Application of Monte Carlo simulations for the calculation of differential capacitance of double electrical layer formed at the metal oxide/electrolyte interface

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Mathematical relations between fundamental quantities describing double electrical layer (surface potential, surface charge density and differential capacitance) were derived by analyzing the definition of the differential capacitance. The obtained relations make it possible to calculate one of these quantities from two others as a function of pH.

We used these relations combined with the Monte Carlo simulation results for surface charge to calculate differential capacitance. Additionally we verified the equations by using experimental data for surface potential. Finally we discussed the pH-dependence of differential capacitance of double layer formed at the metal oxide/electrolyte interface.

1. INTRODUCTION

When a metal oxide is immersed in water, the charge is formed at its surface due to several interfacial processes. It is believed that the major source of the
surface charging in this case is the adsorption of the potential determining ions (H$^+$ for metal oxides). In addition, when the metal is in contact with electrolyte a characteristic space distribution of the charges, called double electrical layer is formed. The model of the electrical double layer (e.d.l.) is often treated as an analog of the plane capacitor. One of conducting plates of the capacitor is the charged surface, the other is the imaginary plane in which ions of background electrolyte are stored. By interpreting the e.d.l. in such a way, the system can be characterized by three quantities: surface potential ($\psi_0$), surface charge density ($\sigma_0$) and differential capacitance ($c_d$). All these quantities can be treated as functions of pH, but in many theoretical models of e.d.l. the $c_d$ is assumed to be constant (for the mathematical convenience).

There are several ways in which capacitance of the double electrical layer can be described. In general, we can distinguish the differential capacitance ($c_d$) and the integral capacitance ($c_i$) which are defined as follows [1]:

$$c_d = \frac{\partial \sigma_0}{\partial \psi_0} \quad \text{and} \quad c_i = \frac{\sigma_0}{\psi_0}$$  \hspace{1cm} (1)

where $\sigma_0$ is surface charge density and $\psi_0$ represents the macroscopic (statistically mean value) potential of the surface. From the physical point of view, we are able to measure only variations in the electrical potential; the absolute electrostatic potential is immeasurable.

Hal et al. [2] have published theory describing the variations of the surface potential as a function of the differential double layer capacitance and the intrinsic buffer capacity (the capability of the surface to store charge as a result of a small change in the H$^+$ concentration at the surface). The results obtained by Hal et al [2] were used by us to examine the mathematical relations between $\sigma_0$, $\psi_0$ and $c_d$ discussed in the next section. In most cases the way of calculating the $c_d$ depends on the theoretical background, and therefore $c_d$ is not purely empirically achievable.

Di Caprio et al. [3] have published some remarkable theoretical results of the differential capacitance calculated by applying the extension of the Gouy-Chapman theory based on a field theoretical approach including the hard sphere effect. They have observed that minimum of $c_d$ is located at pH=PZC. Furthermore, they have observed that for diluted electrolyte. It has been observed that these minima become maxima when the concentration of the electrolyte increases. They have proved that capacitance at these local extrema depends on the size of ions and their concentration in the solution. Lamperski [4] has observed a similar behavior of the function $c_d=f(pH)$ in his theoretical investigation of the adsorption of anions onto a metallic electrode. Despite the
fact that the studies mentioned above are strictly theoretical and concern the e.d.l. formed at the metallic electrode/electrolyte interface the conclusions are general to some extent, for all e.d.l. systems.

The differential capacitance can be measured experimentally by using CS (Capacitance Spectroscopy) [5], but mostly this empirical approach is applied for the e.d.l. formed at a membrane. Krysa et al. [7] have published empirically determined electrical capacitance for the e.d.l. formed at the titanium electrode with a layer of RuO$_2$ and IrO$_2$. The measurement has been carried out by changing the potential of the electrode within the range:-200 mV - 400 mV. Surprisingly, they have observed an exponential decrease of the capacitance without presence of any local extrema. However, the application of a similar method to the cadmium electrode resulted in a curve $c_d=f(y_0)$ with a large number of local extrema [8].

