

Influence of finite size of ions on electrostatic properties of electric double layer

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Abstract. The electric double layer is formed when a charged plane is placed in contact with an electrolyte solution. The ions which are oppositely charged than the plane are attracted by the plane and therefore accumulate near it, while the ions which carry the charge of equal sign as the plane are repelled by the plane and therefore expelled from its vicinity. In this work, some electrostatic properties of the electric double layer are considered. The electrostatic interaction of ions with the mean electric field is taken into account. The finite size of ions and water molecules is considered by means of volume exclusion principle. Starting from the statistical mechanical description, a procedure is proposed in which self consistent expressions for the free energy of the system, ion and water distribution functions and the differential equation for the electric field are derived. It is shown that the classical Gouy-Chapman model of the electric double layer which considers ions and water molecules as dimensionless is a good approximation only for low values of the surface charge density of the charged plane. When the values of the surface charge density are higher the finite size of ions should be considered. The expressions for the ion and water molecules distribution functions and the electric field which are presented here can be due to their simple form used for fitting different experimental data in electrochemistry and physics of biological membranes.

Key words: electric double layer, electric potential, ions, ion distribution function

Vpliv končne velikosti ionov na elektrostatične lastnosti električne dvojne plasti

Povzetek. Električna dvojna plast nastane, ko pride po površini naelektrena plošča v stik z ionsko raztopino. Ione, ki nosijo nasprotno elektrino kot plošča, plošča privlači. Zato se naberejo v bližini naelektrene ravnine, medtem ko enako naelektrene ione plošča odbija in izriva iz svoje bližine. V tem delu obravnavamo nekatere elektrostatične lastnosti električne dvojne plasti. Upoštevamo elektrostatično interakcijo ionov s povprečnim električnim poljem. Končno velikost ionov in vodnih molekul pa upoštevamo s predpostavko, da se prostornine, ki jih zavzemajo posamezne molekule, ne morejo prekrivati. Začenši s statistično mehanskim opisom sistema predpostavimo postopek v katerem izpeljemo med seboj usklajene izraze za prosto energijo sistema, krajevne porazdelitvene funkcije za ione in vodne molekule ter diferencialno enačbo za krajevno odvisnost električnega potenciala v elektrolitski raztopini. Pokažemo, da je klasični Gouy-Chapmanov model električne dvojne plasti, ki obravnava ione in vodne molekule kot točkaste delce, dober približek samo pri majhnih vrednostih površinske gostote elektrine na plošči. Kadar je plošča močnejše naelektrena, moramo upoštevati končno velikost ionov in vodnih molekul. Izpeljani izrazi za krajevno porazdelitev ionov in vodnih molekul ter krajevno odvisnost jakosti električnega polja so relativno preprosti. Zato imajo uporabno vrednost pri tolmačenju rezultatov meritev v elektrokemiji in fiziki bioloških membran.

Ključne besede: električna dvojna plast, električni potencial, ioni, ionska porazdelitvena funkcija

1 Introduction

If the electrolyte solution is in contact with the charged plane with surface charge density σ , the ions which carry the charge of the opposite sign than the plane (counterions) are accumulated near the plane and the ions which carry the charge of the same sign as the plane (coions) are depleted from this region. A diffuse electric dou-

ble layer is thus created (figure 1). The electric double layer is a convenient model for the description of the electrostatics of the cellular membranes, phospholipid bilayers and metals in contact with the electrolyte solution [7,9,10,11,12]. On the basis of the electric double layer theory different physiological processes can be elucidated, such as transport of charged molecules across the biological membranes [6,8,10,11,13], binding of charged molecules to the biological membrane [3,11] and fusion of phospholipid vesicles or liposomes with

