APPROXIMATE CHARGE-POTENTIAL RELATIONSHIP FOR SPHERICAL PARTICLE IN ARBITRARY SALT MEDIUM

Sergey Pivovarov
Institute of Experimental Mineralogy, Russian Academy of Sciences
142432 Chernogolovka, Moscow district, Russia
E-mail: serg@iem.ac.ru

ABSTRACT

The paper presents simple and accurate approximation of charge-potential relationship for spherical particle in electrolyte solution, valid for arbitrary salt medium and applicable for particles and ions. For a particle in arbitrary mixture of 1:1, 1:2, 2:1, and 2:2 electrolytes, the analytical expression was deduced. Within the range covered by numerical studies, the maximum error in surface charge is 0.75 % (for 1:1, 1:2, 1:3, 2:1, and 3:1 electrolytes). This charge-potential relationship was applied to modeling of acid-base properties of oxides. It was found that the planar approach is not applicable for ferrihydrite particles.

INTRODUCTION

If the curvature of the interface is negligible, the charge-potential relation is defined by Gouy-Chapman equation (below all numerical values of constant factors are valid for 25^oC and aqueous medium):

$$\sigma, C/m^2 = (2000RT\varepsilon_0\varepsilon)^{0.5}I^{0.5}Q = 0.0587 \times I^{0.5}Q \text{, or} \tag{1}$$

$$\sigma, \mu eq/m^2 = 0.608 \times I^{0.5}Q \tag{1a}$$

$$Q = sgn(y_d) \times \{1/I^{0.5}\} \times \{\textstyle\sum c_i(exp(-z_iy_d) - 1)\}^{0.5} \tag{2}$$

$$y_d = F\varphi_d/RT \tag{3}$$

$$I = 0.5 \times \textstyle\sum z_i^2 c_i \tag{4}$$

Here φ_d is potential in the head of diffuse layer, y_d is scaled potential, $sgn(y_d)$ is sign of y_d, I is molar ionic strength, c_i is molar concentration of ion in the bulk solution (moles per dm^3), z_i is charge of ion, F is Faraday constant (96484.6 C/mol), R is gas constant (8.3144 $J\times mol^{-1}\times K^{-1}$), T is absolute temperature, ε_o is dielectric constant of free space (8.8541878×10^{-12} $C\times V^{-1}\times m^{-1}$), ε is relative dielectric constant of medium (78.47 for water at 25^oC).

The Eq (2) may be rearranged (Pivovarov, 2009, 2010) as

$$Q = (I_{eff}/I)^{0.5} \times (P_d^{0.5} - 1/P_d^{0.5}) \tag{5}$$

$$P_d = exp(F\varphi_d/RT) = exp(y_d) \tag{6}$$

$$I_{eff} = 0.5 \times \{[A^-] + [An^{2-}](2 + 2P_d) + \cdots [An^{n-}](n + 2(n-1)P_d + \cdots 2P_d^{n-1}) + [M^+] + [Me^{2+}]\left(2 + \frac{2}{P_d}\right) + \cdots [Me^{n+}]\left(n + \frac{2(n-1)}{P_d} + \cdots \frac{2}{P_d^{n-1}}\right)\} \tag{7}$$

Here $[A^-]$, $[An^{2-}]$, and $[An^{n-}]$ are molar concentrations of mono-, bi- and n-valent anions, $[M^+]$, $[Me^{2+}]$, and $[Me^{n+}]$ are molar concentrations of mono-, bi- and n-valent cations.

For symmetric z:z electrolytes, the Eq. 2 is reduced to

$$Q = (2/z)\text{sh}(zy_d/2) \tag{8}$$

Here $\text{sh}(x) = 0.5\{\exp(x)-\exp(-x)\}$ is hyperbolic sinus.

The Gouy-Chapman equation gives the exact charge-potential relation for flat interface, and may be applied if the curvature of interface is negligible. The accuracy of planar approach is 1 % at scaled radius of particle $\kappa a = 100$, and 10 % at scaled radius of particle $\kappa a = 10$, where a is radius of particle and κ is inversed Debye length:

$$\kappa = (2000F^2/RT\varepsilon_0\varepsilon)^{0.5} \times I^{0.5}, \quad \text{or} \tag{9}$$
$$\kappa^{-1}, \text{Å} = 3.04/I^{0.5} \tag{9a}$$

The exact analytical charge-potential relation for spherical particle is not known. At low surface potentials ($|y_d| \ll 1$), the charge-potential relationship is defined by Debye-Hückel equation:

$$\sigma, \mu eq/m^2 \approx 0.608 \times I^{0.5}\left(y_d + \frac{y_d}{\kappa a}\right) = 0.608 \times I^{0.5} \times y_d + 1.85 \times \frac{y_d}{[a,\ \text{Å}]} \tag{10}$$

Here $[a, \text{Å}]$ is radius of particle in angstroms. This is exact asymptotic relation at $y_d \to 0$ and any size of a particle. At $I = 0$, the Eq. (10) is exact relation (Coulomb's law).

