

APPROXIMATE CHARGE-POTENTIAL RELATIONSHIP FOR TWO IDENTICAL OVERLAPPED FLAT DIFFUSE LAYERS IN SYMMETRIC ELECTROLYTE

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ABSTRACT

The values of potential in the middle between two identical charged surfaces in symmetric 1:1 electrolyte solution were calculated numerically for round values of scaled potential at interface and scaled distance between charged surfaces. Based on these calculations, approximate charge-potential relationship for the overlapped diffuse layers was deduced. This relationship was then applied to modeling of acid-base properties. Algorithm of calculations is attached.

INTRODUCTION

It is often suspected, that the results of, e.g., pH measurements in suspension are affected by overlap of diffuse layers. For instance, “pH of suspension” often differs from “pH of overlying solution”. However, this is not the evidence for “suspension effect”. The difference may be conditioned by contamination of overlying solution with micro-molar impurities (mostly, atmospheric carbon dioxide, introduced together with electrodes). Another cause is weak responsibility of ion-selective electrodes at $p[\text{Ion}] > 5$. For pH electrodes, the range of doubtful measurements is 5-9. Homogeneous suspension acts as buffer solution, and the measured values of pH, even in the range 5-9, are close to reality. Contrarily, the measurements of pH in CO₂-free water or NaCl solution in the same pH range are often followed by large errors (up to 1 pH units, depending on model of electrode).

It should be noted, that the “suspension effect” is simply potential jump at the surface of precipitate. This potential jump may be detected with use of two reference electrodes: one immersed into precipitate, and second in overlying solution. Contrarily, equilibrium “suspension effect” cannot be detected with use of pair of ion-selective electrodes (pH, or pNa, or pCl, or etc.). In equilibrium state, the potential jump at the surface of precipitate is completely compensated by concentration difference, and pair of identical ion-selective electrodes gives zero response (see Chernoberezhskii, 1982). Because of potential jump at the surface of precipitate, true values of pH, pNa, or etc. may be obtained, if both ion-selective and reference electrodes are immersed into precipitate, or both in overlying solution.

GOUY-CHAPMANN THEORY. Poisson-Boltzmann equation for flat diffuse layer is:

$$d^2\varphi_x/dx^2 = -\rho_x/\varepsilon_0\varepsilon = -(1000F/\varepsilon_0\varepsilon)\sum z_i c_i \exp(-z_i F\varphi_x/RT) \quad (1) \text{ or}$$

$$d^2y_x/dx^2 = - (1000F^2/\varepsilon_0\varepsilon RT)\sum z_i c_i \exp(-z_i y_x) = - (\kappa^2/2I)\sum z_i c_i \exp(-z_i y_x) \quad (1a)$$

Here ϕ_x and ρ_x are potential (V) and charge density (C/m^3) at distance x (meters) from the head of diffuse layer, ϵ_0 is dielectric constant of free space ($8.8542 \times 10^{-12} F/m = C \times V^{-1} \times m^{-1}$), ϵ is dielectric constant of medium (dimensionless; 78.47 for water at $25^\circ C$), z_i is charge of ion “i”, c_i is molar concentration of ion “i” in the bulk solution (moles per liter), F is Faraday constant ($96485 C/mol$), R is gas constant ($8.314 J \times mol^{-1} \times K^{-1}$), T is absolute temperature (K). The variable y is scaled potential:

$$y = F\phi/RT \quad (2)$$

Parameter κ is inversed Debye length:

$$\kappa = (2000F^2/RT\epsilon_0\epsilon)^{0.5} \times I^{0.5} \quad (3) \text{ or}$$

$$1/\kappa, \text{ \AA} = 3.04/I^{0.5} \quad (3a)$$

Parameter I is ionic strength (moles per liter):

$$I = 0.5 \sum z_i^2 c_i \quad (4)$$

Multiplying both sides of Eq. (1a) by $2dy_x$, one may obtain

$$2dy_x \times d\{dy_x/dx\}/dx = d(dy_x/dx)^2 = - \{\kappa^2/I\} \sum z_i c_i \exp(-z_i y_x) dy_x \quad (5)$$

Integration to $y_x = 0$ (at $x = \infty$) gives the following relation:

$$dy_x/dx = - \text{sgn}(y_x) \times \{\kappa/I^{0.5}\} \times [\sum c_i \{\exp(-z_i y_x) - 1\}]^{0.5} \quad (6)$$

Here $\text{sgn}(X)$ is function “sign of X ”, which is -1 at $X < 0$, $+1$ at $X > 0$ and 0 at $X = 0$. Note that sign of (dy_x/dx) is opposite to that of y_x and $(d^2 y_x/dx^2)$.