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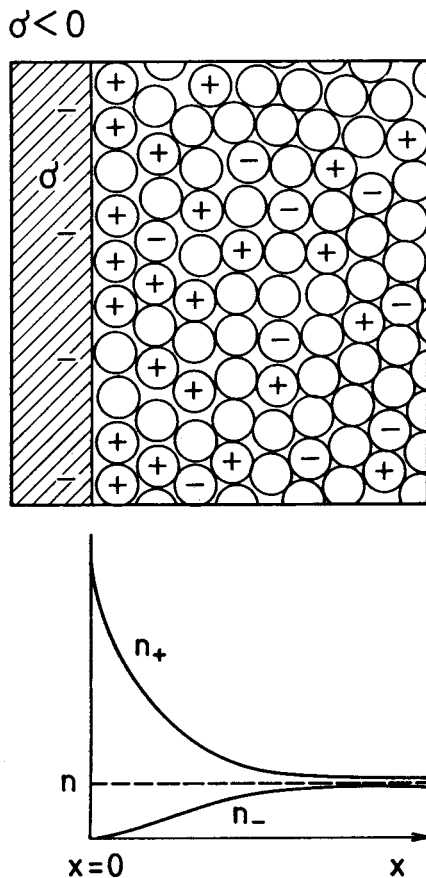


Figure 1. Schematic presentation of the electric double layer. In the presented case the surface charge density σ is negative, therefore cations (counterions) are accumulated near the plane and anions (coions) are depleted from the vicinity of the plane. The x-axis is perpendicular to the plane located at $x = 0$, while the y and z axes lie in the charged plane.

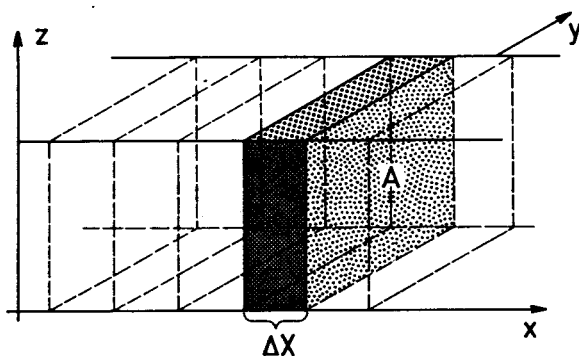


Figure 2. The system is divided into cells.

biological membranes [14,15].

In this work, macroscopic electric properties of an aqueous solution of univalent cations and univalent anions (i.e. an 1-1 electrolyte solution) in contact with a charged plane are considered. Requiring the local thermodynamic equilibrium, ions and water molecules are assumed to be distributed in accordance with the mean

electric field produced by the charged plane and the ions in the solution themselves. Counterions which accumulate in the vicinity of the charged plane, screen its electric field. Since ions and water molecules occupy finite volumes, screening is constrained with the maximal possible concentration of counterions near the charged plane. The electric properties of the system are thus affected by the finite size of particles constituting the solution. In this work, the finite size of ions is described by taking into account the excluded volume effect, i.e. ions and water molecules are assumed to occupy finite volume which can be occupied by only one particle at the same time. By taking into account the excluded volume effect and the electrostatic interactions of ions with the mean electric field, the electrostatic properties of the electric double layer are studied in this work.

2 Theory

Let us imagine a plane extending over an area A which bears on its surface (at $x = 0$) uniformly distributed charge with surface charge density σ (figure 1). The charged plane is in contact with the electrolyte solution which extends into infinity in the positive x direction of the chosen Cartesian coordinate system (figure 2). It is taken, that there is no electric field on the other side of the charged plane. The solution under consideration is composed of univalent anions, univalent cations and water molecules. The presented model of electric double layer is subject to the condition that the whole system, i.e. the charged plane and electrolyte solution together, is electrically neutral. Nonuniformly distributed ions in the solution (figure 1) create an additional electric field to the field generated by the charged plane. However, the electric field and also all other macroscopic properties of the system still depend on the x coordinate only since the boundary effects are neglected.

In order to describe the system, we divide it into cells of equal volume (figure 2),

$$\Delta V = A \Delta x \tag{1}$$

where Δx is the dimension of the cell in the x direction. It is assumed, that Δx is small comparing to the distance over which macroscopic properties of the system change appreciably.

In the particular cell chosen, there are N_w water molecules, N_+ cations and N_- anions. Finite size of particles is introduced in the model by means of excluded volume effect. This means that the particles in one cell are distributed over N_0 sites of equal volume which are all occupied (figure 1),

$$N_+ + N_- + N_w = N_0 \tag{2}$$

In accordance with equation 2 the volume of the cell is proportional to the number of the sites N_0 . It is also assumed, that the total volume of all the particles is conserved if the particles are mixed.

The behaviour of an individual particle in the cell can be described by using statistical mechanical approach.