As it was guessed by Loeb et al. (1961) on basis of their numerical calculations, the charge-potential relationship for symmetric z:z electrolyte at $\kappa a \to \infty$ approaches to (see Eq. 4.50 in Loeb et al., 1961):

$$\sigma, \mu eq/m^2 \approx 0.608 \times c^{0.5}\left\{2\text{sh}(zy_d/2) + \left(\frac{4}{\kappa a}\right)\text{th}(zy_d/4)\right\} \tag{11}$$

Here $\text{th}(x) = \{\exp(x)-\exp(-x)\}/\{\exp(x)+\exp(-x)\}$ is hyperbolic tangent. The uncertainty of the Loeb-Overbeek-Wiersema equation (Eq. 11) is 1 % at $\kappa a \sim 1.7$ and 10 % at $\kappa a \sim 0.27$. At smaller size of particles, uncertainty increases to infinity.

As it was shown by Ohshima et al. (1982), Eq. (11) is exact asymptotic relationship for $\kappa a \to \infty$. Based on perturbation analysis, the second-order charge-potential relationship was also deduced (see Eq. 24 in Ohshima et al., 1982). For symmetric z:z electrolytes:

$$\sigma, \mu eq/m^2 \approx 0.608 \times c^{0.5}\left\{4\text{sh}^2\left(\frac{zy_d}{2}\right) + \left(\frac{32}{\kappa a}\right)\text{sh}^2\left(\frac{zy_d}{4}\right) + \left(\frac{32}{(\kappa a)^2}\right)\ln\left(\text{ch}\left(\frac{zy_d}{4}\right)\right)\right\}^{0.5} \tag{12}$$

Here $\text{ch}(x) = 0.5\{\exp(x)+\exp(-x)\}$ is hyperbolic cosine. Maximum error of this relationship is 1 % at $\kappa a \sim 0.32$ and 10 % at $\kappa a \sim 0.035$. At smaller size of particles, uncertainty increases to infinity.

The Loeb-Overbeek-Wiersema equation (Eq. 11) was extended to arbitrary salt medium by Ohshima (1995):

$$\sigma, \mu eq/m^2 \approx 0.608 \times I^{0.5}\left\{Q + \left(\frac{2}{\kappa a}\right)(U/Q)\right\} \tag{13}$$
$$U = \int_0^{y_d} Q dy_d \tag{14}$$

For symmetric z:z electrolyte,

$$U = \left(\frac{8}{z^2}\right)\text{sh}^2\left(\frac{zy_d}{4}\right) = \left(\frac{4}{z^2}\right)\left\{\text{ch}\left(\frac{zy_d}{2}\right) - 1\right\} \tag{15}$$

The Ohshima equation (Eqs. 13, 14) is also an exact asymptotic relationship in the limit κα → ∞. The accuracy of the Ohshima equation for the arbitrary salt mixtures is expected to be the same as that of the Loeb-Overbeek-Wiersema equation for symmetric z:z electrolytes. The Eq. (12) may also be extended to arbitrary salt mixture (see Eq. 26 in Ohshima, 1995):

$$\sigma, \mu\text{eq/m}^2 \approx 0.608 \times I^{0.5}\left\{Q^2 + \left(\frac{4}{\kappa a}\right)U + \left(\frac{4}{(\kappa a)^2}\right)\int_0^{y_d}(U/Q)\,dy_d\right\}^{0.5} \tag{16}$$

The integral in Eq. (14) may be solved numerically. However, this is not too convenient for practical calculations. At any given conditions, the calculation of the ionic sorption via simultaneous solution of mass balance and mass action law equations requires ~ 100-1000 iteration steps. Accurate numerical integration of Eq. (14) at each iteration step leads to ~ 1000-fold delay. Thus, the analytical solution of Eq. (14) gives significant advantage. Unfortunately, the analytical solution for the Eq. (14) is known solely for the $(M^+, Me^{2+})A^-$ electrolyte (and thus for $M^+(A^-, An^{2-})$ electrolyte; see Eq. 34 in Ohshima et al., 1982).