The surface charge σ_s is related with field strength $E_d = - (d\phi_x/dx)_{x=0}$ in the head of diffuse layer as:

$$\sigma_s = \epsilon_0 \epsilon E_d = - \epsilon_0 \epsilon (d\phi_x/dx)_{x=0} = - \{RT\epsilon_0\epsilon/F\} (dy_x/dx)_{x=0} \quad (7)$$

Combining Eqs. (6) and (7), one may obtain the charge-potential relation for flat interface in the absence of overlap of diffuse layers (Gouy-Chapman equation):

$$\begin{aligned} \sigma_s, C/m^2 &= (2000RT\epsilon_0\epsilon)^{0.5} \times \text{sgn}(y_d) \times [\sum c_i \{\exp(-z_i y_d) - 1\}]^{0.5} = \\ &= 0.0587 \times \text{sgn}(y_d) \times [\sum c_i \{\exp(-z_i y_d) - 1\}]^{0.5} \end{aligned} \quad (8) \text{ or}$$

$$\sigma_s, \mu eq/m^2 = 0.608 \times \text{sgn}(y_d) \times [\sum c_i \{\exp(-z_i y_d) - 1\}]^{0.5} \quad (8a)$$

Here $y_d = F\phi_d/RT$ is scaled potential in the head of diffuse layer ($x = 0$).

For symmetric $z:z$ electrolyte, Eq. (8a) may be reduced to

$$\sigma_s, \mu eq/m^2 = 0.608 \times I^{0.5} \times \{2/z\} \text{sh}(zy_d/2) \quad (9)$$

Here z is valency of symmetric $z:z$ electrolyte, and $\text{sh}(X) = 0.5\{\exp(X) - \exp(-X)\}$ is hyperbolic sinus. In homogeneous suspension, the variable $[y_d - y_m]$ (y_m is potential between particles, i.e., potential of suspension) acts as determining factor. Within the

approach $y_d \equiv y_d - y_m$, maximum error of Eq. (9) in surface charge is 1 % at $\kappa h = 11.9$, and 10 % at $\kappa h = 7.5$, where h is distance between charged surfaces. If, otherwise, the system is determined as equilibrium between suspension and free solution (e.g., between precipitate and overlaying solution), the variable y_d becomes the determining factor. Within the approach $y_{d,h} \equiv y_{d,h=\infty}$, the range of applicability of Eq. (9) is 2-4 times larger: maximum error in surface charge is 1 % at $\kappa h = 5.3$, and 10 % at $\kappa h = 3$, where κh is related to distance between the particles in precipitate. At smaller κh , the error (for both approaches) increases to infinity.

OVERLAP OF DIFFUSE LAYERS: GENERAL. Solution of the Poisson-Boltzmann equation for two identical overlapped diffuse layers is similar (Corkill and Rosenhead, 1939; Verwey, 1940; Verwey and Overbeek, 1948):

$$dy_x/dx = -\text{sgn}(y_x) \times (\kappa/I^{0.5}) \times [\sum c_i \{ \exp(-z_i y_x) - \exp(-z_i y_m) \}]^{0.5} \quad (10)$$

$$\sigma_s, \mu\text{eq}/\text{m}^2 = 0.608 \times \text{sgn}(y_d) \times [\sum c_i \{ \exp(-z_i y_d) - \exp(-z_i y_m) \}]^{0.5} \quad (11)$$

Note here that Eq. (10) is valid for $x = 0 \div h/2$, and it changes sign at $x > h/2$, where h is distance between charged surfaces. The variable $y_m = F\phi_m/RT$ is scaled potential at midplane between two charged surfaces, and $y_d = F\phi_d/RT$, as before, is scaled potential at the head of diffuse layer.

For symmetric z:z electrolyte, Eq. (11) may be reduced to:

$$\sigma_s, \mu\text{eq}/\text{m}^2 = 0.608 \times I^{0.5} \times \text{sgn}(y_d) \times \{1/z\} [2\text{ch}(zy_d) - 2\text{ch}(zy_m)]^{0.5} \quad (12)$$

Here $\text{ch}(X) = 0.5 \{ \exp(X) + \exp(-X) \}$ is hyperbolic cosine.

