CALCIUM-SODIUM EXCHANGE IN COMPACTED CLAY

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ABSTRACT

The Gouy-Chapman model of diffuse layer was applied for estimation of Ca/Na selectivity of compacted clay. The Ca/Na selectivity constant for compacted clay, based on Gouy-Chapman model, is K(Ca/Na) = $\{ECa/ENa^2\}\times\{[Na^+]^2/[Ca^{2+}]\} \approx \{(40\times\sigma/h)^2 + K_\infty{}^2\}^{0.5}$, where σ is surface charge of clay particles (in $\mu eq/m^2$), h is average distance between clay particles (in Å), and K_∞ is selectivity constant for diluted suspension of clay. This relation is consistent with observations.

INTRODUCTION

Ion selectivity coefficient, measured in laboratory, is useful tool for projection of sewage disposal, burial of wastes, etc, etc, etc. However, selectivity coefficient, measured for diluted clay suspension, is not applicable for compacted clay. As shown by Karnland et al (2011), selectivity of clay for Ca ions increases with compaction. Present study is focused on this problem.

GAINES-THOMAS ION EXCHANGE MODEL

The Gaines-Thomas model for Na/Ca exchange in clay may be defined by quasi-reaction:

$$2XNa^+ + Ca^{2+} \Leftrightarrow X_2Ca^{2+} + 2Na^+ \quad (1)$$

Here X is "site" of clay surface, XNa^+ and X_2Ca^{2+} are "surface complexes", Ca^{2+} and Na^+ are free ions in solution. Apparent Ca/Na selectivity constant of this quasi-reaction is:

$$K_{GT} = \{ECa/ENa^2\}/R_{Ca} = \{(1\text{-}ENa)/ENa^2\}/R_{Ca} \quad (2)$$

Here ECa and ENa are equivalent fractions of cations in clay. In accordance with Eq. (1), these values are defined by:

$$ENa = [XNa^+]/\{2[X_2Ca^{2+}] + [XNa^+]\} \quad (3)$$

$$ECa = 1 - ENa = 2[X_2Ca^{2+}]/\{2[X_2Ca^{2+}] + [XNa^+]\} \quad (4)$$

Here $[XNa^+]$ and $[X_2Ca^{2+}]$ are molar concentrations in clay (e.g., in moles per kg of clay).
Factor R_{Ca} in Eq. (2) is "calcium exchange ratio":

$$R_{Ca} = [Ca^{2+}]/[Na^+]^2 \quad (5)$$

Here $[Ca^{2+}]$, $[Na^+]$ and, further, $[Cl^-]$ are molar concentrations of ions in the bulk solution (moles per dm^3 of solution).

"Calcium exchange ratio" may be converted back to ion concentrations in solution:

$$[Na^+] = \{(0.25 + 2R_{Ca}N)^{0.5} – 0.5\}/2R_{Ca} \quad (6)$$

$$[Ca^{2+}] = \{N – [Na^+]\}/2 = R_{Ca}[Na^+]^2 \quad (7)$$

Here N is normality of solution. For Na–Ca–Cl solutions, it is:

$$N = [Na^+] + 2[Ca^{2+}] = [Cl^–] \quad (8)$$

With known exchange constant and calcium exchange ratio, equivalent fractions of cations in clay may be calculated from:

$$ENa = \{(0.25 + K_{GT}\times R_{Ca})^{0.5} – 0.5\}/(K_{GT}\times R_{Ca}) \quad (9)$$

$$ECa = 1 – ENa \quad (10)$$

SURFACE PROPERTIES OF MONTMORILLONITE

Due to small lattice charge, attraction between one-unit-cell layers of montmorillonite is too small to prevent hydration of interlayer cations in contact with water. In result, immersion of montmorillonite into distilled water leads to complete disaggregation of montmorillonite quasi-crystals into one-unit-cell platelets. Because of this, surface properties of montmorillonite may be calculated directly from crystallographic data (see **Tab. 1**). Another feature of montmorillonite is significant variability of molecular weight with humidity. Because of this, any property of montmorillonite, measured "per gram", depends on drying procedure. Mass of calcium is close to doubled mass of sodium ions, and changes in specific properties due to replacement of sodium by calcium are negligible.

Tab. 1 Some relevant properties of Wyoming montmorillonite MX-80.