The Loeb-Overbeek-Wiersema equation (Eq. 11) is well applicable for very fine crystalline particles, whereas the Eq. (12) is extended down to the range of macromolecules. However, there is no accurate approximation applicable down to molecular size.

The aim of present study is to deduce the analytical solution of the Ohshima equation (Eqs. 13, 14) for $(Me^+, Me^{2+})(A^-, An^{2-})$ electrolyte (most important case for majority of applications) and find close approximation for charge-potential relationship, applicable down to molecular range. The present paper is faced to surface complexation studies, and the application of the theory of spherical diffuse layer to surface reactivity is considered in details.

THEORY

The Eqs. (5) is more convenient for integration than Eq. (2). For the $(M^+, Me^{2+})(A^-, An^{2-})$ electrolyte, the Eqs. (7) is

$$I_{eff} = N + [An^{2-}]P_d + [Me^{2+}]/P_d \tag{17}$$

Here $N = [M^+] + 2[Me^{2+}] = [A^-] + 2[An^{2-}]$ is normality of solution. With use of Eqs. (5, 17), the Eq. (14) may be integrated analytically. The result is:

$$U = 2(I_{eff}/I)^{0.5} \times \left(P_d^{0.5} + 1/P_d^{0.5}\right) - 4 + U_{Me} + U_{An} \tag{18}$$

The function U_{Me} is zero at $[Me^{2+}] = 0$; at $[Me^{2+}] > 0$, it is defined by:

$$U_{Me} = 1 - \left(\frac{I_{eff}}{I \times P_d}\right)^{0.5} + 0.5\left(\frac{[M^+]}{(I \times [Me^{2+}])^{0.5}}\right)\ln\left\{\frac{2(I_{eff}[Me^{2+}]/P_d)^{0.5} + 2([Me^{2+}]/P_d) + N}{2(I[Me^{2+}])^{0.5} + 2[Me^{2+}] + N}\right\} \tag{19}$$

Similarly, U_{An} is zero at $[An^{2-}] = 0$; at $[An^{2+}] > 0$, this function is defined by:

$$U_{An} = 1 - \left(\frac{I_{eff}\,P_d}{I}\right)^{0.5} + 0.5\left(\frac{[A^-]}{(I\times[An^{2-}])^{0.5}}\right)\ln\left\{\frac{2\left(I_{eff}\,[An^{2-}]\,P_d\right)^{0.5}+2[An^{2-}]P_d+N}{2(I[An^{2-}])^{0.5}+2[An^{2-}]+N}\right\} \qquad (20)$$

In general case, charge-potential relationship for sphere may be rearranged on a manner of Debye-Hückel equation (see Eq. 10):

$$\sigma,\ \mu eq/m^2 = 0.608 \times I^{0.5}(Q + \Phi/\kappa a) = 0.608 \times I^{0.5}Q + 1.85\,\Phi/[a,\ \text{Å}] \qquad (21)$$

Here $[a,\ \text{Å}]$ is radius of particle in angstroms, and Φ is some unknown function.

The function Φ for 1:1 electrolyte is shown in Fig. 1. At $y_d \to 0$ (and at any κa), as well as at $\kappa a \to 0$ (and at any definite y_d), this function approaches to y_d. At $\kappa a \to \infty$ (and any y_d), as well as at $y_d \to \infty$ (and any definite κa), the function Φ approaches to $4\text{th}(y_d/4) = 2U/Q$. As may be seen, the analysis of charge-potential relationship in terms of the function Φ is more or less simple. The following approximation was found most accurate:

$$\Phi \approx \text{sng}(y_d) \times \left\{(b\kappa aQ)^2 + 4b\kappa aU + y_d^2\right\}^{0.5} - b\kappa aQ \qquad (22)$$

Here $b = 5/3$ is dimensionless fitting parameter. Combined with Eq. (21), it gives the following relationship:

$$\sigma,\ \mu eq/m^2 \approx 0.608 \times I^{0.5}\left((1-b)Q + \text{sng}(y_d) \times \{(bQ)^2 + (4b/\kappa a)U + (y_d/\kappa a)^2\}^{0.5}\right) \qquad (23)$$