2. DIFFERENTIAL CAPACITANCE OF E.D.L. AS A FUNCTION OF $\sigma_0$ AND $\psi_0$

Both surface charge density and surface potential are unique functions of pH. This feature allows us to rewrite the definition of the differential capacitance (1) in the following form:

$$c_d = \frac{\partial \sigma_0}{\partial pH} \cdot \frac{\partial pH}{\partial \psi_0}$$

(2)

Because the $\psi_0=f(pH)$ is unequivocal function of pH (continuous and injective function) it is possible to find the inverse function i.e. $f^{-1}(\psi_0)$, so finally we have:

$$c_d = \frac{\partial \sigma_0}{\partial pH} \cdot \frac{\partial f^{-1}(\psi_0)}{\partial \psi_0}$$

(3)

The derivative of the inverse function is equal to the inverted derivative of the function, which in our case means that: $\frac{\partial f^{-1}(\psi_0)}{\partial \psi_0} = \left(\frac{\partial \psi_0}{\partial \psi_0}\right)^{-1}$. The pH-dependence of surface potential can be measured empirically by using the ISFET technique. It is also possible to assume analytical form of the $\psi_0=f(pH)$, as suggested e.g. by Bousse [9] (correct for small values of the surface potential):
where \( e \) is elementary charge, \( k \) is Boltzmann constant, \( T \) is the absolute temperature and \( \alpha \) is the dimensionless sensitivity parameter of reducing function (4) to the Nernst’s potential (for \( \alpha = 1 \) equation (4) becomes identical with the Nernst’s equation) and finally \( n = 1/\ln(10) \) is a constant value (connected with changing the base in logarithmic functions). The value of \( \alpha \) varies between 0 and 1. According to Hal et al. [2] \( \alpha \) depends on the intrinsic buffer capacity \((\beta_{\text{int}})\) and the differential capacitance \((c_d)\), but in many theoretical approaches is treated as a best-fit parameter [10,11] (so it is often assumed that \( \alpha \) value does not depend on the physical properties of the system). In our studies we assumed that \( \alpha \) is pH independent and can be treated as a parameter chosen \textit{ad hoc}.

The inverse function to the \( \psi_0(pH) \) is given by:

\[
pH \equiv f^{-1}(\psi_0) = PZC - \frac{en}{\alpha kT} \psi_0
\]

Its derivative can be written as:

\[
\frac{\partial f^{-1}(\psi_0)}{\partial \psi_0} = -\frac{en}{\alpha kT}
\]

The function \( \sigma_0 = f(pH) \) is the most frequently obtained information by the experimental studies of the e.d.l. formed at the metal oxide/electrolyte interface. To determine \( \sigma_0 \) the potentiometric titration of the suspension is usually used. We assume that the relation \( \sigma_0 = f(pH) \) is known (i.e. it was obtained empirically or theoretically) and that it is possible to find its derivative \( \frac{\partial \sigma_0}{\partial pH} \). Finally, the appropriate expression for the differential capacitance is given by the following formula:

\[
c_d(pH) = -\frac{en}{\alpha kT} \cdot \frac{\partial \sigma_0}{\partial pH}
\]
3. SURFACE CHARGE DENSITY AS A FUNCTION OF $C_D$ AND $\psi_0$

A similar approach based on equation (1) can be used to derive the expression for $\sigma_0$ as a function of $c_d$ and $\psi_0$. If $c_d=f(pH)$ and $\psi_0=f(pH)$ are known, then it is also possible to obtain the profile of the surface charge density as a function of pH. The appropriate expressions can be derived in two different ways. On one hand, the definition of the differential capacitance can be formulated as an ordinary differential equation. On the other hand, the derivation can based on the properties of the derivative of the inverse function in equation (3). By treating eq. (1) as the ordinary differential equation with separable variables we can rewrite this equation in the following form:

$$c_d(pH) \cdot d\psi_0 = d\sigma_0$$

(8)

where the differentials are defined as:

$$d\psi_0 = (\partial \psi_0 / \partial pH) dpH$$ \quad and \quad $$d\sigma_0 = (\partial \sigma_0 / \partial pH) dpH$$