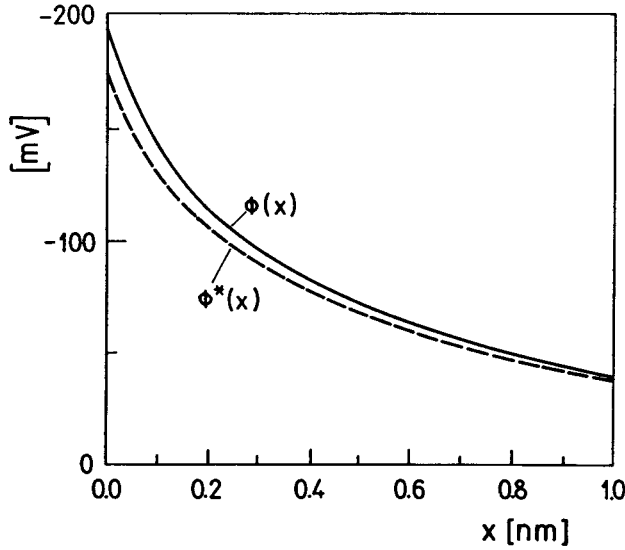


Figure 3. The electric potential Φ in dependence on the distance from the charged plane x calculated by considering the finite size of ions and the corresponding dependence of Φ^* on x calculated using the Gouy-Chapman model. The values of model parameters are $\sigma = -0.5 \text{ As/m}^2$, $n = 0.1 \text{ mol/l}$, $T = 310 \text{ K}$, $\epsilon = 78.5$, $n_0 = \rho_w N_A / M_w$, $M_w = 18 \text{ kg/kmol}$, $\rho_w = 1000 \text{ kg/m}^3$.

The particle partition functions of a m_+ - th univalent cation and a m_- - th univalent anion are respectively [5]

$$q_{m_+} = q_+^0 \exp \left[\frac{-e_0 \Phi(\mathbf{r}_{m_+})}{kT} \right], \quad m_+ = 1, 2, \dots, N_+, \quad (3)$$

$$q_{m_-} = q_-^0 \exp \left[\frac{+e_0 \Phi(\mathbf{r}_{m_-})}{kT} \right], \quad m_- = 1, 2, \dots, N_-, \quad (4)$$

while the partition function of a m_w - th water molecule which is electrically neutral is written as

$$q_{m_w} = q_w^0, \quad m_w = 1, 2, \dots, N_w, \quad (5)$$

where e_0 is the unit charge, $\Phi(\mathbf{r}_{m_j})$ the potential of the electric field at the position \mathbf{r}_{m_j} of the m_j - th ion of the j -th species, while q_j^0 is defined as follows,

$$q_j^0 = \sum_i \exp \left[-\frac{K_{ji}}{kT} \right], \quad j = +, -, w, \quad (6)$$

where index i runs through all possible energy states K_{ji} of the chosen particle of the j -th species. As we can see, all particles of the same species are considered as indistinguishable and equal with respect to the spectrum of the energy states K_{ji} . It is assumed, that the electric field in the system does not influence the energies K_{ji} .

The solution in the chosen cell is considered to be a system with constant volume ΔV and constant number of all species of particles N_+ , N_- and N_w . The system is immersed in a heat bath, so that its temperature

T is constant. Since it is assumed, that the particle-particle correlations are described through the effect of the mean electric field and the excluded volume effect, the particles in the cell are explicitly considered to be independent.

Assuming that the solution in the particular cell is in the thermodynamic equilibrium and taking into account all possible nonequivalent distributions of the particles in the cell, the canonical partition function of the cell Q^c can be written as a product of particle partition functions (see equations 3-5)

$$Q^c = \exp \left[-\frac{\Delta W_{el}}{kT} \right] [q_+^0]^{N_+} [q_-^0]^{N_-} [q_w^0]^{N_w} \cdot \frac{N_0!}{N_+! N_-! N_w!} \quad (7)$$

where all possible nonequivalent distributions of the particles in the single cell are taken into account by the factor $\frac{N_0!}{N_+! N_-! N_w!}$ and where

$$\begin{aligned} \Delta W_{el} &= \sum_{m_+=1}^{N_+} e_0 \Phi(\mathbf{r}_{m_+}) + \sum_{m_-=1}^{N_-} -e_0 \Phi(\mathbf{r}_{m_-}) = \\ &= \frac{1}{2} \epsilon \epsilon_0 E^2 A \Delta x \end{aligned} \quad (8)$$