Clay	Molar weight per formula, g/mol	Surface area, m^2/g	Lattice charge, eq per mol	Surface charge, $\mu eq/m^2$	Exchange capacity, meq/g
Wyoming montmorillonite MX-80 (Na-form, nominal)	373[a]	756[d]	-0.35[a]	-1.24[e]	0.938[f]
Wyoming montmorillonite MX-80 (Na-form, tetrahydrate)	445[b]	633[d]	-0.35[a]	-1.24[e]	0.787[f]
Wyoming montmorillonite MX-80 (Na-form, ignited)	355[c]	794[d]	-0.35[a]	-1.24[e]	0.986[f]
Wyoming montmorillonite MX-80 (Ca-form, nominal)	372[g]	758[d]	-0.35[h]	-1.24[e]	0.941[f]

[a] formula $Na_{0.35}(Al_{1.56}Mg_{0.24}Fe^{III}_{0.1}Fe^{II}_{0.09}Ti^{IV}_{0.01})[Si_{3.97}Al_{0.03}]O_{10}(OH)_2$ from data of Karnland et al (2011)
[b] formula for nominal Na-montmorillonite plus 4 H_2O
[c] formula for nominal Na-montmorillonite minus H_2O
[d] surface area of one-unit-cell crystal; from lattice parameters a_o = 5.2 and b_o = 9 Å, it is $10^{-20}a_ob_oN_A/M$
[e] from lattice parameters a_o = 5.2 and b_o = 9 Å, and lattice charge –0.35, it is $– 0.35\times10^{20}/\{a_ob_oN_A)$ eq/m^2
[f] exchange capacity of one-unit-cell crystal; from lattice charge –0.35, and molar weight, it is 0.35/M eq/g
[g] difference between molar weights of Na-form and Ca-form is 0.35×23 – 0.35×40/2 = 1 g/mol
[h] the same as for Na-form

Ca/Na EXCHANGE IN DIFFUSE LAYER IN ABSENCE OF OVERLAP

In the absence of overlap of diffuse layers, composition of diffuse layer in equilibrium with Na-Ca-Cl salt solution may be calculated from (Pivovarov, 2013):

$$[DNa^+],\ \mu mol/m^2 = \qquad (11)$$

$$= \{0.304/R_{Ca}^{0.5}\}\times\ln[\{2([Ca^{2+}]I_{eff}\times\exp(-y_s))^{0.5}+2[Ca^{2+}]\times\exp(-y_s)+N\}/\{2([Ca^{2+}]I)^{0.5}+2[Ca^{2+}]+N\}]$$

$$[DCa^{2+}],\ \mu mol/m^2 = 0.304\times\{(I_{eff}\times\exp(-y_s))^{0.5} - I^{0.5}\} - 0.5[DNa^+] \qquad (12)$$

$$[DCl^-],\ \mu mol/m^2 = 0.608\times\{(I_{eff}\times\exp(y_s))^{0.5} - I^{0.5}\} \qquad (13)$$

Here $0.608 = 10^6(2000RT\varepsilon_o\varepsilon/F^2)^{0.5}$ is Gouy-Chapman constant (0.304 is exactly 0.608/2), 10^6 is mol-to-μmol conversion factor, 1000 is m^3-to-dm^3 conversion factor, R is gas constant (8.314 J/molK is gas constant), T is absolute temperature (Kelvin), ε_o is electric permeability of free space (8.8542×10^{-12} Farads/m ≡ Coulomb×$Volt^{-1}\times m^{-1}$), ε is relative electric permeability of water (= 78.47 at 25°C), F is Faraday constant (96485 Coulombs/mol), N is normality of solution (see Eq. 8), I is ionic strength of solution:

$$I = 0.5\{[Na^+] + 4[Ca^{2+}] + [Cl^-]\} = [Cl^-] + [Ca^{2+}] \qquad (14)$$

I_{eff} is intermediate variable ("effective ionic strength"):

$$I_{eff} = 0.5\{[Na^+] + (2+2\times\exp(-y_s))[Ca^{2+}] + [Cl^-]\} = [Cl^-] + [Ca^{2+}]\times\exp(-y_s) \qquad (15)$$

y_s is scaled potential in the head of diffuse layer (scaled "surface potential"):

$$y_s = F\varphi_s/RT \qquad (16)$$

φ_s is potential in the head of diffuse layer (in Volts).

Scaled potential in the head of diffuse layer (scaled "surface potential") is defined by Gouy-Chapman equation:

$$\sigma_s,\ \mu eq/m^2 = 0.608\,\mathrm{sgn}(y_s)\{[Na^+](\exp(-y_s)-1)+[Ca^{2+}](\exp(-2y_s)-1)+[Cl^-](\exp(y_s)-1)\}^{0.5}$$

$$= 0.608\times I_{eff}^{0.5}\{\exp(y_s/2) - \exp(-y_s/2)\} \qquad (17)$$

Here $\mathrm{sgn}(y_s)$ is sign of surface potential.