Within the range covered by numerical studies (Loeb et al., 1961, Zhou and Zhang, 2012; 1:1 electrolyte: $\kappa a = 0.009\text{-}10$, $F\varphi_d/RT = 0\text{-}9.5$ and $\kappa a = 0.1\text{-}20$, $F\varphi_d/RT = 0\text{-}16$; 2:1 and 3:1 electrolytes: $\kappa a = 0.009\text{-}10$, $F\varphi_d/RT = 0\text{-}9.5$; 1:2 electrolyte: $(4/3)^{0.5}\kappa a = 0.1\text{-}20$, $F\varphi_d/RT = 0\text{-}4$; 1:3 electrolyte: $1.5^{0.5}\kappa a = 0.1\text{-}20$, $F\varphi_d/RT = 0\text{-}8/3$), maximum uncertainty in surface charge is 0.75 %. Similar accuracy is expected for electrolyte mixtures.
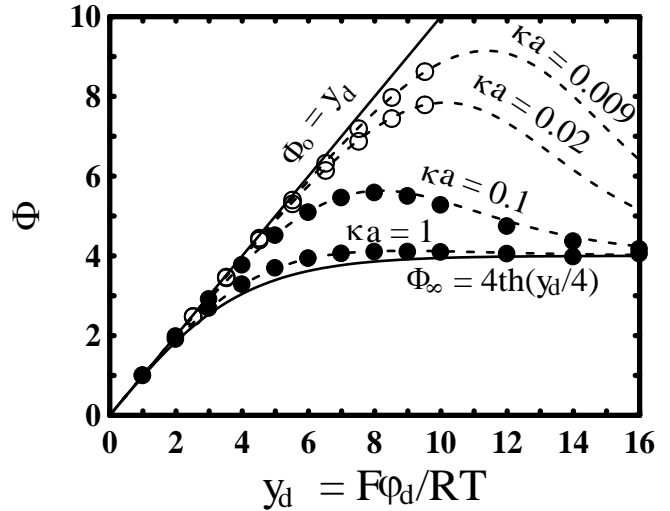

Fig. 1 The function Φ for spherical particle in 1:1 electrolyte. Symbols: numerical calculations from Loeb et al (1961, solid circles) and Zhou and Zhang (2012, open circles). Dashed curves: Eq. (22)

COMBINATION WITH STERN MODEL

In accordance with the Stern model, the head of diffuse layer is separated from the surface by some distance λ (familiarly, it is radius of counter ion), and all above relations are valid for imaginary particle with radius $a + \lambda$.

Thus the charge of diffuse layer, related to the surface area at the head of diffuse layer is defined by:

$$\sigma_d, \mu eq/m^2 = -0.608 \times I^{0.5}\big(Q + \Phi/\kappa(a + \lambda)\big) \tag{24}$$

$$\Phi \approx sng(y_d) \times \big\{(b\kappa(a + \lambda)Q)^2 + 4b\kappa(a + \lambda)|U| + y_d^2\big\}^{0.5} - b\kappa(a + \lambda)Q \tag{25}$$

The equations for Q and U stand the same (Eqs. 2 or 5 or 8 for Q, and 14 or 15 or 18-20 for U). As above, $b = 5/3$. It should be noted that the function U is always positive (or zero at $y_d = 0$). However, at the calculations of ionic sorption, the model bulk solution often deviates from electrical neutrality (e.g., "adsorption of 1 mM Ca from 0.1 M NaCl"), and small errors introduced by this simplification are neglected. At the deviation of the bulk solution from electrical neutrality (even in terms of last digits), the function U may have small negative values. To avoid the failure of calculations (error: square root of negative number), this function should be taken by modulus.

The charge of particle (in Coulombs) is equal by modulus to total charge of diffuse layer. In terms of surface charge, this balance equation may be expressed as

$$\sigma_s = -(1 + \lambda/a)^2 \sigma_d \tag{26}$$

In accordance with the Coulomb's law, the surface potential is related with potential at the head of diffuse layer via relation
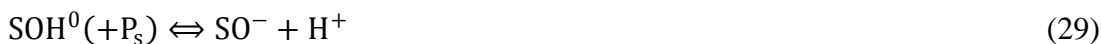
$$\varphi_s = \varphi_d + (\sigma_s/\varepsilon_0\varepsilon) \times \{\lambda a/(\lambda + a)\} = \varphi_d + \sigma_s/C \tag{27}$$