(9)

Integrating both sides of equation (8) leads to the expression for the surface charge density which is indefinite integral of $c_d$:

$$\sigma_0(pH) \equiv \int d\sigma_0 = \int c_d(pH) \cdot \frac{d\psi_0}{dpH} dpH$$

(10)

By assuming analytical form of the $\psi_0$ (4), the above expression can be rewritten in the form:

$$\sigma_0(pH) = -\alpha \frac{kT}{en} \int c_d(pH) dpH = -\alpha \frac{kT}{en} C_d(pH) + C^*$$

(11)

where $C_d(pH)$ is a primitive function (antiderivative of the integrand function) and $C^*$ is the integration constant. The integration constant can be found by using physical properties of the system (the boundary condition for the differential equation). At $pH=PZC$ $\sigma_0$ is equal to zero, thus by using this condition we can write the following expression for integration constant:

$$C^* = \alpha \frac{kT}{en} C_d(pH = PZC)$$

(12)
4. THE SURFACE POTENTIAL AS A FUNCTION OF $C_D$ AND $\sigma_0$

Analogously, if the functions: $c_d = f(pH)$ and $\sigma_0 = f(pH)$ are known, we can calculate the function $\psi_0$. A suitable expression for the surface potential is derived from the definition of the differential capacitance:

$$d\psi_0 = \frac{d\sigma_0}{c_d(pH)} \quad \Rightarrow \quad \frac{\partial \psi_0}{\partial pH} dpH = \frac{1}{c_d(pH)} \frac{\partial \sigma_0}{\partial pH} dpH$$

(13)

By integrating both sites of eq. (13) we obtained:

$$\psi_0(pH) = \int \frac{1}{c_d(pH)} \frac{\partial \sigma_0}{\partial pH} dpH + C'$$

(14)

We assumed that $c_d(pH=\text{PZC}) \neq 0$, which is the necessary condition for the existence of the right hand of equation (14) (this condition is generally satisfied). The integration constant $C'$ can be obtained by taking advantage of PZC at which $\psi_0(pH = \text{PZC}) = 0$ i.e.:

$$C' = \left[ \int \frac{1}{c_d(pH)} \frac{\partial \sigma_0}{\partial pH} dpH \right]_{pH = \text{PZC}}$$

(15)

The mathematical relations between surface charge density, surface potential and differential capacitance (3,10,14) are unique and general for any e.d.l. model. For example, from calculated $c_d$ (by using eq. (3)) we can recreate the input surface charge density (by using eq. (10)) or the surface potential (by using the eq. (14)).

5. CALCULATIONS OF $\sigma_0 = f(pH)$ FROM THE MONTE CARLO SIMULATIONS

Despite the fact that $\sigma_0 = f(pH)$ is frequently obtained experimentally in the potentiometric titration in this paper we present strictly theoretical approach in which the surface charge is obtained from the Grand Canonical Monte Carlo (GCMC) simulation of the double electrical layer formed at the metal oxide/electrolyte interface [12,13]. According to the classical 1-pK mechanism of the proton adsorption [14], the surface complexes are formed according to the following surface reactions:
For each of the equations (16a,b,c) we can write a suitable microscopic equilibrium constant:

\[
K_H^* = \frac{[SOH_2^{1/2}]}{[SOH^{-1/2}][H^+]},
\]

\[
K_C^* = \frac{[SOH^{-1/2}C^+]}{[SOH^{-1/2}][C^+]},
\]

\[
K_A^* = \frac{[SOH_2^{1/2}A^-]}{[SOH_2^{1/2}][A^-]}.
\]

In practice, we used the desorption constant instead of the adsorption constants (17), the desorption constants are obtained simply by inverting the constants from eq. (17) i.e.:

\[
K_H = \frac{1}{K_H^*}, \quad K_C = \frac{1}{K_C^*}, \quad K_A = \frac{1}{K_A^*}.
\]