At $[Ca^{2+}] = 0$, $I_{eff} = I$, and surface concentrations of ions in equilibrium with NaCl solution are

$$[DCl^-],\ \mu mol/m^2 = 0.608\times I^{0.5}(\exp(y_s/2) - 1\} =$$

$$= (0.608^2\times I + 0.25[\sigma_s,\ \mu eq/m^2]^2)^{0.5} - 0.608\times I^{0.5} + 0.5[\sigma_s,\ \mu eq/m^2] \qquad (18)$$

$$[DNa^+],\ \mu mol/m^2 = 0.608\times I^{0.5}(\exp(-y_s/2) - 1\} =$$

$$= (0.608^2\times I + 0.25[\sigma_s,\ \mu eq/m^2]^2)^{0.5} - 0.608\times I^{0.5} - 0.5[\sigma_s,\ \mu eq/m^2] \qquad (19)$$

$$y_s = 2\ln\{0.5[\sigma_s, \mu eq/m^2]/(0.608\times I^{0.5}) + (0.25[\sigma_s, \mu eq/m^2]^2/(0.608^2\times I) + 1)^{0.5}\} \quad (20)$$

Majority of ion exchange studies are based on “anion subtraction” convention. Practically, precipitate is separated from solution, and the exchangeable cations are extracted from precipitate (e.g., by 1 M NH_4NO_3, several times), and then, total amount of extracted cations is corrected on their quantity in the solution remaining in the wet clay prior to extraction. For the chloride medium, amount of resident solution in sample of precipitate may be estimated from total amount of chloride ions in the extracts. Alternatively, prior to analysis, chloride (together with “odd” cations) may be removed from sample of precipitate by redispersion in distilled water or alcohol, with hope about negligible change of Ca-Na ratio in clay (less accurate variant).

The exchangeable fractions of cations, defined by “anion subtraction” convention, may be calculated from:

$$ENa_{AS} = \{[DNa^+] - ([Na^+]/[Cl^-])\times[DCl^-]\}/|\sigma| \quad (21)$$

$$ECa_{AS} = 1 - ENa_{AS} = 2\{[DCa^{2+}] - ([Ca^{2+}]/[Cl^-])[DCl^-]\}/|\sigma| \quad (22)$$

The conventional Gaines-Thomas selectivity coefficient is then defined by:

$$K(Ca/Na)_{AS} = \{ECa_{AS}/ENa_{AS}^2\}/R_{Ca} = \{(1 - ENa_{AS})/ENa_{AS}^2\}/R_{Ca} \quad (23)$$

The exchange fraction of sodium ion in clay, based on “anion subtraction” convention, may be estimated from Eriksson equation:

$$ENa_{Eriksson} = \{0.304/[|\sigma_s|, \mu q/m^2]R_{Ca}^{0.5}\}\ln\{a+(a^2+1)^{0.5}\} \quad (24)$$

$$a = \{[|\sigma_s|, \mu eq/m^2]/0.304\}[Ca^{2+}]^{0.5}/\{[Na^+] + 4[Ca^{2+}]\}$$

$$= \{[|\sigma_s|, \mu eq/m^2]/0.304\}R_{Ca}^{0.5}/\{1 + 8R_{Ca}N\}^{0.5} \quad (25)$$

For arbitrary salt mixture $M^+A^- + Me^{2+}An^{2+}$, Eriksson equation (Eqs. 24, 25) gives exact fraction of surface charge, balanced by positive adsorption of univalent cation and negative adsorption of univalent anion, i.e., $\{[DM^+] - [DA^-]\}/|\sigma|$. Error of Eriksson equation (assuming $ENa_{AS} \approx ENa_{Eriksson}$) in application to NaCl + $CaCl_2$ salt mixture is negligible at low salt concentrations. However, error increases with ionic strength and calcium exchange ratio. Up to $[Cl^-] = 1$ M maximum error of Eriksson equation at $\sigma_s = -1\div2$ $\mu eq/m^2$ and $[Cl^-]$ 0.01÷1 M is 24 % for Ca/Na selectivity coefficient.

Closer result for NaCl + $CaCl_2$ mixture may be obtained with following approximation for Eq. (25):

$$a = \{[|\sigma_s|, \mu eq/m^2]/0.304\}R_{Ca}^{0.5}/\{1+bR_{Ca}N\}^{0.5} \quad (26)$$

$$b = 8 - 0.562[Cl^-]/(1+0.43[Cl^-]) - 2.775\{[Cl^-]R_{Ca}\}^{0.5}/(1+1.686\{[Cl^-]R_{Ca}\}^{0.5}) \quad (27)$$

Maximum error of this approximation at $\sigma_s = -$ 1-2 $\mu eq/m^2$ and $[Cl^-]$ 0.01÷1 M is 1.1 % for Ca/Na selectivity coefficient.