is the the electric potential energy of all ions in the cell. The ions are assumed to be immersed in a medium with permittivity ϵ . The symbol ϵ_0 denotes the permittivity of the free space, while E is the electric field strength which points in the direction of the x -axis. The validity of equation 8 is limited by the assumption that Δx is small comparing to the distance over which macroscopic properties of the system change appreciably, so that electric field is considered to be constant everywhere in the cell. While calculating ΔW_{el} , it is taken into account that the potential at the site of a given ion is created by all other ions in the whole solution and the charged plane as well.

Knowing the canonical partition function Q^c , using equations 1 and 2 and applying the Stirling approximation for large N_+ , N_- , N_w and N_0 , the expression for the Helmholtz free energy of the solution in the chosen cell ΔF can be obtained by using the statistical mechanical relation $\Delta F = -kT \ln Q^c$:

$$\Delta F = \left[\frac{1}{2} \epsilon \epsilon_0 E^2 + kT \Sigma \right] A \Delta x, \quad (9)$$

$$\Sigma = \left[n_+ \ln \frac{n_+}{n_0 q_+^0} + n_- \ln \frac{n_-}{n_0 q_-^0} + n_w \ln \frac{n_w}{n_0 q_w^0} \right],$$

where the densities of the number of particles n_j as well as the density of the number of sites n_0 are introduced,

$$n_+ = \frac{N_+}{\Delta V}, \quad n_- = \frac{N_-}{\Delta V}, \quad n_w = \frac{N_w}{\Delta V}, \quad n_0 = \frac{N_0}{\Delta V}. \quad (10)$$

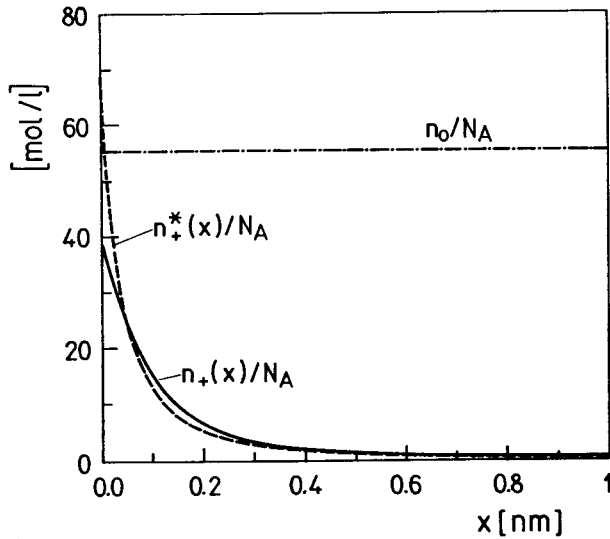


Figure 4. The density of number of univalent counterions (cations) n_+ in dependence on the distance from the charged plane x calculated by considering the finite sizes of ions and the corresponding dependence of n_+^* on x calculated using the Gouy-Chapman model. The values of model parameters are the same as in figure 3.

In order to derive an expression for the free energy of the whole system F^S , the contributions of all the cells which constitute the system are integrated,

$$F^S = \int_0^\infty \left[\frac{1}{2} \epsilon \epsilon_0 E^2(x) + kT \Sigma \right] A dx, \quad (11)$$

where it is taken into account that $E \rightarrow E(x)$ and $n_j \rightarrow n_j(x)$, $j = +, -, w$. The free energy of the system expressed by equation 11 includes interactions of ions with the mean electric field due to all the charges in the system and the entropy of mixing of all the particles in the system.