In accordance with Eq. (10), the potential profile may be found from:

$$\kappa|x - h/2| = I^{0.5} \times \int_{y_m}^{y_x} [\sum c_i \{ \exp(-z_i y) - \exp(-z_i y_m) \}]^{-0.5} dy \quad (13)$$

For $(y_x - y_m) \rightarrow 0$ (at $x \rightarrow h/2$), in symmetric z:z electrolyte, Eq. (13) may be reduced to

$$\kappa|x - h/2| \approx [2z(y_x - y_m)/\text{sh}(zy_m)]^{0.5} \quad (14) \text{ or}$$

$$y_x - y_m \approx \{ \text{sh}(zy_m)/2z \} \times (\kappa x - \kappa h/2)^2 \quad (14a)$$

As may be seen, in vicinity of midplane (at $x \rightarrow h/2$), the potential profile is parabola.

In general case, in accordance with Eqs. (13) and (3a), the distance between charged interface and midplane is defined by

$$h/2, \text{ \AA} = 3.04 \times \int_{y_m}^{y_d} [\sum c_i \{ \exp(-z_i y) - \exp(-z_i y_m) \}]^{-0.5} dy \quad (15)$$

As may be seen, charge-potential relationship for the overlapped diffuse layers may be obtained via iterative solution of Eqs. (11) and (15). However, this is almost inapplicable in the most of cases. Prior to use in some calculations, it is better to perform accurate integration of Eq. (15), and approximate numerical results by some analytical function. The tables of (y_d, y_m, h) relation for 1:1 electrolyte may be found in Verwey and Overbeek (1948; $\kappa h/2 = 0.00434 \div 4.366$, $y_d = 0.5 \div 10$, and $y_m = 0.1 \div 9.9$).

DEBYE-HÜCKEL APPROACH. One may guess that, at small potentials, the potential profile between two charged surfaces is superposition:

$$y_x \sim \text{const} \times \{\exp(-\kappa x) + \exp(-\kappa(h-x))\} \quad (16)$$

The factor “const” in Eq. (16) may be found from equality $y_x = y_d$ at $x=0$:

$$y_x \approx y_d \times \{\exp(-\kappa x) + \exp(-\kappa(h-x))\} / \{1 + \exp(-\kappa h)\} \quad (17)$$

Eq. (17) is exact asymptotic potential-distance relation for the case of small potentials. From Eq. (17), one may obtain relation between h , y_d and y_m , valid for $y_d, y_m \rightarrow 0$, and arbitrary salt medium (Corkill and Rosenhead, 1939):

$$y_d \approx y_m \times \text{ch}(\kappa h/2) \quad (18)$$

Eq. (18) is exact asymptotic relation. From Eq. (12) and (18), applying equality $\text{ch}(X) \sim 1 + X^2/2$ (for small X), one may obtain the following charge-potential relations (also for $y_d, y_m \rightarrow 0$; arbitrary salt medium):

$$\sigma_s, \mu\text{eq}/\text{m}^2 \approx 0.608 \times I^{0.5} \times \text{th}(\kappa h/2) \times y_d \quad (19)$$

$$\sigma_s, \mu\text{eq}/\text{m}^2 \approx 0.608 \times I^{0.5} \times \{1/\text{th}(\kappa h/4)\} \times \{y_d - y_m\} \quad (20)$$

Here $\text{th}(X) = \{\exp(X) - \exp(-X)\} / \{\exp(X) + \exp(-X)\}$ is hyperbolic tangent. Note that Eqs. (19, 20) give exact limiting slope, and thus, any empirical approximation should be consistent with these relations.

ELECTROLYTE-FREE SYSTEMS. Eq. (15) may be integrated analytically for the case of zero ionic strength, if the surface charge is compensated by the only kind of counter ions (Langmuir, 1938; Verwey 1940; Verwey and Overbeek, 1948):

$$\begin{aligned} h/2, \text{ \AA} &= 6.08 \times |1/z_c c_{c,m}^{0.5}| \times \arccos[\exp\{z_c(y_d - y_m)/2\}] = \\ &= 6.08 \times |1/z_c c_{c,m}^{0.5}| \times \text{artg}[(\exp\{-z_c(y_d - y_m)\} - 1)^{0.5}] \end{aligned} \quad (21) \text{ or}$$

$$y_d = y_m + (2/z_c) \ln[\cos\{z_c c_{c,m}^{0.5} [h/2, \text{ \AA}]/6.08\}] \quad (22)$$

Here z_c is charge of counter ion, and $c_{c,m}$ is concentration of counter ion at midplane, $\arccos(X)$ is arc cosine, $\text{artg}(X)$ is arc tangent, and $\cos(X)$ is cosine. Note equality (for $|X| < 1$): $\arccos\{|X|\} = \text{artg}\{(1/X^2 - 1)^{0.5}\}$. Note also that the sign of z_c is always opposite to that of $(y_d - y_m)$, and thus $z_c(y_d - y_m)$ is always negative.