Tab. 2. Fractions of surface charge (σ_s = – 1 and – 2 μeq/m^2) balanced by Na^+, Ca^{2+}, and Cl^- ions, scaled surface potential y_s, and selectivity coefficient $K(Ca/Na)_{AS}$ for flat diffuse layer at the absence of overlap.

σ_s	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
– 1 μeq/m^2	0.01 M	0	0.942883	18418.9×[Ca^{2+}]	0.0571169	5.607684	1.84303
		0.01	0.925404	0.0175733	0.0570226	5.581683	1.82198
		0.1	0.815423	0.128245	0.0563317	5.408488	1.68945
		1	0.516645	0.430336	0.0530196	4.827384	1.33399
		10	0.227341	0.728017	0.0446421	4.017029	1.04227
		100	0.0779301	0.886337	0.0357332	3.466180	0.985293
		∞	11.0368×[Na$^+$]	0.970333	0.0296670	3.149425	1.01990
	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
	0.1 M	0	0.843426	215.939×[Ca^{2+}]	0.156574	3.367886	2.19070
		0.01	0.823749	0.0205519	0.155699	3.341987	2.17605
		0.1	0.702286	0.148106	0.149607	3.175780	2.09460
		1	0.391651	0.481153	0.127196	2.701139	1.99653
		10	0.143724	0.755460	0.100817	2.278383	2.13831
		100	0.0461656	0.865249	0.0885857	2.104019	2.29384
		∞	2.06295×[Na$^+$]	0.917449	0.0825509	2.020102	2.39717
	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
	1 M	0	0.679187	4.79920×[Ca^{2+}]	0.320813	1.500080	5.44082
		0.01	0.642219	0.0438532	0.313928	1.474104	5.52700
		0.1	0.463485	0.257342	0.279173	1.348630	6.04977
		1	0.196143	0.580437	0.223421	1.160438	7.30317
		10	0.0652189	0.739826	0.194955	1.067051	8.24876
		100	0.0207996	0.794012	0.185188	1.034994	8.64384
		∞	0.294923×[Na$^+$]	0.819398	0.180602	1.019899	8.84471
σ_s	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
– 2 μeq/m^2	0.01 M	0	0.970523	72529.6×[Ca^{2+}]	0.0294767	6.988471	7.25356
		0.01	0.909391	0.061222	0.0293872	6.894570	6.94750
		0.1	0.680389	0.290722	0.0288892	6.486653	5.78098
		1	0.360413	0.612518	0.0270685	5.664957	4.09406
		10	0.146421	0.830771	0.0228077	4.755190	3.03053
		100	0.049245	0.932429	0.0183265	4.172073	2.76004
		∞	6.96021×[Na$^+$]	0.984721	0.0152793	3.840569	2.77591
	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
	0.1 M	0	0.913024	758.996×[Ca^{2+}]	0.0869755	4.702272	7.60735
		0.01	0.849897	0.0639861	0.0861170	4.608791	7.32560
		0.1	0.614838	0.303590	0.0815722	4.213130	6.32056
		1	0.292331	0.638922	0.0687465	3.509587	5.26599
		10	0.102196	0.842980	0.0548239	2.995286	5.18143
		100	0.0325550	0.918991	0.0484543	2.792133	5.36643
		∞	1.45178×[Na$^+$]	0.954683	0.0453171	2.695170	5.51143
	[Cl⁻]	R_{Ca}	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$K(Ca/Na)_{AS}$
	1 M	0	0.781163	10.5779×[Ca^{2+}]	0.218837	2.544916	11.0156
		0.01	0.701656	0.0868275	0.211516	2.454861	10.9982
		0.1	0.439962	0.377634	0.182404	2.145674	11.3897
		1	0.169601	0.686006	0.144393	1.810805	12.9683
		10	0.0550391	0.818612	0.126349	1.664956	14.2598
		100	0.0174455	0.862297	0.120258	1.616500	14.8051
		∞	0.246734×[Na$^+$]	0.882590	0.117409	1.593899	15.0829

In **Tab. 2** the composition of diffuse layer and Ca/Na selectivity coefficients ("anion subtraction" convention) are given, as calculated from Eqs. (11-23).

In **Fig. 1**, the data on Ca/Na exchange on Wyoming montmorillonite SWy-1 are shown, as measured by Amrhein and Suarez (1991). As may be seen, Gouy-Chapman model is generally consistent with observations (see solid curves). Thus, Ca and Na ions are adsorbed in the diffuse layer, and specific binding of these ions by surface sites is negligible. The dashed gray curves in **Fig. 1** were calculated with use of Eriksson equation. As may be seen, in the range R_{CA} 0.01÷100, deviation of Eriksson equation from exact relation is small even at $[Cl^-] = 1$.