The equation 11 describes how the free energy of the system is expressed with the particle distribution functions and the electric field in the system. However, the explicit expressions for the functions $n_+(x)$, $n_-(x)$, $n_w(x)$ and $E(x)$ are not known. To derive the explicit expressions for these functions, the condition for the free energy minimum ($\delta F^S = 0$) is applied, where the following constraints must be satisfied:

- (a) the condition, that all of N sites in each cell are occupied (equation 2), i.e. that for any x :

$$n_0 = n_+(x) + n_-(x) + n_w(x), \quad (12)$$

- (b) the conditions that the total number of the particles for each species N_{Tj} in the whole system is constant while the variation is performed,

$$\int_0^\infty n_j(x) A dx = N_{Tj}, \quad j = +, -, w, \quad (13)$$

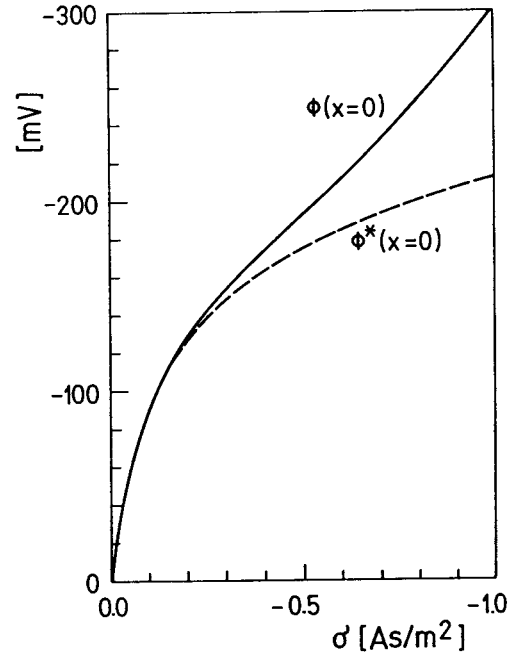


Figure 5. The electric potential near the charged plane $\Phi(x=0)$ in dependence on the charge area density of the $x=0$ plane σ considering the finite size of particles in the solution and the corresponding dependence of $\Phi^*(x=0)$ on σ calculated by using the Gouy-Chapman model. The values of n , T , ϵ and n_0 are the same as in figure 3.

- (c) the validity of the Gauss law at any x ,

$$\epsilon \epsilon_0 \frac{\partial E}{\partial x} = e_0 n_+(x) - e_0 n_-(x). \quad (14)$$

The requirement that the variation of F^S is zero, taking into account the conditions 12-14 and the boundary condition

$$E(x \rightarrow \infty) = -\frac{d\Phi}{dx}(x \rightarrow \infty) = 0, \quad (15)$$

formulates an isoparametric problem. The condition 15 takes into account that the effect of the charged plane is screened by the ions and that far from the plane the density of the number of cations $n_+(x \rightarrow \infty)$ equals the density of the number of anions $n_-(x \rightarrow \infty)$,

$$n_+(x \rightarrow \infty) = n_-(x \rightarrow \infty) \equiv n. \quad (16)$$

After some calculation we obtain the solution of the above isoparametric problem,

$$n_+(x) = \frac{n_0 n \exp\left(\frac{-e_0 \Phi(x)}{kT}\right)}{n_{w\infty} \left[1 + \frac{2n}{n_{w\infty}} \operatorname{ch}\left(\frac{e_0 \Phi(x)}{kT}\right) \right]}, \quad (17)$$

$$n_-(x) = \frac{n_0 n \exp\left(\frac{e_0 \Phi(x)}{kT}\right)}{n_{w\infty} \left[1 + \frac{2n}{n_{w\infty}} \operatorname{ch}\left(\frac{e_0 \Phi(x)}{kT}\right) \right]}, \quad (18)$$

$$n_w(x) = \frac{n_0}{1 + \frac{2n}{n_{w\infty}} \operatorname{ch}\left(\frac{e_0 \Phi(x)}{kT}\right)}, \quad (19)$$

$$\frac{d^2\Phi}{dx^2} = \frac{2e_0n_0n \operatorname{sh}\left(\frac{e_0\Phi(x)}{kT}\right)}{\epsilon\epsilon_0n_w\infty\left[1 + \frac{2n}{n_w\infty}ch\left(\frac{e_0\Phi(x)}{kT}\right)\right]}, \quad (20)$$

where we take into account $E(x) = -\frac{d\Phi(x)}{dx}$ and chose $\Phi(x \rightarrow \infty) = 0$. The distribution functions 17 - 19 and the differential equation 20 were obtained also by Freise (1952) by applying a thermodynamical approach. The thermodynamical approach can however not prove that the distribution functions are consistent with the differential equation for the electric potential, which can be done by applying the presented method.