For symmetric $z:z$ electrolyte, Eq. (22) gives approximate equality (note that z is always positive):

$$y_d \approx y_m - \text{sgn}(y_m)(2/z) \ln[\cos\{\exp(z|y_m|/2)\kappa h/4\}] \quad (23)$$

From Eqs. (11) and (21), the charge-potential relation for electrolyte-free system (e.g., suspension plus counter ions with no added salt) is:

$$\begin{aligned} \sigma_s, \mu\text{eq}/\text{m}^2 &= 0.608 \times \text{sgn}(y_d) \times c_{c,m}^{0.5} \{\exp(-z_c(y_d - y_m)) - 1\}^{0.5} = \\ &= -0.608 \times \{6.08/z_c [h/2, \text{ \AA}]\} \times \arccos[\exp\{z_c\{y_d - y_m\}/2\}] \times \{\exp(-z_c(y_d - y_m)) - 1\}^{0.5} = \end{aligned}$$

$$= -0.608 \times \{6.08/z_c[h/2, \text{Å}]\} \times \text{artg}[\{\exp(-z_c\{y_d - y_m\}) - 1\}^{0.5}] \times \{\exp(-z_c(y_d - y_m)) - 1\}^{0.5} \quad (24)$$

Here, as above, z_c is charge of counter ion. Again, note that $z_c(y_d - y_m)$ is always negative and z_c is always opposite to surface charge. For symmetric z:z electrolyte, Eq. (24) gives approximate equality:

$$\begin{aligned} \sigma_s, \mu\text{eq}/\text{m}^2 &\approx \\ &\approx 0.608 \times I^{0.5} \times \text{sgn}(y_d - y_m) \times \{4/\kappa h\} \times \{1/z\} \arccos[\exp(-z|y_d - y_m|/2)] \times \{\exp(z|y_d - y_m|) - 1\}^{0.5} = \\ &= 0.608 \times I^{0.5} \times \text{sgn}(y_d - y_m) \times \{4/\kappa h\} \times \{1/z\} \text{artg}[\{\exp(z|y_d - y_m|) - 1\}^{0.5}] \times \{\exp(z|y_d - y_m|) - 1\}^{0.5} \end{aligned} \quad (25)$$

In the limit $\kappa h \rightarrow 0$, Eq. (25) is exact relation. Maximum error of Eq. (25) is 1 % at $\kappa h = 0.66$, and 10 % at $\kappa h = 2.3$.

SUBJECT OF PRESENT WORK. In present work, Eq. (15) was solved numerically for round values of κh and y_d , which is more convenient for practical needs than the tables given by Verwey and Overbeek (1948). Based on these calculations, the approximate charge-potential relationship for overlapped diffuse layer was deduced. This relationship was then applied to modeling of acid-base properties (algorithm of calculations is attached).

METHODS

Eq. (15) can not be integrated accurately near by $y - y_m = 0$. Thus, first ten steps of integration were approximated by Eq. (14):

$$\begin{aligned} \Delta h_{n=10}, \text{Å} &= 6.08 \times \left| \int_{y_m}^{y_{n=10}} [\sum c_i \{\exp(-z_i y) - \exp(-z_i y_m)\}]^{-0.5} dy \right| \approx \\ &\approx \{6.08/I^{0.5}\} [2z(y_{n=10} - y_m)/\text{sh}(zy_m)]^{0.5} \end{aligned} \quad (26)$$