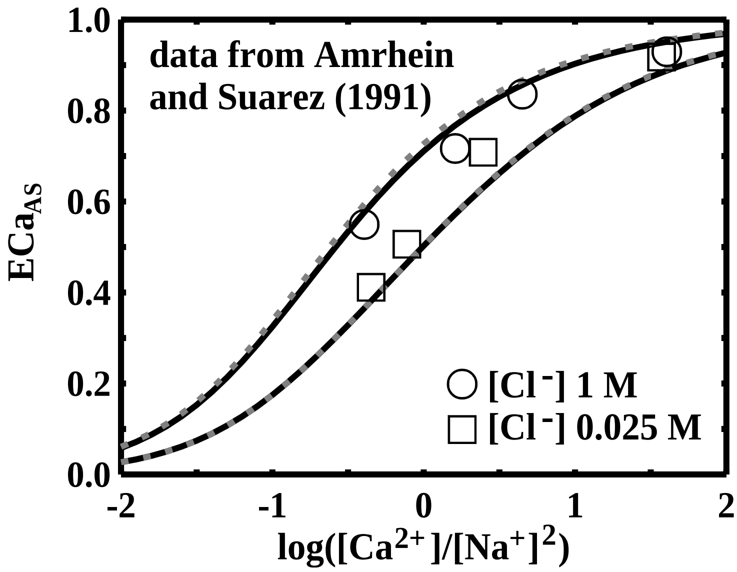

Fig. 1. Ca/Na exchange on Wyoming montmorillonite SWy-1. Data from Amrhein and Suares (1991). Solid curves: Gouy-Chapman model. Dashed grey curves: Eriksson equation.

Na/Ca EXCHANGE IN THE OVERLAPPED DIFFUSE LAYERS

In the limit of zero distance between charged planes, Ca/Na exchange coefficient may be deduced analytically. Electric potential in the slit between two negatively charged surfaces becomes strongly negative. Because of this, highly compacted clay in equilibrium with bulk solution is almost free of anions. Thus, negative adsorption of chloride in equilibrium with Ca-Na-Cl solution may be estimated simply as $-[Cl^-]\times w$, where w is water content in clay. Consequently, negative adsorption of Cl^- in highly compacted clay approaches to:

$$[DCl^-],\ \mu mol/m^2 \approx 0.1\times[Cl^-]\times\{\exp(y_a)-1\}\times[h/2,\ Å] \approx -0.1\times[Cl^-]\times[h/2,\ Å] \qquad (28)$$

Here 0.1 is scaling factor, y_a is "average" scaled potential in the slit between charged surfaces ("very negative" value), and h/2 is a half of distance between charged surfaces. Similarly, the values of adsorbed Na^+ and Ca^{2+} in highly compacted clay are defined by:

$$[DNa^+],\ \mu mol/m^2 \approx 0.1\times[Na^+]\times\{\exp(-y_a)-1\}\times[h/2,\ Å] \qquad (29)$$

$$[DCa^{2+}],\ \mu mol/m^2 \approx 0.1\times[Ca^{2+}]\times\{\exp(-2y_a)-1\}\times[h/2,\ Å] \qquad (30)$$

Consequently, on basis of "anion subtraction" convention (see Eqs 21, 22), exchange fractions of Na^+ and Ca^{2+} in highly compacted clay are defined by:

$$ENa_{AS} \approx 0.1\times[Na^+]\times\exp(-y_a)\times[h/2,\ Å]/[|\sigma_s|,\ \mu eq/m^2] \qquad (31)$$

$$ECa_{AS} \approx 0.1\times2\times[Ca^{2+}]\times\exp(-2y_a)\times[h/2,\ Å]/[|\sigma_s|,\ \mu eq/m^2] \qquad (32)$$

Thus, selectivity coefficient of Ca/Na exchange in the limit $h \to 0$ is:

$$K(Ca/Na)_{AS} = \{ECa_{AS}/ENa_{AS}^2\}/R_{Ca} \approx 40\times[|\sigma_s|, \mu eq/m^2]/[h, Å] \quad (33)$$

Note here that Eq. (33) is exact asymptotic relation in the limit h → 0. To obtain closer estimations, one may apply approximation:

$$K(Na/Ca)_{AS} \approx \{(40\times[|\sigma_s|, \mu eq/m^2]/[h, Å])^2 + K_\infty^2\}^{0.5} \quad (34)$$

Here K_∞ is selectivity coefficient for diluted suspension (see **Tab. 2**). As may be found from numerical integration of Poisson-Boltzmann equation (see **Appendixes A and B**), maximum error of Eq. (34) for selectivity constant at $[Cl^-] = 0.01\div1$ M and $\sigma_s = -1\div2$ $\mu eq/m^2$ is 10.6 %.