If it is assumed that the electrolyte solution is very dilute everywhere in the system, i.e. that for any x

$$n_+(x) + n_-(x) \ll n_w(x), \quad (21)$$

the ion distribution functions 17 and 18 transform into

$$n_+^*(x) = n \exp\left(\frac{-e_0\Phi^*(x)}{kT}\right), \quad (22)$$

$$n_-^*(x) = n \exp\left(\frac{+e_0\Phi^*(x)}{kT}\right), \quad (23)$$

while the differential equation 20 becomes

$$\frac{d^2\Phi^*}{dx^2} = \frac{ne_0}{\epsilon\epsilon_0} \operatorname{sh}\left(\frac{e_0\Phi^*(x)}{kT}\right). \quad (24)$$

Equations 22 -24 are known as Gouy - Chapman model of the electric double layer [1,4] (denoted by asteriks). It can be noted that in contrast to the expressions 17 - 20, the corresponding expressions 22 - 24 do not depend on the density of the number of sites n_0 , i.e. on the volume occupied by a single particle in the solution. This means that the particles in the Gouy-Chapman model are considered as dimensionless and there is no upper limit posed upon the concentration of particles. To avoid unreasonably high concentrations of counterions near the charged plane it should be kept in mind that the use of the Gouy Chapman model is justified only within the assumption 21 that the concentration of ions is very small everywhere in the system. If the surface charge density $|\sigma|$ is high, many counterions are attracted in the vicinity of the charged plane and therefore condition 21 may be violated there even if the concentration of ions far from the charged plane is very low.

3 Results and discussion

In order to obtain the explicit dependencies of n_+ , n_- , n_w and Φ on the distance x from the charged plane, we must first solve the differential equation 20 subject to the condition 15 and to the condition $\Phi(x \rightarrow \infty) = 0$. The charged plane at $x = 0$ (figure 1) is taken into account by an additional boundary condition at $x = 0$ [12],

$$\frac{d\Phi}{dx}(x=0) = -\frac{\sigma}{\epsilon\epsilon_0}. \quad (25)$$

Equation 20 can be integrated to obtain

$$\left(\frac{d\Phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_0} \ln\left[\frac{1 + \frac{2n}{n_w\infty}ch\left(\frac{e_0\Phi}{kT}\right)}{1 + \frac{2n}{n_w\infty}}\right] \quad (26)$$

By taking into account 25 and 26, an analytic expression for the surface potential $\Phi(x=0)$ is obtained

$$\phi(x=0) = \frac{kT}{e_0} \operatorname{Arch}\Upsilon, \quad (27)$$

$$\Upsilon = \left[\frac{n_w\infty}{2n} \left[\left(1 + \frac{2n}{n_w\infty}\right) \exp\left[\frac{\sigma^2}{2\epsilon\epsilon_0kTn_0}\right] - 1 \right]\right].$$

The corresponding densities of the number of ions at $x = 0$, $n_+(x=0)$ and $n_-(x=0)$, respectively, can be then obtained from equations 17 and 18 by inserting $\Phi(x=0)$ from equation 27. To obtain the dependence of Φ on x and the corresponding distributions $n_+(x)$ and $n_-(x)$, equation (26) must be solved numerically.

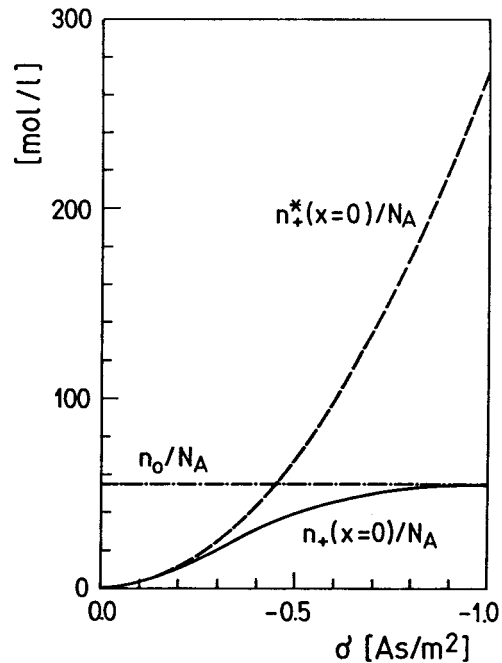


Figure 6. The density of number of univalent counterions (cations) near the charged plane $n_+(x=0)$ in dependence on the charge area density of the $x=0$ plane σ considering the finite sizes of particles in the solution and the corresponding dependence of $n_+^*(x=0)$ on σ calculated by using the Gouy-Chapman model. The values of n , T , ϵ , and n_0 are the same as in figure 3.