These constants (18) are linked with the adsorption energy as follows:

\[
pK_{H} = n\epsilon_H, \quad pK_{C} = n\epsilon_C, \quad pK_{A} = n\epsilon_A.
\]

where \(pK_i = -\log[K_i]\). During the simulation process, the \(pK_i\) values are associated with the chemical potential and the probability of adsorption/desorption process are used. The acceptance/rejection rule is based on the Metropolis algorithm. In order to describe lateral interactions between adsorbed species we used the interaction potential suggested by Borkovec et al.
which consist of coulombic $W_c(r_{ij})$ and polarization $W_p(r_{ij})$ contributions:

$$W(r_{ij}) = W_c(r_{ij}) + W_p(r_{ij}) = q_i q_j \left[ \frac{e^2}{2\pi \epsilon_0 \epsilon_w} \exp(-\kappa r_{ij}) + \frac{\epsilon_s}{2\pi \epsilon_0} \left( \frac{d}{\epsilon_s} + \frac{1}{\epsilon_w} \right)^2 \frac{e^2}{r_{ij}^3} \right]$$

where $d$ is the depth of the charge buried inside the solid, $\epsilon_0$ is permittivity of free space, $\epsilon_s$ is dielectric constant of the interfacial layer and $\epsilon_w$ is the dielectric constant of bulk phase respectively, $\kappa$ is the Debye's parameter (inversion of the e.d.l. thickness), $q_i$ and $q_j$ are the formal effective charges for the surface complexes at sites $i$ and $j$ respectively. We assume that the effective charges are: $q_H = q_C = +1/2$ (cationic and protonic complexes) and $q_A = -1/2$ (anionic complexes).

In the calculations we take into account the influence of the electrolyte concentration on the thickness of double electrical layer.

It is well known that really existing, and practically used adsorbents (especially metal oxides) are energetically heterogeneous [17]. The lack of energetic uniformity is responsible for difference between the adsorption energies of different adsorption sites. In our studies we assume random topography of the surface sites and the quasi-Gaussian distribution functions of the adsorption energy ($pK_i$ values):

$$\Gamma_i(pK_i) = \frac{m_i}{F_i} \frac{10^{m_i(pK_i - pK_i)}}{1 + 10^{m_i(pK_i - pK_i)}} \text{ for } i \in \{H, C, A\}$$

where $m_i$ is the heterogeneity parameter and $F_i$ is the normalization constant in the energetic domain $[pK_i - z, pK_i + z]$ (where $z$ is the cut-off parameter of the $\Gamma_i$ functions). The lower value of $m_i$, the more heterogeneous the surface is.

We present results for $m_H = m_C = m_A = 0.2$.

From GCMS we directly obtained adsorption isotherms for each type of ions ($\theta_H$, $\theta_C$, $\theta_A$). The surface charge is obtained from $\theta_i$ by using the following equation:

$$\sigma_0 = B \left( \theta_H + \theta_C - \frac{1}{2} \right)$$
where \(B = eN_s\) and \(N_s\) is the density of the surface sites ([sites/nm\(^2\)]). The density of the surface sites is connected with the GCMC simulation parameter \(d_s\) i.e. with the distance between sites on a square lattice \((N_s = 1/d_s^2)\). The details of the presented simulations can be found in our previous papers [12,13].

6. RESULTS

In Figure 1 the results of Monte Carlo simulations are shown. They were obtained for the strongly heterogeneous surface \((m_H = m_C = m_A = 0.2)\). The other parameters used in the simulations have the following values: \(pK_H = 6.0\), \(pK_C = pK_A = -0.75\), \(av = 20\) (averaging cycles), \(mcs = 20\) (monte carlo steps), \(L = 100\) (linear dimension of the lattice cell), \(d = 1.1\) nm (distance between sites), \(z = 25\) (cut-off parameter of the energy distribution function), \(\rho = 0.25\) nm, \(1/\kappa = 0.43\) nm and the dielectric constants are equal to \(\varepsilon_w = 80\) and \(\varepsilon_s = 3\). The physical meaning of these parameters can be found in our previous papers [12,13].