APPLICATION

To estimate parameter h in Eqs. (33, 34), one may calculate average distance between particles:

$$d, Å = 2\times10^7/\{[S, m^2/g][Load, g/dm^3]\} \quad (35)$$

Here [S m^2/g] is specific surface area of clay (see Tab. 1) and [Load, g/dm^3] is solid-to-solution ratio ("solid load") in suspension or paste, expressed in grams of clay per dm^3 of solution.

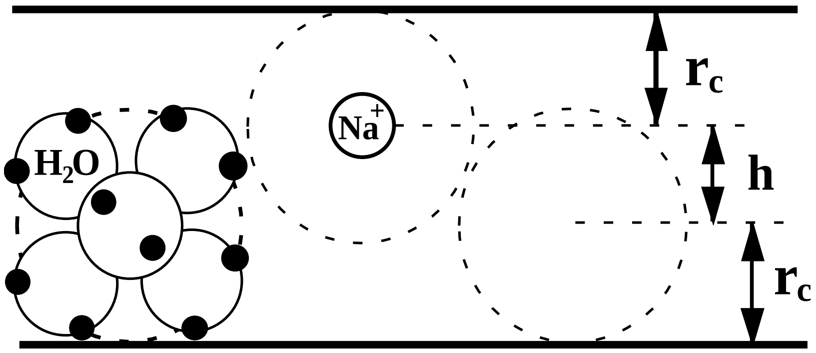

Fig. 2 Layer of solution between charged surfaces in accordance with Stern approach.

In accordance with Stern approach (see **Fig. 2**), the head of diffuse layer is separated from charged surface by radius of counter ion, r_c, and thus, parameter "h" in Eq. (34) may be estimated from:

$$h \approx d - 2\times r_c \quad (36)$$

Radius of counter ion, r_c , may be estimated from data on swelling pressure. In accordance with Gouy-Chapman model of diffuse layer, swelling pressure in homo-ionic clay paste in equilibrium with symmetric z:z electrolyte may be calculated from (see Pivovarov, 2016a):

$$P_{sw}\text{, bar} \approx 24.79\times\{C_m + C^2/C_m - 2C\} \quad (37)$$

$$C_m \approx (C_{m0}^2 + C^2)^{0.5} \quad (38)$$

$$C_{m0} \approx \{20\times[|\sigma_s|, \mu eq/m^2]/z[h, Å]\}/\{1 + 0.05488\times\alpha - 0.01008\times\alpha/(1 + 0.049\times\alpha)\} \quad (39)$$

$$\alpha = z\times[|\sigma_s|, \mu eq/m^2]\times[h, Å] \quad (40)$$

Here 24.79 = RT/100 is Van't Hoff constant, C_m is molar concentration of counter-ion at mid-plane between charged surfaces, C^2/C_m is molar concentration of co-ion at mid-plane, C is molar concentration in the bulk solution, and C_{m0} is molar concentration of counter-ion at mid-plane in equilibrium with pure water.

In **Fig. 3**, the data on swelling pressure in Wyoming montmorillonite MX-80 (Karnland et al 2006) are shown. In original, the values of "dry density" (mass of clay per volume of paste) were given. These values were converted to average distance between particles with use of specific surface area 756 m^2/g and particle density 2.78 g/cm^3. As may be seen, Gouy-Chapmann model (dashed curves in **Fig. 3**: Eqs. 37-40 with h = d) is not consistent with observations at d < 10 Å. Applying Stern approach with r_c = 2 Å (gray curves in **Fig. 3**), one may obtain much closer agreement with observations. Thus, parameter h may be estimated as [d, Å] – 4.

