) and thus derive the adsorption isotherm, and surface charge density function. The mean number of adsorbed ions per particle is equal to the ratio between the total number of adsorbed ions and the total number of colloid particles

$$\bar{\nu} = \frac{N_0 \int_0^\infty \nu \cdot \exp \left(\frac{-\Delta G_{ch,1}^\ominus \cdot \nu}{R T} + \nu \ln a - \frac{\nu^2 z^2 e^2 L}{8 \pi \epsilon r R T} \right) d \nu}{N_0 \int_0^\infty \exp \left(\frac{-\Delta G_{ch,1}^\ominus \cdot \nu}{R T} + \nu \ln a - \frac{\nu^2 z^2 e^2 L}{8 \pi \epsilon r R T} \right) d \nu} \tag{8}$$

By solving these integrals the following relation is obtained

$$\bar{\nu} = \frac{A}{2 D} + \frac{1}{[1 + \Phi (A/2 \sqrt{D})] \sqrt{\pi D} \exp (A^2/4 D)} \tag{9}$$

where

$$A = \frac{-\Delta G_{ch,1}^\ominus}{R T} + \ln a$$

$$D = z^2 e^2 L / 8 \pi \epsilon r R T$$

and the function Φ is given by

$$\Phi (A/2 \sqrt{D}) = \frac{2}{\sqrt{\pi}} \int_0^{A/2 \sqrt{D}} \exp (-t^2) dt$$

The integral $\Phi (x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp (-t^2) dt$ is the well known probability

function. The values of $\Phi (x)$ are between -1 and $+1$ for $x = -\infty$ and $x = \infty$, respectively. At $x = 0$, $\Phi (x) = 0$, and the significant change of $\Phi (x)$ are in the region $-1.5 < x < 1.5$. The values of $\Phi (x)$ are represented graphically in Figure 1. By analysing the relation (9) it can be concluded that at relatively large activities of p. d. i. $\bar{\nu}$ can be calculated as

$$\bar{\nu} = A/2 D = \frac{-\Delta G_{ch,1}^\ominus}{z^2 e^2 L} + \frac{R T}{z^2 e^2 L} \ln a \tag{10}$$

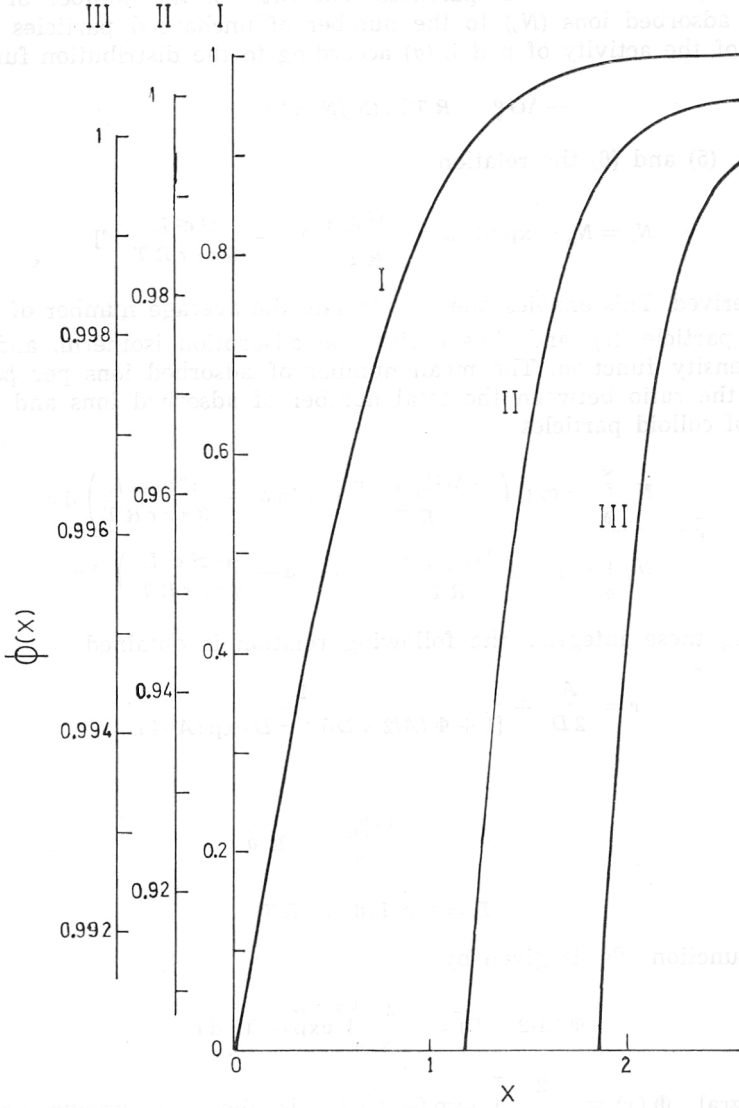


Figure 1.