Here, as above, z is valency of symmetric z:z electrolyte. Other steps of integration were recovered using Simpson (parabolic) method:

$$h, \text{Å} \approx \Delta h_{n=10} + \{1/6\} \sum_{n=11}^n \{f_{n-1} + 4f_{n-0.5} + f_n\} \{y_d - y_m\} / 1000000 \quad (27)$$

$$f_{n-1} = 6.08 \times [\sum c_i \{\exp(-z_i y_{n-1}) - \exp(-z_i y_m)\}]^{-0.5} \quad (28)$$

$$f_{n-0.5} = 6.08 \times [\sum c_i \{\exp(-z_i y_{n-0.5}) - \exp(-z_i y_m)\}]^{-0.5} \quad (29)$$

$$f_n = 6.08 \times [\sum c_i \{\exp(-z_i y_n) - \exp(-z_i y_m)\}]^{-0.5} \quad (30)$$

$$y_{n-1} = y_m + (n-1) \times (y_d - y_m) / 1000000 \quad (31)$$

$$y_{n-0.5} = y_m + (n-0.5) \times (y_d - y_m) / 1000000 \quad (32)$$

$$y_n = y_m + n \times (y_d - y_m) / 1000000 \quad (33)$$

To estimate accuracy, integration was also performed in accordance with rectangle method:

$$h, \text{ \AA} \approx \Delta h_{n=10} + \frac{\sum_{n=0.5}^{n=10.5} f_n \times (y_d - y_m)}{1000000} \quad (34)$$

The difference between parabolic and rectangle methods was considered as a round estimate for accuracy of integration. In all calculations, double accuracy (16 digits) was applied.

RESULTS

The results of numerical integration of Eq. (15) for “NaCl” solution are presented in **Tab. 1**, and **Fig. 1**. In general, results of integration by rectangle and parabolic methods coincide within 6-10 digits, and the data in **Tab. 1** are probably exact within the last digit. Limiting slope of all curves in **Fig. 1** is defined by Eq. (18). At high y_d , the midplane potential y_m approaches to plateau. This behavior is consistent with approximation (see also Eq. 18):

$$y_m \approx (4/z) \text{th}(zy_d/4) / \text{ch}(\kappa h/2) \quad (35)$$

Eq. (35) is roundly applicable for symmetric z:z electrolytes down to $\kappa h = 1$ (see solid curves in **Fig. 1**). Down to $\kappa h = 1$, maximum error in surface charge in accordance with Eqs. (35) and (12) is 2.9 %. At smaller κh , error in surface charge (with use of Eqs. 35 and 12) increases to infinity. In the limit $\kappa h \rightarrow \infty$, Eq (35) is exact relation.

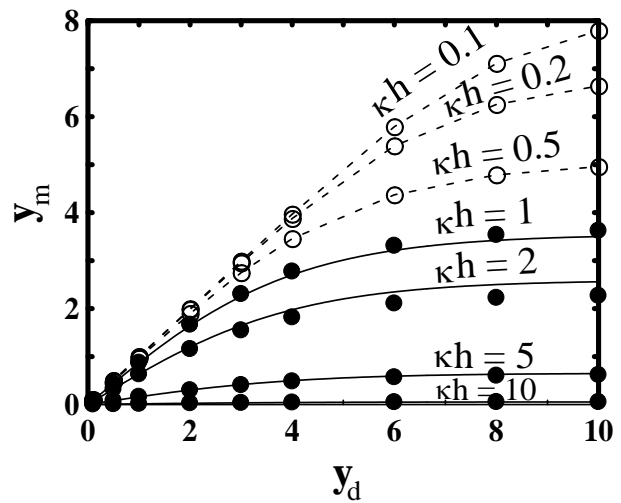


Fig. 1. Dependence of y_m (scaled midplane potential) on y_d (scaled potential in the head of diffuse layer) at round κh (scaled distance between charged surfaces) for symmetric 1:1 electrolyte. Down to $\kappa h = 1$ (solid symbols), data are consistent with Eq. (35, solid curves). For $\kappa h < 1$ (open symbols, connected with dashes for guidance), Eq. (35) fails.

Tab. 1. Results of numerical integration of Eq. (15) for 1:1 electrolyte.

y_d	y_m						
	$\kappa h = 0.1$	$\kappa h = 0.2$	$\kappa h = 0.5$	$\kappa h = 1$	$\kappa h = 2$	$\kappa h = 5$	$\kappa h = 10$
0.1	0.099875	0.099501	0.096950	0.088668	0.064785	0.016303	0.001347
0.5	0.499349	0.497407	0.484179	0.441656	0.321460	0.081043	0.006703
1	0.998533	0.994161	0.964679	0.872787	0.628213	0.159221	0.013201
2	1.995484	1.982144	1.896399	1.662575	1.156080	0.297967	0.024904
3	2.987607	2.951889	2.746788	2.302804	1.546654	0.405698	0.034224
4	3.966818	3.876862	3.457329	2.772817	1.815158	0.482539	0.041031
6	5.788567	5.391881	4.371228	3.309323	2.106434	0.567758	0.048756
8	7.110619	6.253520	4.786867	3.534510	2.223359	0.602101	0.051923
10	7.795446	6.640393	4.956961	3.622906	2.268069	0.615184	0.053138