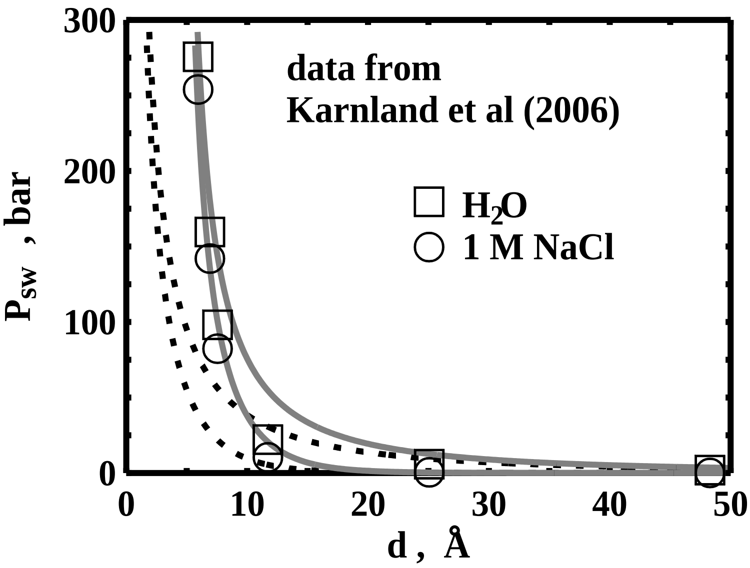

Fig. 3 Swelling pressure in Wyoming montmorillonite MX-80 (Na-form) in equilibrium with water (boxes) and 1 M NaCl (circles). Data from Karnland et al (2006). Dashed curves: Gouy-Chapman model (Eqs. 37-40 with h = d). Grey curves: Stern approach (Eqs. 37-40 with h = [d, Å] – 4).

In **Fig. 4**, the data on Ca/Na selectivity of compacted Wyoming montmorillonite MX-80 are shown, as measured by Karnland et al (2011). In original study, the values of water-to-solid mass ratio were reported. These values were converted to average distance between particles with use of specific surface area 756 m^2/g. Calcium exchange ratios in the outflowing solutions at test termination (at 110th day) were measured at 1.64÷3.84 (2.63, on average), whereas normality (as $[Na^+] + 2[Ca^{2+}]$) was measured at 0.033÷0.062 M (0.047 M, on average). From surface charge, σ_s = – 1.24 μeq/m^2, and Eqs. (11-23), exchange coefficient for diluted clay at these conditions is ~ 2.12 (1.92÷2.31). As may be seen, the Gouy-Chapman model (Eq. 34 with h = d; black curve) is consistent with observations. Contrarily, Stern model (Eq. 34 with h = [d, Å] – 4; gray curve) failed.

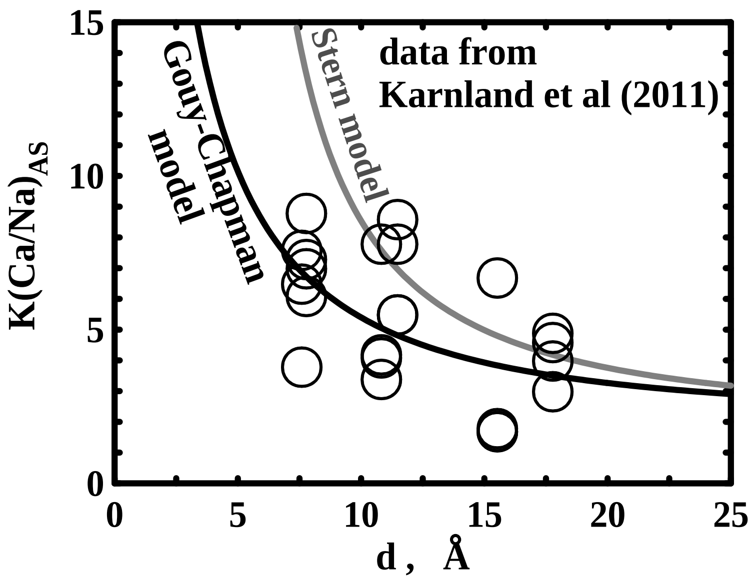

Fig. 4 Ca/Na selectivity coefficient for compacted Wyoming montmorillonite MX-80. Data from Karnland et al (2011). Black curve: Gouy-Chapman model (Eq. 34 with h = d). Gray curve: Stern model (Eq. 34 with h = [d, Å] – 4).

Of course, due to large scatter in **Fig. 4**, disproof of Stern model looks questionable. Nevertheless, if Stern model is really wrong, deviation of measured swelling pressure from Gouy-Chapman model (see **Fig. 3**) should arise due to some unknown effect. As guessed in previous study (Pivovarov 2016b), an additional pressure may arise due to attraction of water molecules to interface. An idea is that the overlap of surface force fields generates positive "wetting pressure" in the slit between two interfaces:

$$P_{wet} = -\{2\omega_{ws}/\lambda\}\exp\{-0.5\times d/\lambda\} \quad (41)$$

Here ω_{ws} is surface energy of water in contact with solid, and λ is decay length of force field.

