

THEORY OF ELECTROPHORESIS AND INTRODUCTION TO PHANTOM MODELING OF SPECIFIC ADSORPTION

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ABSTRACT

Published electrophoretic data are consistent with semi-empirical relation (for symmetric z:z electrolyte):

$$U_{\text{eph}}, \text{ m}^2/\text{Vs} = \{4/\alpha\} \times \{\varepsilon_0 \varepsilon / \eta_0\} \times \{4RT/zF\} \times \tanh(zF\varphi_s/4RT)$$

Here U_{eph} is electrophoretic mobility of charged particle (m/s per V/m), α is Stokes constant ($\alpha \sim 4$ for oil droplet, $\alpha \sim 6$ for silica particles, $\alpha \sim 10-12$ for ferric (hydr)oxides), $\varepsilon_0 = 8.8542 \times 10^{-12}$ C/Vm is dielectric constant of free space, ε is relative dielectric constant of water (78.47 at 25°C), η_0 is viscosity of water (0.0008902 Pa×s at 25°C), $R = 8.3144 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1}$ is gas constant, T is absolute temperature (Kelvins), $F = 96485 \text{ C/mol}$ is Faraday constant, φ_s is surface potential (Volts), defined by diffuse layer charge-potential relation.

INTRODUCTION TO PHANTOM MODELING OF SPECIFIC SORPTION

Charge-potential relationship for spherical particle is defined by Loeb-Overbeek-Wiersema equation (Loeb et al., 1961). For symmetric z:z electrolyte, it is:

$$\sigma, \text{ C/m}^2 = (2000RT\varepsilon_0\varepsilon)^{0.5} \times c^{0.5} \times 2 \times \sinh(zy_s/2) + (RT\varepsilon_0\varepsilon/Fr) \times (4/z) \times \tanh(zy_s/4) \quad (1) \text{ or}$$

$$\sigma, \mu\text{eq/m}^2 = 0.608 \times c^{0.5} \times \{\exp(zy_s/2) - \exp(-zy_s/2)\} + \{1.85/[r, \text{Å}]\} \times (4/z) \times \{\exp(zy_s/4) - \exp(-zy_s/4)\} / \{\exp(zy_s/4) + \exp(-zy_s/4)\} \quad (1a)$$

Here $R = 8.3144 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1}$ is gas constant, T is absolute temperature (Kelvins), $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C} \times \text{V}^{-1} \times \text{m}^{-1}$ is dielectric constant of free space, ε is relative permeability of substance (78.47 for water at 25°C), c is molar concentration of electrolyte (moles per liter), $F = 96485 \text{ C/mol}$ is Faraday constant, $\tanh(X) = \{\exp(X) - \exp(-X)\} / \{\exp(X) + \exp(-X)\}$ is hyperbolic tangent, r is radius of particle, and y_s is scaled surface potential:

$$y_s = F\varphi_s/RT \quad (2)$$

Here φ_s is surface potential (Volts). The first term in Eq (1) is Gouy-Chapman equation for flat interface, and last term is correction on curvature of spherical particle. Radius of spherical particle is may be estimated from:

$$r, \text{ Å} = 30000 / \{[S, \text{ m}^2/\text{g}][\rho, \text{ g/cm}^3]\} \quad (3)$$

Here S is specific surface area, and ρ is specific density of solid. Eq. (3) is valid also for cubic particles with side length $2r$.

The Loeb-Overbeek-Wiersema equation is almost exact relation for spherical charged particle with radius larger than Debye length, κ^{-1} Å:

$$r, \text{ \AA} > 1/\kappa = 3.04/I^{0.5} \quad (\text{at } 25^\circ\text{C}) \quad (4)$$

Here I is molar ionic strength of solution:

$$I = 0.5 \times \sum z^2 [\text{Ion}^z] \quad (5)$$

Here $[\text{Ion}^z]$ is molar concentration of ion with charge z in solution.

Surface charge of silica particles may be modeled with use of surface reaction:



Eq. (6) gives equalities:

$$[\equiv\text{SiO}^-] = [\equiv\text{SiOH}^0] \times K_{\text{SiO}} \times P_s \times 10^{\text{pH}} \quad (7)$$

$$\text{TS} = [\equiv\text{SiOH}^0] + [\equiv\text{SiO}^-] \quad (8)$$

Here $\text{TS} = 7.56 \mu\text{mol}/\text{m}^2$ is site density of silica surface (Iler, 1979), and P_s is “potential function”:

$$P_s = \exp(y_s) = \exp(F\phi_s/RT) \quad (9)$$

Surface charge, arising due to formation negatively charged surface species $\equiv\text{SiO}^-$, should be balanced by charge of diffuse layer. For convenience, Loeb-Overbeek-Wiersema equation may be rearranged as (25°C and 1:1 electrolyte):

$$[\text{D}^-], \mu\text{mol}/\text{m}^2 = 0.608 \times \{c \times P_s\}^{0.5} + \{7.4/[r, \text{ \AA}]\} / \{1 + 1/P_s^{0.5}\} \quad (10)$$

$$[\text{D}^+], \mu\text{mol}/\text{m}^2 = 0.608 \times \{c/P_s\}^{0.5} + \{7.4/[r, \text{ \AA}]\} / \{1 + P_s^{0.5}\} \quad (11)$$

$$[\equiv\text{SiO}^-] + [\text{D}^-] = [\text{D}^+] \quad (12)$$

Eqs (7-12) may be easily solved with use of iterative relations:

$$[\equiv\text{SiOH}^0]_{\text{next approach}} = [\equiv\text{SiOH}^0] \times \text{TS} / ([\equiv\text{SiOH}^0] + [\equiv\text{SiO}^-]) \quad (13)$$

$$P_{s, \text{ next approach}} = P_s \times \{[\text{D}^+] / ([\equiv\text{SiO}^-] + [\text{D}^-])\}^{1/(1+a)} \quad (14)$$

Here a is “delay factor” (optimum value, $a = 3$).