We would like to compare the calculated values of $\Phi(x=0)$, $n_+(x=0)$ and $n_-(x=0)$ with the corresponding Gouy-Chapman values calculated from equations 22, 23 and 24. Equation 24 can be integrated twice to obtain an analytic expression for $\Phi^*(x)$ [12]. The surface potential $\Phi^*(x=0)$ is

$$\Phi^*(x=0) = \frac{kT}{e_0} \operatorname{Arch}\left[1 + \frac{\sigma^2}{2\epsilon\epsilon_0kTn_0}\right]. \quad (28)$$

The corresponding densities of number of ions at $x = 0$, $n_+^*(x = 0)$ and $n_-^*(x = 0)$, respectively, can be obtained from equations 22 and 23 by inserting $\Phi^*(x = 0)$ from equation 28.

Figure 3 shows the dependence of the electric potential Φ on the distance from the charged plane x and the corresponding dependence of Φ^* on x calculated by using the Gouy - Chapman model. The potential is negative since the potential of the negatively charged plane is negative. The counterions which are attracted by the charged plane accumulate near it and screen its potential, so that the absolute value of the potential diminishes with increasing distance from the charged plane. Considering the finite size of ions causes $\Phi(x)$ to be more negative than the corresponding $\Phi^*(x)$, the difference $\Phi(x) - \Phi^*(x)$ diminishing with increasing distance from the charged plane.

Figure 4 shows the dependence of the density of the number of counterions n_+ on the distance from the charged plane x and the corresponding dependence of the Gouy-Chapman model $n_+^*(x)$. The number of counterions is the largest in the vicinity of the charged plane and diminishes monotonously with the distance from the plane. Considering the finite size of ions causes $n_+(x = 0)$ to be lower than $n_+^*(x = 0)$ since the particles in the Gouy - Chapman model are considered to be dimensionless and their number density therefore unlimited. However, at certain distance from the charged plane $n_+^*(x)$ falls below $n_+(x)$ due to the effect of the electric potential for which $|\Phi(x)| > |\Phi^*(x)|$ (figure 3).

Figure 5 shows the dependence of the electric potential at $x = 0$ plane $\Phi(x = 0)$ and the corresponding dependence of the Gouy - Chapman model $\Phi^*(x = 0)$ on the charge area density of the charged plane σ . Both potentials become more negative with increasing $|\sigma|$.

Figure 6 shows the dependence of the density of the number of counterions at $x = 0$, $n_+(x = 0)$ and the corresponding dependence of the Gouy - Chapman model $n_+^*(x = 0)$ on the charge area density of the charged plane σ . The discrepancy between both curves increases with increasing $|\sigma|$. It can be seen that $n_+(x = 0)$ saturates at high values of $|\sigma|$, attaining the value of the density of the number of sites n_0 while the corresponding curve of the Gouy - Chapman model $n_+^*(x = 0)$ increases unlimitedly and therefore exceeds the density of the number of sites n_0 . For higher $|\sigma|$ the Gouy-Chapman approach is no more justified, because the condition 12 is not fulfilled in the vicinity of the charged plane and finite size of ions must be taken into account in order to describe the system in a more realistic way.

4 Conclusions

Comparing the results of presented model of electric double layer and classical Gouy-Chapman model it was shown that the Gouy-Chapman model of electric double layer is a good approximation only when concentrations of ions are low everywhere in the solution, including the region near the charged plane. It was shown that this condition can be fulfilled only for low values of surface

charge density of the charged plane. Namely, for higher values of the surface charge density ($|\sigma| > 0.2 \text{ As/m}^2$) many counterions accumulate near the charged plane in order to fulfill the electroneutrality condition, so the concentration of ions in the vicinity of charged plane may become very high and the use of the Gouy-Chapman model can not be justified. Therefore when surface charge density of charged plane in contact with electrolyte solution is higher than 0.2 As/m^2 , the presented more general expressions for the electric potential and ion concentration functions should be considered.

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