The values of the integral

$$\varphi(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt.$$

For negative x values:

$$\varphi(-x) = -\varphi(x)$$

The functions I, II, and III are identical, but the corresponding scales are different, i. e. curve I corresponds to scale I, etc.

and the surface potential defined as $\psi = \overline{v z e / 4 \pi \epsilon r}$ in this p. d. i. activity region becomes then

$$\Psi = \frac{-\Delta G_{\text{ch},1}^{\circ}}{z F} + \frac{R T}{z F} \ln a \quad (11)$$

In the p. d. i. activity region where a is not very much greater than $\exp(\Delta G_{\text{ch},1}^{\circ} / R T)$ all terms in equation (9) should be taken into consideration, so that v should approach the zero value as a is lowered.

DISCUSSION

In the theoretical treatment of equilibrium in colloid systems one can see the advantage of applicability of laws which are valid for molecular systems as well as for macroscopic particles. In this paper Born's equation, which is valid for macroscopic particles, was used together with the reaction isotherm describing the equilibrium of molecular systems. The Born equation⁸ has a limitation of free charge distribution within the particle. At equilibrium the charges are at the surface so that this equation can be applied to the adsorption of ions. However, it can be applied exactly only when the adsorbed ions are nearly equidistant. It was stated that ϵ is the permittivity in the »effective space« and this is in the region of mutual repulsive interaction between the adsorbed charges. This region includes the solid phase of the colloid particle and the liquid phase near the surface, so that ϵ will have a value between those for two phases. Because of the specific state of the liquid phase at the surface the permittivity in this part of effective region need not be the same as in the bulk of solution. Large changes can be expected in the case of adsorption of organic molecules (surface active agents, dyes etc.) at the particle surface. In this case the value of ϵ will decrease and consequently, at low ionic strengths the adsorption capacity of p. d. i., the electric mobility of the particles will drop. Of course, this might cause a change in $\Delta G_{\text{ch},1}^{\circ}$ which again will cause a shift in the potential function.

According to the model treated in this study the evaluated adsorption isotherm can be applied also to colloid systems formally similar to ideally reversible electrodes (e. g. AgI) under the following conditions: low electrolyte concentrations, the p. d. i. activity region far enough from p. z. c., where adsorption of only one kind of ionic species can be assumed. For adsorption of Γ^{-} on AgI particles a low surface coverage was found⁶ which also contributes to the fact that under these conditions equation (9) can be applied. Mirnik and Musić⁷ have recently presented experimental results of adsorption of Γ^{-} on the AgI colloid (small particles, low ionic strength) and they found (i) that $n_{\text{ads}}(\Gamma^{-})/n_{\text{tot}}(\text{AgI})$ is a linear function of $\ln a(\Gamma^{-})$ for the Γ^{-} activity greater than 10^{-8} , (ii) that the slope of the straight lines depends on the radius of primary particles, (iii) that all extrapolated lines intersect in one point, and (iv) that the coordinates of this intersection are $n_{\text{ads}}(\Gamma^{-})/n_{\text{tot}}(\text{AgI}) = 0$ and $a(\Gamma^{-}) = 4 \cdot 10^{-10}$. For Γ^{-} activities lower than 10^{-8} the adsorbed amount of ions approaches zero. This values yields *via* equation (10) for adsorption of the first Γ^{-} ion $\Delta G_{\Gamma}^{\circ} \approx \Delta G_{\text{ch},1}^{\circ} = -53$ kJ/mol.

In conclusion one can say that the derived expressions for the adsorption isotherm can be applied to stable lyophobic colloids when adsorption of one

kind of ions is dominant. Relation (9) describes also the dissociation charging mechanism, but then ν represents the mean number of dissociated groups on one particle. The quantity $\Delta G_{\text{ch},1}^{\circ}$ corresponds to the dissociation of the first group on the surface. The derived expressions enable also the treatment of colloid systems which do not show the properties of ideally reversible electrodes.

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SAŽETAK

Adsorpcija iona na malim sfernim česticama pri niskoj ionskoj jakosti

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Izvedena je adsorpcijska izoterma iona na malim sfernim česticama za nisku ionsku jakost. Izvod se temelji na razmatranju reverzibilne reakcije iona s koloidnim česticama. Elektrostatsko odbijanje adsorbiranih iona uključeno je primjenom Bornove teorije. Izvedeni su izrazi prikladni za koloidne sisteme koji pokazuju različita svojstva u odnosu na reverzibilne elektrode.

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