In Fig. 1a, Eqs. (7-12) with best fit constant $K_{\text{SiO}} = 10^{-8.4}$ are compared with experimental measurements of surface charge of amorphous silica (Bolt, 1957). Radius of particles, $r = 76 \text{ \AA}$, was estimated from Eq. (3), with use of measured surface area $S = 180 \text{ m}^2/\text{g}$ (Bolt, 1957) and density of particles, $2.2 \text{ g}/\text{cm}^3$ (Iler, 1979). As may be seen, consistence of this approach with data is very weak. Significant improvement may be obtained with use of Stern approach. In accordance with Stern model, diffuse layer is separated from interface by “charge-free” layer, which gives correction to surface potential. As may be estimated from modeling of surface charge curves, thickness of “charge-free” layer is about 2-3 Å, which is comparable with radii of ions. However, due to numerous contradictions with observations, to date, Stern approach is

upgraded to variety of “multilayer” Surface Complexation models. Besides, as it was recently found from modeling of Ca/Na ionic exchange in compact clays (with average separation between charged particles down to 7 Å), thickness of “charge free” layer is zero. And thus, it is likely, that the Gouy-Chapman theory of diffuse layer gives true estimates for surface potential at flat interface, whereas Stern model is just approximation of some unknown phenomenon (Pivovarov, 2017).

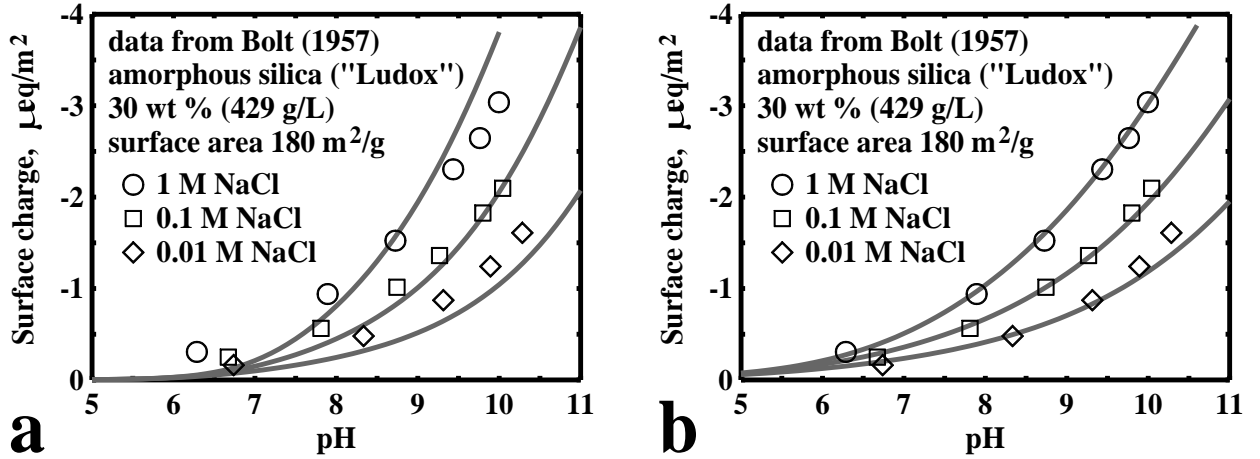


Fig. 1 Surface charge of amorphous silica in NaCl solutions (Bolt, 1957). Solid curves (a): Eqs (7-12) with $K_{SO} = 10^{-8.4}$, and (b): Eqs. (8-12, 15) with $K_{SO} = 10^{-8.95}$.

In Fig. 1b, data were modeled with use of Eqs (8-12) and, instead of Eq (7), with use of semi-empirical “phantom model”:

$$[\equiv\text{SiO}^-] = [\equiv\text{SiOH}^0] \times \{K_{\text{SiO}} \times P_s \times 10^{\text{pH}}\}^{0.5} \quad (15)$$

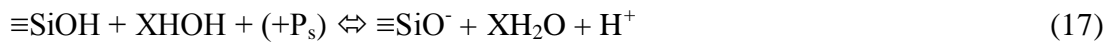
The value of surface acidity constant was adjusted to $K_{\text{SiO}} = 10^{-8.95}$. Similarly to model curves in Fig. (1a), radius of particles $r = 76 \text{ \AA}$, and site density $\text{TS} = 7.56 \text{ } \mu\text{mol}/\text{m}^2$ were used.

Eq. (15) corresponds to “quasi-reaction”:



Generally speaking, Eq. (16) seems to be senseless. However, taking into account for the absence of adjusting parameters (apart from K_{SiO}), close correlation of Eq. (15) with data should mean something.

Various hypotheses may be generated from Eq. (15). First, Eq. (16) may be rearranged into more relevant reaction:



Here XHOH is “phantom” of neutral site, and XH_2O is “phantom” of negative surface species.