CHARGE-POTENTIAL RELATIONSHIP

In the most of cases, pH is measured in homogeneous suspension, because the buffer capacity of particles leads to stabilization of the electrode response. Thus, the variable $[y_d-y_m]$ acts as determining factor. So on, for practical needs, the charge- $[y_d-y_m]$ relation is most relevant.

Combining exact asymptotic relations for $\kappa h \rightarrow \infty$ and $\kappa h \rightarrow 0$, Eqs. (9) and (25), and taking into account for limiting slope, as defined by Eq. (20), one may obtain the following approximation, valid for symmetric z:z electrolytes:

$$\sigma_s, \mu\text{eq/m}^2 \approx 0.608 \times I^{0.5} \times \left\{ \text{th}(\kappa h/4) \right\} \times \left\{ 2/z \right\} \times \text{sh}(z(y_d-y_m)/2) + \\ + \text{sgn}(y_d-y_m) \times \left\{ 2/\text{sh}(\kappa h/2) \right\} \times \left\{ 1/z \right\} \text{artg} \left[\left\{ \exp(z|y_d-y_m|)-1 \right\}^{0.5} \right] \left\{ \exp(z|y_d-y_m|)-1 \right\}^{0.5} \right\} \quad (36)$$

Note that $2/\text{sh}(\kappa h/2) = 1/\text{th}(\kappa h/4) - \text{th}(\kappa h/4)$ and thus, the limiting slope of Eq. (36) coincides with that of Eq. (20). In both limits, $\kappa h \rightarrow \infty$ and $\kappa h \rightarrow 0$, Eq. (36) is exact relation. Maximum error of Eq. (36) in surface charge is 3.6 %.

EXTENSION TO STERN MODEL

Within the Stern approach, the head of diffuse layer is separated from the surface by some distance λ (familiarily, it is radius of counter ion), and all above relations are valid for $h_{\text{corr}} = h - 2\lambda$. Thus Eq. (36) should be rewritten as:

$$\sigma_s, \mu\text{eq/m}^2 \approx 0.608 \times I^{0.5} \times \left\{ \text{th}(\kappa(h-2\lambda)/4) \right\} \times \left\{ 2/z \right\} \times \text{sh}(z(y_d-y_m)/2) + \\ + \text{sgn}(y_d-y_m) \left\{ 2/\text{sh}(\kappa(h-2\lambda)/2) \right\} \left\{ 1/z \right\} \text{artg} \left[\left\{ \exp(z|y_d-y_m|)-1 \right\}^{0.5} \right] \left\{ \exp(z|y_d-y_m|)-1 \right\}^{0.5} \right\} \quad (37)$$

In accordance with the Coulomb's law, the surface potential is related with potential at the head of diffuse layer via relation

$$\varphi_s = \varphi_d + \left\{ \sigma_s / \varepsilon_0 \varepsilon \right\} \times \lambda = \varphi_d + \sigma_s / C \quad (38)$$

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

$$P_s = P_d \exp \left[\left\{ F\sigma_s / RT\varepsilon_0\varepsilon \right\} \times \lambda \right] \quad (39) \text{ or}$$

$$P_s = P_d \exp \left\{ 0.541 \times [\sigma_s, \mu\text{eq/m}^2] \times [\lambda, \text{\AA}] \right\} \quad (39a)$$

Note that Coulomb's law factor 0.541 is related with Gouy-Chapman constant exactly as $0.541 = 0.2/0.608^2$.