In Figure 1 D are shown the curves of the surface charge density obtained by using eq. (22). While looking at Figure 1 we can see lower values of the surface coverage \(q_C, q_A\) for \(c = 0.01\) mol/dm\(^3\) compared with the coverage obtained for \(c = 0.1\) mol/dm\(^3\) (Fig. 1 B, C).

As we can see in Figure 2 the maximum of \(c_d\), does not lay at pH=PZC. The position of the maximum does not depend on the \(\alpha\) parameter, but is sensitive to the concentration of the electrolyte. The higher the concentration of the background electrolyte, the higher the maximum value of the \(c_d\) (for the same \(\alpha\) value) is. The curves \(c_d = f(\sigma_0)\) (Fig. 3) are inverted with relation to the PZC in comparison with Figure 2. The inversion of the maxima is caused by the fact that \(\sigma_0\) is decreasing function of pH (Fig. 1 D).

The maximum at \(c_d = f(pH)\) determines the value of pH, at which the capacitor exhibits the highest capacitance efficiency. In other words, at this point the surface charge is the most sensitive to the pH changes.

The pH\(^{cd}\) value and the corresponding \(\sigma_0^{cd}\) value which describe maximum \(c_d\) (in Figs 3, 4) determine also the point on the curve \(\sigma_0 = f(pH)\) where the differential capacitance reaches the maximum value. Similarly, the maximum of \(c_d\) shown in Figure 4 is placed at \(\psi_0\) which corresponds to pH\(^{cd}\) (the axis of abscissae in Figure 4 is shifted and inverted by eq. (4) in comparison to the axis of abscissae in Fig. 2).
Fig. 1. Adsorption isotherms for protons (A), cations (B) and anions (C) (obtained from GCMC simulations) and surface charge density $\sigma_0$ (D) as functions of pH. The PZC values are 3.02 (c=0.1 mol/dm$^3$) and 3.18 (c=0.01 mol/dm$^3$).

Fig. 2. Differential capacitance as function of pH for a few values of parameter $\alpha$ (eq. (4)). The results correspond to the concentration of electrolyte equal to: (A) 0.1 mol/dm$^3$ and (B) 0.01 mol/dm$^3$. 
According to the results published by Di Caprio et al. [3] the extremal value of $c_d$ for the metallic electrode is placed at pH=PZC, whereas for the metal oxide electrode the extremal value of $c_d$ is shifted with respect to pH=PZC (Fig. 5A, Figs 3, 4). In addition, only for the metallic electrode the value of $c_d$ changes with increasing concentration of the background electrolyte, whereas for the metal oxide electrode we can observe changes in both value of $c_d$ and its position.
Hal et al. [2] have carried out measurements of $\Delta \psi_0$ as function of pH, then they determined the shape of the surface potential $\psi_0=f(pH)$ (to that purpose they have applied the c.d.l. model based on the MUSIC mechanism and the Gouy-Chapman-Stern scheme). They have used the same theoretical background to determine $c_d$ as function of pH. The dependence $\psi_0$ found by Hal et al. has a linear shape (Fig. 18 in ref. [2]). We found the following expression for this function:

$$\psi_0(pH) = \text{const} \cdot (\text{PZC} - pH) \quad \text{where} \quad \text{const} = 0.5673$$  \hspace{1cm} (23)$$

The PZC obtained by Hal et al. is equal to 8.46 and the curves $\psi_0(pH)$ were independent of the concentration of electrolyte, so the same equation (23) was used by us in both cases: $c=0.1\text{mol/dm}^3$ and $c=0.01\text{mol/dm}^3$. The curves $c_d=f(pH)$ obtained by Hal et al. [2] are shown in Figure 5 A. The functions $\sigma_0=f(pH)$ are derived by using eq. (11). The integral constants ($C^*$) was fund by using the condition (12), and they are equal to 0.2577 ($c=0.1 \text{mol/dm}^3$) and 0.2282 ($c=0.01 \text{mol/dm}^3$) respectively.