Second hypothesis may be guessed from ionic adsorption in diffuse layer. Indeed, Gouy-Chapman equation for flat interface in NaCl solution (see first term in Eq. 1) may be rearranged to:

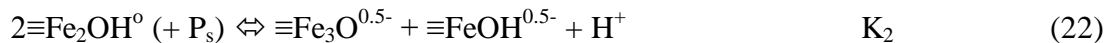
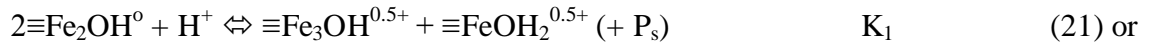
$$[\text{DCI}^-], \text{ } \mu\text{mol}/\text{m}^2 = 0.608 \times \{[\text{Cl}^-] \times P_s\}^{0.5} \quad (18)$$

$$[\text{DNa}^+], \text{ } \mu\text{mol}/\text{m}^2 = 0.608 \times \{[\text{Na}^+] / P_s\}^{0.5} \quad (19)$$

$$\sigma_s, \text{ } \mu\text{eq}/\text{m}^2 = [\text{DCI}^-] - [\text{DNa}^+] \quad (20)$$

As may be seen, theoretical Eqs (18, 19) are closely similar to empirical Eq. (15). Thus, one may guess that the surface charge is diffusely distributed within the subsurface layer of solid, similarly to counter-ions in aqueous diffuse layer (see Pivovarov, 2009). Indeed, as known from electrochemistry, total interfacial potential is Nernstian one, and evolution from surface potential (at interface) to Nernstian potential (inside of, e.g., metallic electrode) cannot be explained without existence of free charge density inside of subsurface layer of solid. Thus, ultimately, “internal diffuse layer” must exist.

Third, one may suggest, that the specific adsorption causes reconstruction of interface. For instance, surface charge of hydrous ferric oxide may be successfully modeled with use of Loeb-Overbeek-Wiersema equation (Eq. 1) and MUSIC model (Hiemstra et al, 1989ab), assuming reactions:



Here $\equiv\text{Fe}_2\text{OH}^0$ is doubly coordinated hydroxide (element $\text{Fe}^{0.5+}$ is 1/6 of 6-coordinated lattice ion Fe^{3+}), $\equiv\text{FeOH}_2^{0.5+}$ is proton, adsorbed by singly coordinated hydroxide, $\equiv\text{Fe}_3\text{OH}^{0.5+}$ is triply coordinated hydroxide (“phantom” of adsorbed proton), etc. Solid curves in Fig. 2 were calculated, assuming surface area $499 \text{ m}^2/\text{g Fe}(\text{OH})_3 = 600 \text{ m}^2/\text{g FeOOH}$ (Dzombak and Morel, 1990). Acidity constants, $K_1 = 10^{6.3}$, $K_2 = 10^{9.9}$, radius of particles 20 \AA , and site density $7.6 \text{ }\mu\text{mol}/\text{m}^2$ were adjusted.

So on, it is possible, that the “phantom model” reflects some reality. Independently on its reliability, it gives close approximation for surface charge, and thus, gives true estimates for surface potential, and this gives possibility for accurate modeling of electroforesis.

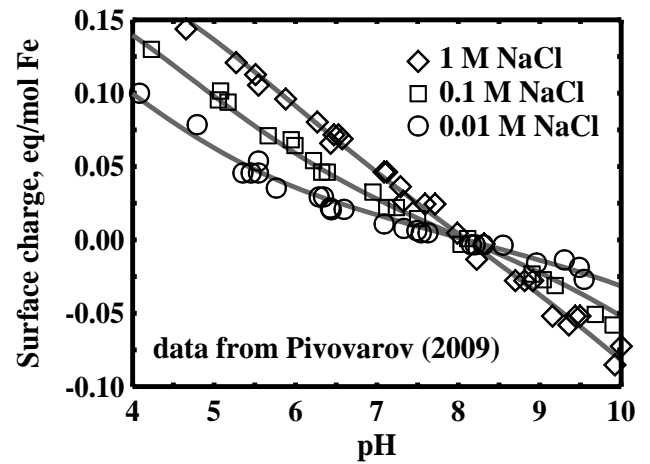


Fig. 2 Surface charge of ferrihydrite. Curves: “phantom model” with surface area $600 \text{ m}^2/\text{g FeOOH}$, acidity constants $K_1 = 10^{6.3}$, $K_2 = 10^{9.9}$ (see Eqs 21, 22), site density $7.6 \text{ }\mu\text{mol}/\text{m}^2$, and radius of particles 20 \AA .

THEORY OF ELECTROPHORESIS

Under applied electric field, E ($\text{V}/\text{m} = \text{N}/\text{C}$), charged particle in water moves with velocity v (m/s). Resulting conventional electrophoretic mobility of particle, U_{eph} (m^2/Vs), is:

$$U_{\text{eph}} = -v/E \quad (23)$$

Sign “minus” reflects very old tradition, in which sign of conventional electrophoretic mobility always coincides with sign of charge of particle (~~due to the same “very old tradition”, pole of battery, charged by free electrons, always marked by sign “+”~~ : error, sorry, all is o’k with battery, \oplus is plus, \ominus is minus : author, 4.10.2019).