Here C ($C \times m^{-2} \times V^{-1}$ = F/m^2) is electric capacitance, related to the surface of particle. Consequently, the factor $P_s = exp(F\varphi_s/RT)$ is related with P_d as

$$P_s = P_d exp[(F\sigma_s/RT\varepsilon_0\varepsilon) \times \{\lambda a/(\lambda + a)\}] , \text{ or} \tag{28}$$

$$P_s = P_d exp\big[(1/1.85) \times [\sigma_s, \mu eq/m^2] \times [\lambda, Å] \times a/(a + \lambda)\big] \tag{28a}$$

If the surface charge is generated by dissociation of some acidic surface site, it may be simulated by reaction:

$$SOH^0(+P_s) \Longleftrightarrow SO^- + H^+ \tag{29}$$

$$K_a^0 = 10^{-pH} \times [SO^-]/([SOH^0] \times P_s) \tag{30}$$

Traditionally, the factor $P_s^z = exp(zF\varphi_s/RT)$ is considered as an "activity coefficient" of surface species with charge z (in present case, SO^-), and this leads to a willing to follow a common way for calculation of activity coefficients (speciation → activity coefficients → speciation → etc). However, this algorithm is not too convenient, taking into account for huge magnitude of this variable (from zero to infinity). From the other hand, as may be seen from Eq. (29-30), the factor P_s acts as a component of reaction, and thus, it may be calculated on a manner of activity of some component, together with activities of all other species, i.e. within a single iteration cycle. To apply this algorithm, it is necessary to introduce the charge balance equation (if to follow the common way, it is satisfied

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automatically). For this purpose, let us split the total charge of diffuse layer (Eq. 24) into positive and negative branches:

$$\sigma_d = \theta_M - \theta_A \qquad (31)$$

It should be noted that θ_M and θ_A are operational variables. The values θ_M and θ_A should be positive, and they should satisfy the Eq. (31). Variety of functions complies with these conditions. The convenient variant is a following:

$$\theta_M, \mu eq/m^2 = 0.608\{I_{eff}/P_d\}^{0.5} + \{1.85/[a+\lambda, Å]\} \times \{(\Phi^2/4 + 1)^{0.5} - \Phi/2\} \qquad (32)$$
$$\theta_A, \mu eq/m^2 = 0.608\{I_{eff} \times P_d\}^{0.5} + \{1.85/[a+\lambda, Å]\} \times \{(\Phi^2/4 + 1)^{0.5} + \Phi/2\} \qquad (33)$$

Thus, the charge balance equation (see Eq. 26) may be rearranged as

$$[SO^-] + (1+\lambda/a)^2 \times \theta_A = (1+\lambda/a)^2 \times \theta_M \qquad (34)$$

Because θ_M and θ_A are positive variables, Eq (34) may be used similarly to any other balance equation.

APPLICATION

In Fig. 2, the charge of silica surface (data from Bolt, 1957) is shown in comparison with model calculations. The values of $pK_a^o = 7.85$, and radius of counter ion $\lambda = 1.5$ Å were adjusted, the site density was fixed at $TS = 7.56$ $\mu mol/m^2$ (based on surface structure of tridymite, see Iler, 1979). The radius of particles $a = 76$ Å was calculated from:

$$a, Å = 30000 \times [\rho, g/cm^3]^{-1} \times [s, m^2/g]^{-1} \qquad (35)$$

Here $[\rho, g/cm^3]$ is density (assuming $\rho \sim 2.2$ g/cm^3, see Iler, 1979), and $[s, m^2/g]$ is specific surface area ($s = 180$ m^2/g, as measured by Bolt, 1957). For the comparison, the calculations with use of planar model are shown (the same values of model parameters were applied except that the radius of particle was changed to 1 m, whereas the "radius of counter ion" was changed to $\lambda = 1.5 \times 76/77.5 = 1.47$ Å, in order to retain the same value of specific capacitance, see Eq. 27). All curves correspond to a single spherical particle in the infinite volume of solution, and the overlap of diffuse layers is neglected. The effect of dissolution of silica is significant at pH>9.5, and the deviation of model curves from data at pH>9.5 (except the lowest ionic strength) is close to that expected from general chemistry of silica (solubility of amorphous silica ~ 1.7-2.5 mM, and dissociation constant of H_2SiO_3, $pK_a^o \sim 9.8$, see
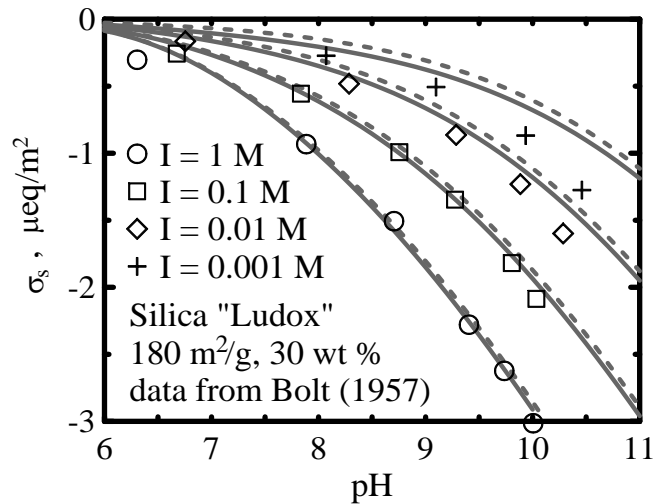