Hal et al. [2] have determined the empirical dependence only for the surface potential $\psi_0=f(pH)$. The functions $c_d=f(pH)$ presented by them were calculated by means of the surface complexation model with the c.d.l. theory. Regardless of the way in which $c_d=f(pH)$ was obtained by Hal et al., we calculated the $\sigma_0=f(pH)$ corresponding to their models by using eq. (10).

The shape of the curve $\sigma_0$ obtained by applying eq. (10) is physically correct, as well as the calculated PZC for the aluminum oxide is. A similar results ($\sigma_0=f(pH)$) for the Al$_2$O$_3$ were published by Ruiz-Reina et al. [18].

The fact that curves $c_d=f(pH)$ obtained by for MC simulations show maximum whereas the curves obtained by Hal et al. have minima should not be treated as a problem. Namely, for the same adsorption system (e.g. SiO$_2$) Hal et al. [2] have obtained both the maximum (Fig. 5 in ref [2]), and minimum in $c_d$ (Fig. 13 in ref [2]). These differences come from the level of theory used to calculate the $\psi_0=f(pH)$ and $c_d=f(pH)$ from $\Delta \psi_0=f(pH)$ measured in ISFET. In addition, the curves $\sigma_0=f(pH)$ (Figure 5B) calculated by using eq. (3) and the empirical potential determined by Hal et al. [2] can perfectly recreate the empirical dependence $c_d=f(pH)$. This fact proves that the solutions obtained in this study are unique.

In our investigation we assumed that the surface potential decreases linearly with increasing pH, which is in agreement with the Bousse’s suggestion (eq. (4)). There are also papers in which theoretically (or empirically) calculated surface potential $\psi_0$ is not a decreasing linear function of pH, for instance the studies of Fe$_2$O$_3$ in water and alcoholic solution presented by Mustafa et al. [19].
Fig. 5. Application of eq. (10) to obtain $\sigma_0 = f(pH)$. The $c_d = f(pH)$ and $\psi_0 = f(pH)$ were determined empirically by Hal et al. [2] for $\text{Al}_2\text{O}_3$ by using the ISFET measurements and the MUSIC model and the Gouy-Chapman-Stern theory of e.d.l. (A) the differential capacitance $c_d$ found by Hal et al. (Fig. 21 in ref. [2]). (B) the surface charge densities obtained by using the $c_d$ (from (A)) and empirically obtained $\psi_0$ by Hal et al. (Fig. 18 in ref. [2]).

5. CONCLUSIONS

A few simple mathematical relations between physicochemical quantities of the e.d.l. ($\sigma_0, \psi_0, c_d$) were derived from the definition of the differential capacitance. In addition, by treating equation (1) as an ordinary differential equation it is possible to determine the behavior of one quantity if the others are known. The presented results have universal character, and the presented mathematical relations may be applied for any e.d.l. system. Equations (3, 10, 14) may be also useful in further empirical and theoretical studies.

We showed an application of the methodology in two cases: a) in order to find $c_d = f(pH)$ we used the analytical expression for $\psi_0$ (eq. 4) and the data from the computer simulations for $\sigma_0 = f(pH)$, b) in order to determine the $\sigma_0 = f(pH)$ we used the experimental data for the surface potential published by Hal et al. [2].

Results of this paper are in agreement with the previously published theoretical results, in which the parameter $\alpha$ was treated as the best-fit parameter. The maximum value of $c_d$ depends on the concentration of the electrolyte and is located near the PZC point.

If we have two from three discussed pH-dependencies ($\sigma_0 = f(pH)$, $\psi_0 = f(pH)$, $c_d = f(pH)$) we are able to accurately calculate the remaining one. The methodology presented by us may be fruitful, especially when the empirical values of these quantities are known. Generally speaking we are able to obtain
Application of Monte Carlo simulations for the calculation of $\psi_0=f(pH)$ without solving the Poisson-Boltzmann equation or ISFET measurements, as well as we are able to obtain $\sigma_0=f(pH)$ without complicated calculations or potentiometric titrations. In addition we proved the well known property of e.d.l. that the differential capacitance is not constant with pH.

REFERENCES


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