In accordance with Stokes law, friction force for spherical particle is:

$$f_{fr} = -\alpha \times \pi \times \eta_0 \times (vr) \quad (24)$$

Here α is Stokes constant ($\alpha = 4$ for hydrophobic particles, and $\alpha = 6$ for hydrophilic particles), $\pi = 3.14159265441\dots$, η_0 is viscosity of medium (0.0008902 Pa×s for water at 25°C), r is radius of particle. Sign minus denotes here that the friction force is directed against velocity of particle.

The electric force, applied to charged particle is:

$$f_{el} = -q \times E \quad (25)$$

Sign minus means that negatively charged particle moves in direction of rising potential, i.e., toward the positively charged electrode. Thus, from equality $f_{fr} + f_{el} = 0$, one may calculate conventional electrophoretic mobility of charged particle:

$$U_{eph} = q / \alpha \pi \eta_0 r \quad (26)$$

With elementary charge, $e = 1.6022 \times 10^{-19}$ C, and $\alpha = 6$, conventional electrophoretic mobility of “hydrophilic ion” at 25°C is:

$$U_{eph}, m^2/Vs = 9.548e-8 \times z / [r, \text{Å}] \quad (27)$$

Note here that, in reality, Cl^- moves toward positively charged electrode, and sign of velocity of Cl^- always coincides with sign of $E = d\phi/dL$. Because of this, “common sense” electrophoretic mobility of charged particle is always opposite to Eq. (26). Conventional electrophoretic mobilities of sodium and chloride ions in water at 25°C are: 5.19×10^{-8} m²/Vs for Na^+ , and -7.91×10^{-8} m²/Vs for Cl^- (see Erdey-Grúz, 1974). From Eq. (27), one may calculate “Stokes ionic radii”: $r_{Na} = 1.84$ Å, $r_{Cl} = 1.21$ Å. Sum of these values (3.05 Å) is comparable with Na-Cl distance in NaCl crystal (2.82 Å). Thus, Eq. (26) is roundly applicable for small charged particles.

Charge of spherical particle is related with its surface charge as:

$$q = 4\pi r^2 \times \sigma \quad (28)$$

Thus, conventional electrophoretic mobility of small charged particle in water is:

$$U_{eph} = \{4/\alpha\} \times \sigma \times r / \eta_0 \quad (29)$$

Applying Coulomb’s law, one may estimate surface potential of small charged particle:

$$\varphi_s, V = (1/4\pi\epsilon_0\epsilon)q/r = \sigma \times r / \epsilon_0\epsilon \quad (30)$$

Here $\epsilon_0 = 8.8542 \times 10^{-12}$ C×V⁻¹×m⁻¹ is dielectric constant of free space, ϵ is relative permeability of substance (78.47 for water at 25°C). Substitution of Eq (30) into Eq (29) gives relation:

$$U_{eph} = \{4/\alpha\} \times \{\epsilon_0\epsilon/\eta_0\} \times \varphi_s \quad (31)$$

Generally speaking, Eq (31) is weakly applicable. To obtain “exact” relation, one may introduce “apparent surface potential”, so-called “zeta potential”, ζ . With use of this variable, and applying Stokes constant $\alpha = 6$, one may obtain Hückel equation for electrophoretic mobility of charged hydrophilic particles:

$$U_{\text{eph}} = \{4/6\} \times \{\epsilon_o \epsilon / \eta_o\} \times \zeta_{\text{Hü}} \quad (32) \text{ or}$$

$$U_{\text{eph}, \text{ m}^2 \times \text{V}^{-1} \times \text{s}^{-1}} = 0.05203 \times 10^{-8} \times [\zeta_{\text{Hü}}, \text{ mV}] \quad (\text{at } 25^\circ\text{C}) \quad (32a)$$

Here $\zeta_{\text{Hü}}$ is “Hückel zeta potential”.

Most popular relation is Smoluchowski electrophoretic equation, which is equivalent to Hückel equation for hydrophobic particles (i.e., Eq. 31 with $\alpha = 4$):

$$U_{\text{eph}} = \{\epsilon_o \epsilon / \eta_o\} \times \zeta_{\text{Sm}} \quad (33) \text{ or}$$

$$U_{\text{eph}, \text{ m}^2 \times \text{V}^{-1} \times \text{s}^{-1}} = 0.07805 \times 10^{-8} \times [\zeta_{\text{Sm}}, \text{ mV}] \quad (\text{at } 25^\circ\text{C}) \quad (33a)$$

Here ζ_{Sm} is “Smoluchowski zeta potential”.

Generally speaking, Coulomb’s law (see Eq. 30) is weakly applicable for spherical charged particles in aqueous solution. Much closer relation is given by Loeb-Overbeek-Wiersema equation (Eq. 1). At low salt concentration, Eq (1) may be reduced to:

$$\sigma, \text{ C/m}^2 = (RT\epsilon_o\epsilon/\text{Fr}) \times (4/z) \times \tanh(zF\phi_s/4RT) \quad (34)$$