Fig. 2 Surface charge of silica in NaCl solutions. Data from Bolt (1957). Solid curves: Stern model with spherical diffuse layer. Dashed curves: Stern model with planar diffuse layer

Iler, 1979). As may be seen, even for relatively large particles with radius 76 Å, the effect of curvature is not negligible, and the neglecting of curvature leads to overestimation of surface acidity constant by 0.1-0.3 log units.

In Fig. 3, the surface charge of ferrihydrite is shown (data from Pivovarov, 2009). The solid curves were calculated with use of the same model as for silica. To simulate the positive branch of the surface charge, it was assumed that the lattice of ferrihydrite has positive permanent charge $[LCh^+] = 0.5TS$. Thus the surface charge is defined as

$$\sigma_s = [LCh^+] - [SO^-] \quad . \tag{36}$$

Consequently, the charge balance equation (see Eqs. 26 and 34) is defined by

$$[S^-] + (1+\lambda/a)^2 \times \theta_A = [LCh^+] + (1+\lambda/a)^2 \times \theta_M \tag{37}$$

Note that this model is numerically equivalent to 1-pK$_a$ model (SOH$^{0.5+}$ ⇔ SO$^{0.5-}$; see Van Riemsdijk et al., 1986), or model with reaction SOH$_2^+$ ⇔ SOH^o, if permanent lattice charge is equal to minus 0.5TS.

The values $pK_a = 8.05$, $\lambda = 2.4$ Å, $a = 23$ Å, and TS = 10 $\mu mol/m^2$ were adjusted. The equimolar mixture of FeOOH (as goethite) and H_2O has density $(89+18)/(89/4.3 + 18/1) \sim 2.77$ g/cm^3. This value was considered as an estimate for hypothetical solid "Fe(OH)$_3$", and the specific surface area of ferrihydrite, 471 m^2/g Fe(OH)$_3$ (equivalent to 566 m^2/g FeOOH) was calculated from Eq. (35).

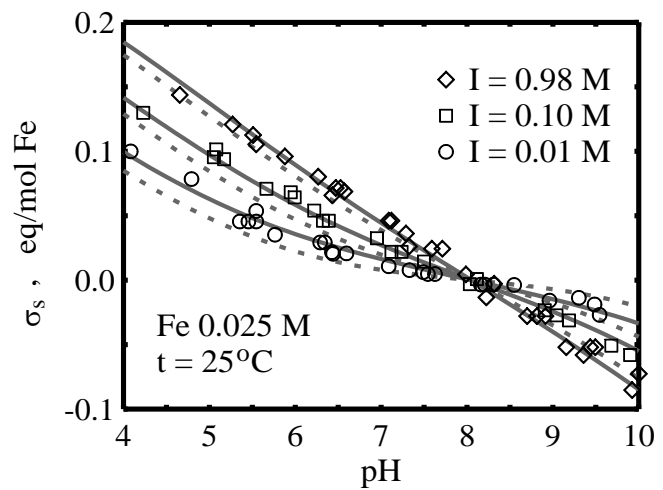The dashed curves in Fig. 3 were calculated with use of planar model of diffuse layer (radius of

Fig. 3 Surface charge of ferrihydrite in NaCl + 0.01 M NaNO$_3$ solutions. Data from Pivovarov (2009). Solid curves: Stern model with spherical diffuse layer. Dashed curves: Stern model with planar diffuse layer

particle was changed to 1 m, and "radius of counter ion" λ was changed to $2\times(23/25.4) = 2.17$ Å, in order to keep the same value of electrical capacitance as for spherical model, see Eq. 27). As may be seen from comparison of model curves, for particles with radius 23 Å, the effect of curvature is large, and can not be simply neglected.