MASS ACTION LAW AND BALANCE EQUATIONS

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



$$K_a^0 = 10^{-\text{pH}}[\text{SO}^-]/([\text{SOH}^0]P_s) \quad (41)$$

To introduce charge balance equation, let us split the total charge of diffuse layer into positive and negative branches:

$$\sigma_s = - \{ \sigma_M - \sigma_A \} \quad (42)$$

$$\sigma_M = \{ (\sigma_s^2/4 + 1)^{0.5} - \sigma_s/2 \} \quad (43)$$

$$\sigma_A = \{ (\sigma_s^2/4 + 1)^{0.5} + \sigma_s/2 \} \quad (44)$$

Here σ_M and σ_A are positive variables, corresponding to excess values of cations (M) and anions (A) near the surface. Note also that the total charge of diffuse layer is opposite to surface charge. With use of these variables, the charge balance equation may be written as

$$[\text{SO}^-] + \sigma_A = \sigma_M \quad (45)$$

Note that the variables σ_M and σ_A are always positive, and Eq (45) may be treated similarly to any other mass balance equation.

APPLICATION

In **Fig. 2**, the surface charge of silica is shown, as measured by Bolt (1957). Solid curves were calculated with accounting for overlap of diffuse layer. Dashed curves were calculated neglecting suspension effect. As may be seen, even at so high surface load ($180 \text{ m}^2/\text{g} \times 429 \text{ g/L} = 77220 \text{ m}^2/\text{L}$), the “suspension effect” is negligible down to $I = 0.01 \text{ M}$. It should be also noted that theoretical curves for $I = 0.001 \text{ M}$ and less coincide each other. In addition, geometry of space between the particles is rather different from space between two parallel planes. Thus, the present model gives just rough description. To estimate distance between particles, the following obvious relation was used

$$[h, \text{Å}] = 2 \times 10^7 / \{ [\text{SL}, \text{g/L}] \times [\text{S}, \text{m}^2/\text{g}] \} \quad (46)$$

Here $[\text{SL}, \text{g/L}]$ is solid load ($30 \text{ wt \%} = 429 \text{ g/L}$), and $[\text{S}, \text{m}^2/\text{g}]$ is specific surface area ($S = 180 \text{ m}^2/\text{g}$, as measured by Bolt, 1957). Thus, average distance between particles was $h = 259 \text{ Å}$.

The algorithm of calculations of surface charge in **Fig. 2** at given pH, constant of deprotonation ($\text{p}K_a^0 = 7.75$), site density of the silica surface ($\text{TS} = 7.5 \text{ } \mu\text{mol}/\text{m}^2$), ionic strength (I, M ; 1:1 electrolyte), radius of counter ion ($[\lambda, \text{Å}] = 1.5$), solid load ($[\text{SL}, \text{g/L}] = 429$), specific surface area ($[\text{S}, \text{m}^2/\text{g}] = 180$):

- Apply: $P_{s-m} = 1, P_{d-m} = 1, B = 0, \alpha = 1$

- Calculate:

$$[h, \text{Å}] = 2 \times 10^7 / \{ [\text{SL}, \text{g/L}] \times [\text{S}, \text{m}^2/\text{g}] \}$$

$$\kappa d = \{ I^{0.5} / 3.04 \} \times \{ [h, \text{Å}] - 2[\lambda, \text{Å}] \}$$

$$\text{if } \kappa d < 60 \text{ then } \alpha = \{ \exp(\kappa d/4) - \exp(-\kappa d/4) \} / \{ \exp(\kappa d/4) + \exp(-\kappa d/4) \}$$

- Cycle. Calculate:

$$P_{d-m} = P_{s-m} \times \exp(-B)$$

$$y_{d-m} = \ln(P_{d-m})$$

$$\sigma_s = 0.608 \times I^{0.5} \times \alpha \times (P_{d-m}^{0.5} - 1/P_{d-m}^{0.5}) + 0.608 \times I^{0.5} \times \{1/\alpha - \alpha\} \times \text{sgn}(y_{d-m}) \times \text{artg}[\{\exp(|y_{d-m}|-1)\}^{0.5}] \times \{\exp(|y_{d-m}|-1)\}^{0.5}$$

$$\sigma_M = \{(\sigma_s^2/4 + 1)^{0.5} - \sigma_s/2\}$$

$$\sigma_A = \{(\sigma_s^2/4 + 1)^{0.5} + \sigma_s/2\}$$

$$[SO^-] = TS \times 10^{(pH - pK_a^0)} \times P_{s-m} / (1 + 10^{(pH - pK_a^0)} \times P_{s-m})$$

$$PLUS = \sigma_M$$

$$MINUS = [SO^-] + \sigma_A$$

$$P1_{s-m} = P_{s-m} \times (PLUS/MINUS)$$

$$P_{s-m} = (P_{s-m} \times P1_{s-m})^{0.5}$$

- Compare P_{s-m} and $P1_{s-m}$; if necessary, repeat cycle
- Calculate
 - $B1 = 0.541 \times [\lambda, \text{Å}] \times \{-[SO^-]\}$
 - $B = (3 \times B + B1)/4$
- Compare B1 and B; if necessary, repeat cycle
- Calculate: [Surface charge, $\mu\text{eq}/\text{m}^2$] = - [SO⁻]

Here variable $P_{d-m} = \exp(y_{d-m})$, $y_{d-m} = y_d - y_m$, $P_{s-m} = \exp(y_{s-m})$, and $y_{s-m} = y_s - y_m$.