Substitution of Eq. (34) into Eq. (29) gives electrophoretic mobility of spherical charged particle in diluted symmetric z:z electrolyte:

$$U_{\text{eph}} = (4/\alpha) \times (\epsilon_o \epsilon / \eta_o) \times \{4RT/zF\} \times \tanh(zF\phi_s/4RT) \quad (35) \text{ or}$$

$$U_{\text{eph}, \text{ m}^2/\text{Vs}} = 5.347 \times 10^{-8} \times (1/z) \times \tanh(zy_s/4) \quad (\text{for hydrophilic particles at } 25^\circ\text{C}) \quad (35a) \text{ or}$$

$$U_{\text{eph}, \text{ m}^2/\text{Vs}} = 8.201 \times 10^{-8} \times (1/z) \times \tanh(zy_s/4) \quad (\text{for hydrophobic particles at } 25^\circ\text{C}) \quad (35b)$$

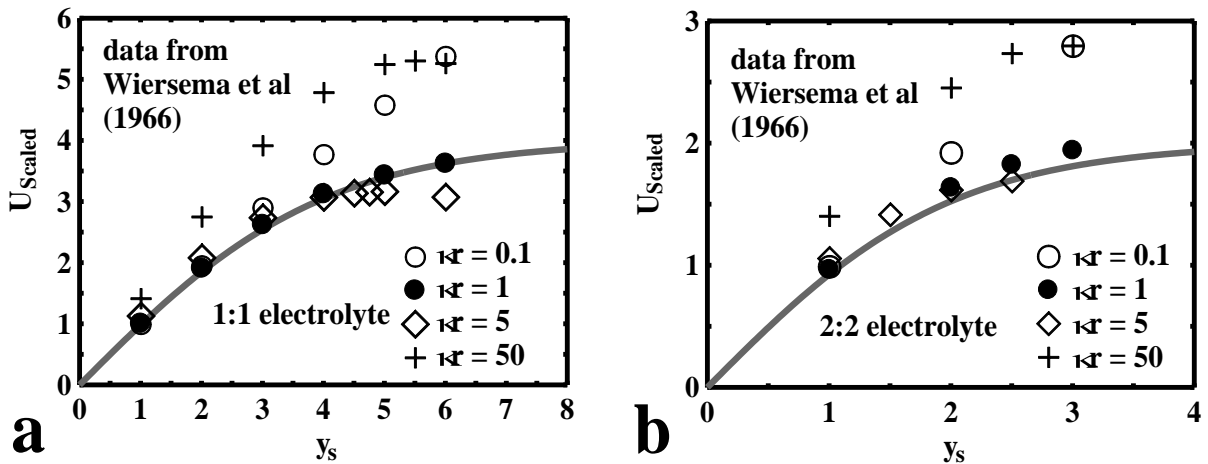


Fig. 3 Scaled electrophoretic mobility of spherical particles at various scaled radii kr as function of surface potential in (a) 1:1 and (b) 2:2 electrolytes, as calculated by Wiersema, et al (1966). Solid curve: Eq. (37).

In Fig. 3, the “computer results” from Wiersema et al (1966) are shown. Numerical calculations were performed for spherical particles with scaled radii $kr = 0.1 \div 50$:

$$kr = \{I^{0.5}/3.04\} \times [r, \text{ \AA}] \quad (36)$$

Here κ is inversed Debye length. From Eq. (35), scaled mobility of particle in symmetric z:z electrolyte is:

$$U_{\text{Scaled}} = U_{\text{ep}} \times (\alpha/4) \times (\eta_0/\epsilon_0\epsilon) \times \{F/RT\} = (4/z) \times \tanh(z\eta_s/4) \quad (37)$$

As may be seen, Eq. (37) is well applicable for “computer particles” at scaled radius $\kappa r = 1$. Maximum deviation of Eq. (37) from numerical results of Wiersema et al (1966) is 38 %.

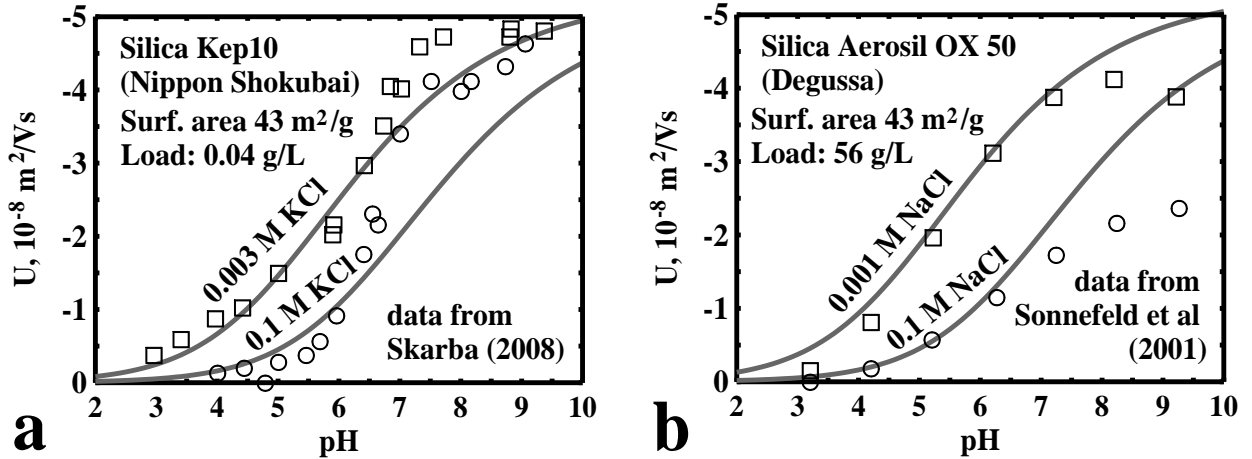


Fig. 4 Electrophoretic mobility of silica particles with average radii 317 Å at 25°C. Data (a) from Scarba (2008) and (b) from Sonnefeld et al (2001). Curves: Eq. (35a) and Eqs. (8-12, 15) with $K_{SO} = 10^{-8.95}$.