The algorithm of calculations at given pH, $[M^+]$, $[Me^{2+}]$, $[A^-]$, $[An^{2-}]$, K_a^o, particle size a (Å), radius of counter ion λ (Å), site density TS ($\mu mol/m^2$), and positive lattice charge $[LCh^+]$, $\mu eq/m^2$:

Calculate: $I = 0.5\{[M^+] + 4[Me^{2+}] + [A^-] + 4[An^{2-}]\}$; $N = [M^+] + 2[Me^{2+}]$; κ, Å^{-1} = $I^{0.5}/3.04$
Define: $P_s = 1$, $P_d = 1$, $B = 0$, $U_{Me} = 0$, $U_{An} = 0$
Cycle. Calculate:

$\qquad$ $P_d = P_s \times exp(-B)$; $y_d = ln(P_d)$; I_{eff} = (see Eq. 17); Q = (see Eq. 5)
$\qquad$ If $[Me^{2+}] > 0$, U_{Me} = (see Eq. 19)
$\qquad$ If $[An^{2+}] > 0$, U_{An} = (see Eq. 20)
$\qquad$ U = (see Eq. 18)
$\qquad$ Φ = (see Eq. 20); θ_M = (see Eq. 32); θ_A = (see Eq. 33)
$\qquad$ $[SO^-] = K_a^o \times TS \times P_s \times 10^{pH}/(1 + K_a^o \times P_s \times 10^{pH})$
$\qquad$ PLUS = $[LCh^+] + (1 + \lambda/a)^2 \times \theta_M$

$$\text{MINUS} = [SO^-] + (1 + \lambda/a)^2 \times \theta_A$$
$$P_{s1} = P_s \times \text{PLUS/MINUS}$$
$$P_s = (P_{s1} \times P_s)^{0.5}$$

Compare P_s and P_{s1}; if necessary, repeat cycle

Calculate $B_1 = \{1/1.85\} \times \{\lambda a/(\lambda+a)\} \times \{[LCh^+] - [SO^-]\}$
              $B = \{B_1 + 3 \times B\}/4$

Compare B_1 and B; if necessary, repeat cycle

Calculate σ_s , $\mu eq/m^2 = [LCh^+] - [SO^-]$

It should be noted that the constant capacitance term (see Eqs. 27-28) cannot be solved within the single iteration, and this part of the surface potential should be calculated with use of double iteration cycle (as above).

CONCLUDING REMARKS

At the specific surface area more than ~ 200 m²/g, the planar approach becomes inapplicable. However, the correction of the diffuse double layer model on curvature of the interface is not too complex. In arbitrary $(M^+, Me^{2+})(A^-, An^{2-})$ salt medium, and for particles of arbitrary size, it may be performed analytically.

REFERENCES

Bolt GH (1957) Determination of the charge density of silica sols. J Phys Chem 61: 1166-1169.

Loeb AL, Overbeek JThG, Wiersema PH (1961) The electrical double layer around a spherical colloidal particle. MIT Press, Cambridge.

Iler RK (1979) The chemistry of silica, Wiley, New York.

Ohshima H, Healy TW, White LR (1982) Accurate analytic expressions for the surface charge density/surface potential relationship and double-layer potential distribution for a spherical colloidal particle. J Colloid Interface Sci 90: 17-26.

Ohshima H (1995) Surface charge density/surface potential relationship for a spherical colloidal particle in a solution of general electrolytes. J Colloid Interface Sci 171: 525-527.

Pivovarov S (2009) Diffuse sorption modeling. J Colloid Interface Sci 332: 54-59.

Pivovarov S (2010) Diffuse sorption modeling: ionic adsorption on silica. J Colloid Interface Sci 352: 158-162.

Van Riemsdijk WH, Bolt GH, Koopal LK, Blaakmeer J (1986) Electrolyte adsorption on heterogeneous surfaces: adsorption models. J Colloid Interface Sci 109: 219-228.

Zhou S, Zhang G (2012) Approximate analytic solution of the non-linear Poisson-Boltzmann equation for spherical colloidal particle immersed in a general electrolyte solution. Colloid Polym Sci 290: 1511-1526.