In **Fig. 3**, the values of midplane potential are shown as function of surface charge, ionic strength, and solid load (sign of midplane potential coincides with that of surface charge). These values were calculated iteratively via simultaneous solution of Eqs (12) and (36), but with $h_{\text{corr}} = h - 2\lambda$ instead of h . As may be seen, at the ionic strength more than 0.01 M, or surface load less than 30 000 m^2/L , the “suspension effect” is negligible. At $|\sigma| > \sim 0.2 \mu\text{eq}/\text{m}^2$, the “suspension effect” is almost independent of surface charge. Practically, the effect of overlap (“suspension effect”) is less than 1 log unit (59 mV) at $\kappa h = 2$ and less than 0.1 log unit (6 mV) at $\kappa h = 7$. At the ionic strengths 0.1, 0.01 and 0.001 mole/L, it is less than 0.1 log unit at surface load less than 300 000, 94 000, and 30 000 m^2/L , correspondingly.

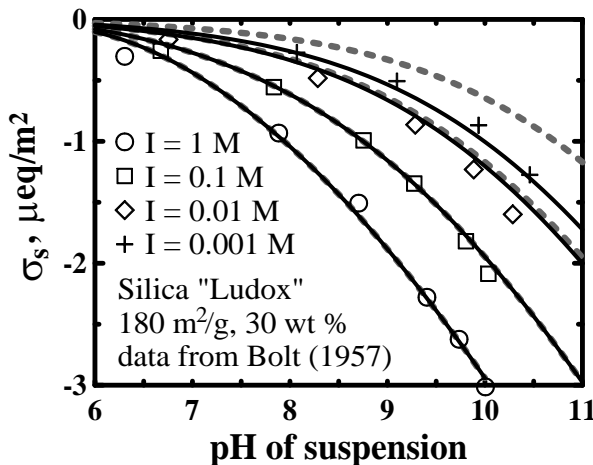


Fig. 2. Surface charge of silica in NaCl solutions. Data from Bolt (1957). Solid curves: Stern model with correction on overlap of diffuse layers. Dashed curves: Stern model without overlap of diffuse layers.

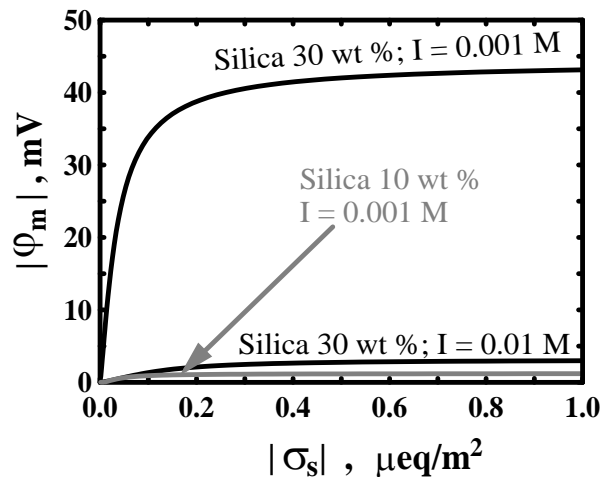


Fig. 3. Calculated “suspension effect” ($\phi_m, \text{mV} = 25.7 \times y_m$) for 30 wt % (429 g/L) suspension of amorphous silica ($S = 180 \text{ m}^2/\text{g}$) at 0.001 and 0.01 M ionic strength (black curves). And for 10 wt % (111 g/L) suspension at 0.001 M ionic strength (grey curve).

CONCLUDING REMARKS

In the most of laboratory cases, the “suspension effect” is negligible. However, the “suspension effect” may be significant, e.g., for compact clays. For instance, the compact clays should be more selective for polyvalent metal ions than the same clay in dilute suspension (in both cases, with respect to withdrawn solutions).

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