Fig. 4 shows electrophoretic mobility of amorphous silica particles with surface area 43 m²/g (a: data from Scarba, 2008; b: data from Sonnefeld et al, 2001). From Eq. (3), radius of particles was $r = 317 \text{ \AA}$. As may be seen, Eq. (35a) is roundly applicable for silica particles with radius 317 Å (scaled radius $\kappa r = 3.3 \div 33$).

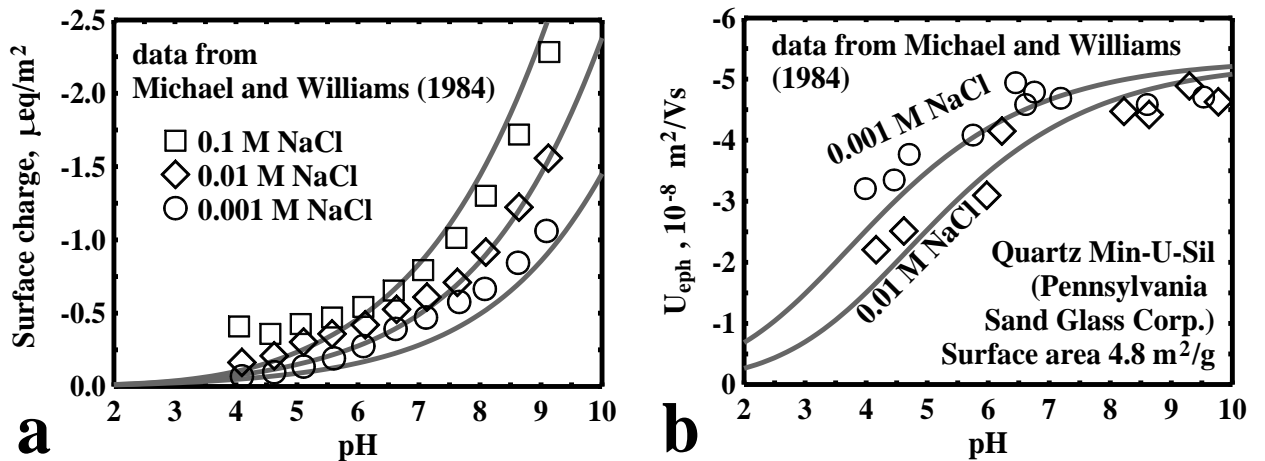


Fig. 5 Surface charge (a) and electrophoretic mobility (b) of quartz particles ($r = 2360 \text{ \AA}$) in NaCl solutions at 25°C. Data from Michael and Williams (1984). Curves: Eq. (35a) and Eqs. (8-12, 15) with $K_{SO} = 10^{-7.5}$.

Fig. 5a shows surface charge of quartz “Min-U-Sil” (Pennsylvania Sand Glass Corp.) in NaCl solutions, as measured by Michael and Williams (1984). As compared with amorphous silica, quartz is ~ 30 times more acidic. Solid curve was calculated from Eqs (8-12, 15) with

acidity constant, adjusted to $K_{SO} = 10^{-7.5}$. From surface area, $4.8 \text{ m}^2/\text{g}$ (Michael and Williams, 1984), and density of quartz, $2.648 \text{ g}/\text{cm}^3$ (Clark, 1966) radius of particles is 2360 \AA . Fig. 5b shows electrophoretic mobility for the same sample of quartz (Michael and Williams, 1984). As may be seen, Eq. (35a) is roundly applicable for large particles.

Fig. 6 shows electroosmotic mobility of solution at 0.02 M ionic strength (various buffer solutions of sodium salts) in fused-silica capillary with inner radius 250000 \AA , as measured by Zhou and Foley (2006). Solid curve in Fig. 6 is quartz electrophoretic mobility, multiplied by factor -1.5 :

$$U_{eos} = - (6/\alpha) \times (\epsilon_o \epsilon / \eta_o) \times \{4RT/zF\} \times \tanh(zF\phi_s/4RT) \quad (38) \text{ or}$$

$$U_{eos}, \text{ m}^2/\text{Vs} = - 8.201 \times 10^{-8} \times \tanh(y_s/4) \quad (\text{with } \alpha = 6 \text{ and } z = 1) \quad (38a)$$

Due to opposite charge, solution in fused-silica capillary moves in opposite direction with respect to quartz particles. Electroosmotic mobility of solution is 1.5 times larger (by modulus) than electrophoretic mobility of quartz particles (see dashed curve in Fig. 6). Smaller (by modulus) mobility of quartz particles arises due to frontal resistance, which is taken into account by Stokes law.

Neglecting curvature of interface, electroosmotic mobility of solution in large capillary, U_{eos} , may be calculated from dynamic equilibrium of charged layer of solution, parallel to flat charged interface (Fridrihsberg, 1974). Electric tag for this layer is

$$f_{el} = - E \times \rho_x \times dx \quad (39)$$

Here dx is thickness of layer, and ρ_x is free charge density at distance x from charged interface. Poisson equation is:

$$\rho_x = - \epsilon_o \epsilon \{d^2\phi_x/dx^2\} \quad (40)$$

Note here that sign of $\{d^2\phi_x/dx^2\}$ coincides with sign of ϕ_s and opposite to sign of free charge of solution. Thus, Eq. (39) may be rewritten as:

$$f_{el} = E \times \epsilon_o \epsilon \{d^2\phi_x/dx^2\} \times dx \quad (41)$$

Electric tag is equilibrated by friction force:

$$f_{fric} = \{d^2(\eta_x v_x)/dx^2\} \times dx \quad (42)$$

Here η_x and v_x are viscosity and velocity of layer, located at distance x from interface. Note here, that sign of d^2v_x/dx^2 is always opposite to sign of electroosmotic flow.

From equality $f_{el} + f_{fric} = 0$, one may obtain:

$$d^2(\eta_x v_x)/dx^2 = - E \times \epsilon_o \epsilon \{d^2\phi_x/dx^2\} \quad (43)$$

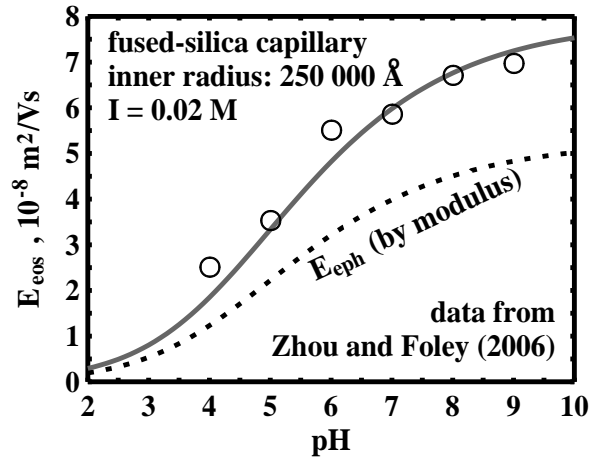


Fig. 6 Electroosmotic mobility of solution at $I = 0.02 \text{ M}$ in fused-silica capillary (inner radius 250000 \AA). Data from Zhou and Foley (2006). Solid curve: Eq. (38a). Dashed curve: modulus of electrophoretic mobility of quartz particle under the same conditions.

Integration of Eq (43) from $x = \infty$ to $x = 0$, applying $v_\infty = 0$ and $\phi_\infty = 0$, gives electroosmotic equation for hydrophilic interface:

$$v_{osm} = -v_s = E \times \epsilon_0 \epsilon \times \phi_s / \eta_s \quad (44)$$

Here v_s is velocity of interface with respect to solution, whereas v_{eos} is velocity of solution respect to interface, i.e. electroosmotic velocity. Replacement of v_{eos} by $U_{eos} = -v_{eos}/E$ gives conventional electroosmotic mobility of solution in hydrophilic capillary:

$$U_{eos} = -(\epsilon_0 \epsilon / \eta_s) \times \phi_s \quad (45)$$

Viscosity of water at interface should be larger than in the bulk solution dew to “viscoelectric effect” (Lyklema and Overbeek, 1961). Indeed, attraction of charged solution to charged interface causes “swelling pressure” (see Pivovarov, 2016a), and thus, “viscoelectric effect” must exist. As may be guessed from Eqs (45) and (38), viscosity of water at interface is:

$$\eta_s = \eta_0 \times \{zF\phi_s/4RT\} / \tanh(zF\phi_s/4RT) = \eta_0 \times \{zy_s/4\} / \tanh(zy_s/4) \quad (46)$$

In Fig. 7, typical data on electrophoretic mobility of oil droplets (xylene, $(CH_3)_2C_6H_4$) in 0.001 M NaCl solution (Marinova et al, 1996) are compared with mobility of amorphous silica particles (dashed curve). Radius of droplets was $\sim 5000 \text{ \AA}$, concentration of emulsion was 0.05 vol % ($= 0.575 \text{ g/L}$). Similar results were obtained also for some other oils, and thus, as deduced by Marinova et al (1996) “electrophoretic mobility is almost independent of the type of specific nonpolar oil”. As may be seen, maximum (by modulus) electrophoretic mobility of hydrophobic droplets is ~ 1.5 times larger than for silica, which is consistent with Eq. (35b). Close consistence with silica mobility (multiplied by factor 1.5) leads to conclusion, that the potential of oil-water interface (and thus, surface charge), is close to that of silica. The electrophoretic mobility of H_2 bubbles is also comparable with that of silica particles (see Yang et al, 2001). Thus, it is possible, that the surface charge of hydrocarbon-water interface (and, may be, that of silica-water interface), arises due to interfacial dissociation of water. Due to existence of such an effect, production of petroleum from borehole may be enhanced by application of electric field. Of course, the effect seems to be too small, to be profitable. However, who knows?

Fig. 8 shows electrophoretic mobility of hydrous ferric oxide in 0.01 M NaCl (data from Su and Suarez, 2000; Goldberg et al, 1996). As may be seen, observed mobility of hydrous ferric oxide is ~ 2 times smaller than predicted by Eq. (35a; see dashed curve). Solid curve was calculated from Eq. (35), with surface potential, estimated from “phantom model” (see Fig. 2), and applying “effective” Stokes constant for ferrihydrite:

$$\alpha(\text{ferrihydrite}) = 11.7 \quad (47)$$

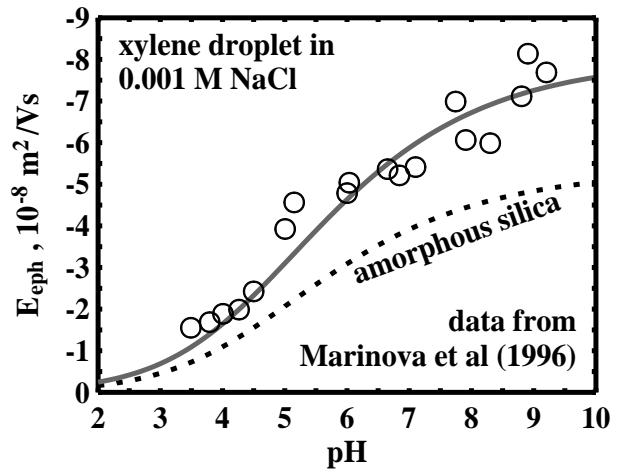


Fig. 7 Electrophoretic mobility of xylene droplets ($r \sim 5000 \text{ \AA}$) in 0.001 M NaCl solution (Marinova et al, 1996) at 22°C . Dashed curve: model for silica particles. Solid curve: same but multiplied by 1.5.

As may be seen, particles of ferrihydrite are “super-hydrophilic”.

Fig. 9 shows electrophoretic mobility of hematite particles ($r \sim 350 \text{ \AA}$) in 0.005 and 0.05 M KCl solutions, as measured by Liang (1988). Solid curves in Fig 9 were calculated from Eq. (35), applying “effective” Stokes constant for hematite:

$$\alpha(\text{hematite}) = 10 \tag{48}$$

Surface potential was calculated with use of the same model as for ferrihydrite (see Fig. 2), but with adjustment of acidity constants by 0.4 units (i.e. to $K_1 = 6.7$ and $K_2 = -10.3$; see Eqs 21, 22), in order to reproduce $\text{pH}_{\text{zpc}} = 8.5$ of hematite (Liang, 1988), and with actual radius of particles ($r = 350 \text{ \AA}$; Liang, 1988).

Perhaps, additional compression of water at metal oxide/water interface is result of interfacial “wetting pressure” (see Pivovarov, 2016b, 2017).

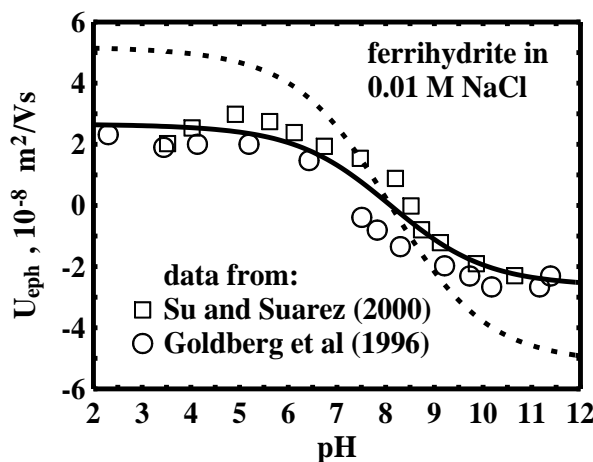


Fig. 8 Electrophoretic mobility of ferrihydrite particles in 0.01 M NaCl solutions, as measured by Su and Suarez (2000), and by Goldberg et al (1996). Radius of particles $\sim 20 \text{ \AA}$. Dashed curve: Eq. (35a). Solid curve: Eq. (35) with $\alpha = 11.7$.

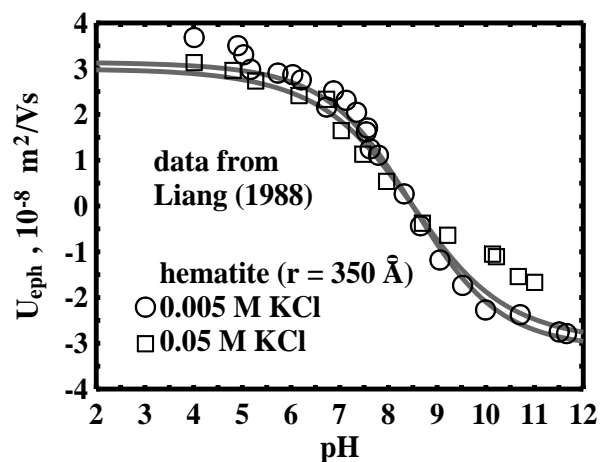


Fig. 9 Electrophoretic mobility of hematite particles ($r = 350 \text{ \AA}$) in KCl solutions, as measured by Liang (1988). Solid curves: Eq. (35) with $\alpha = 10$.

CONCLUDING REMARKS

Due to huge contradiction between “Smoluchowski zeta potential” and “Gouy-Chapman surface potential”, modern theories of ionic adsorption are reduced to multi-layer Ion Exchange models with very small and almost decorative diffuse layer. Indeed, “effective charge of particle”, which may be estimated from its electrophoretic mobility, is just a very small fraction of measurable surface charge. This leads to impression, that the surface charge is almost completely balanced by surface complexes of counter ions. However, apparent contradiction may be successfully eliminated by “viscoelectric effect”. Thus, Gouy-Chapman model of charged interface may be completely rehabilitated.

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