As estimated from data on capillary elevation, surface energy of water in contact with glass and quarts is $\omega_{ws} \approx -0.0665$ J/m^2 (negative sign corresponds to attraction of water molecules to interface). With use of this value, "wetting pressure" in slit is:

$$P_{wet}\text{, bar} = \{13300/[\lambda, Å]\}\exp\{-0.5\times d/\lambda\} \quad (42)$$

In **Fig. 5**, data on swelling pressure in Wyoming montmorillonite MX-80 (Karnland et al, 2006) are shown again. Curves in **Fig. 5** were calculated as sum of Gouy-Chapman swelling pressure (Eqs. 37-40 with h = d) and "wetting pressure" (Eq. 42, with best-fit decay length λ = 0.64 Å). As may be seen, "wetting pressure" is really good idea.

If so, this idea may be applied for explanation of various phenomena, such as much easier development of fractures in the wetted glass (as compared with dry one). For instance, in accordance with Eq. (42), applying d = 3÷6 Å and λ = 0.64 Å, one may estimate "disjoining pressure" in the wetted leader of fracture at 0.2÷2 kbar.

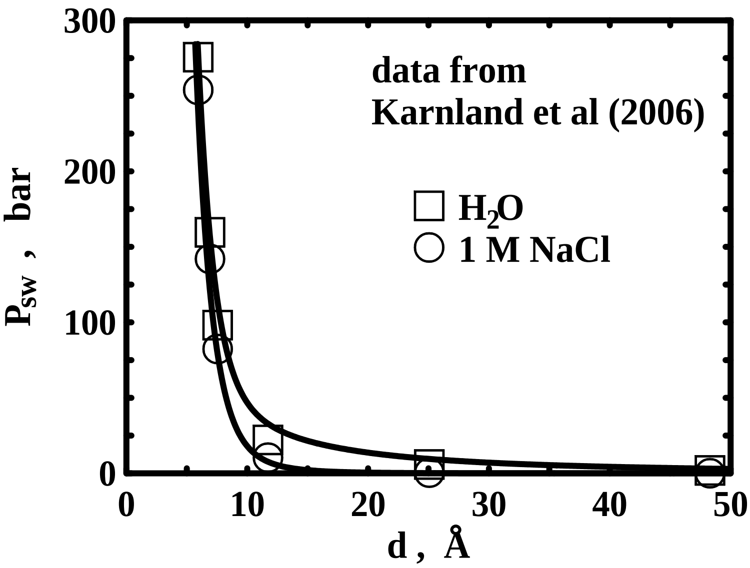

Fig. 5 Swelling pressure in Wyoming montmorillonite MX-80 (Na-form) in equilibrium with water (boxes) and 1 M NaCl (circles). Data from Karnland et al (2006). Curves: Gouy-Chapman swelling pressure (Eqs. 37-40 with h = d) plus wetting pressure (Eq. 42 with λ = 0.64 Å).

CONCLUDING REMARKS

Ion selectivity of compacted clay is consistent with Gouy-Chapman theory of diffuse layer. Contrarily, Stern approach is failed. Alternatively to Stern approach, swelling pressure in highly compacted clay may be explained by action of surface energy (plus minor contribution from Gouy-Chapman swelling pressure). Thus, it is possible that the Gouy-Chapman model gives true estimates for surface potential, whereas constant capacitance term in the Stern approach is just an approximation for action of surface energy.

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APPEDIX A: Results of numerical integration of Poisson-Boltzmann equation

Tab. A1. Surface charge $\sigma_s = -1$ μeq/m^2 and chloride concentration [Cl$^-$] = 1 M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s , and mid-plane, y_m , potentials, and exchange constant $K(Ca/Na)_{AS}$ at various distances, h, between charged surfaces.

$\sigma_s = -1$ μeq/m^2; [Cl$^-$] = 1 M; $R_{Ca} \to 0$; [Na$^+$] = 1 M; [Ca^{2+}] → 0 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.952498	40.1637×[Ca^{2+}]	0.0475024	3.086007	2.953758	40.2587
2	0.909960	20.3261×[Ca^{2+}]	0.0900404	2.483410	2.224868	20.5062
3	0.872286	13.8218×[Ca^{2+}]	0.127714	2.168669	1.789896	14.0772
5	0.810763	8.81485×[Ca^{2+}]	0.189237	1.838425	1.238590	9.19332
10	0.722679	5.62122×[Ca^{2+}]	0.277321	1.568600	0.543821	6.17586
20	0.682269	4.84095×[Ca^{2+}]	0.317731	1.502750	0.106667	5.47641
30	0.679356	4.80118×[Ca^{2+}]	0.320644	1.500180	0.020629	5.44247
∞	0.679187	4.79920×[Ca^{2+}]	0.320813	1.500080	0	5.44082
$\sigma_s = -1$ μeq/m^2; [Cl$^-$] = 1 M; R_{Ca} = 0.1; [Na$^+$] = 0.854102 M; [Ca^{2+}] = 0.0729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.348157	0.607385	0.044458	2.302453	2.172009	41.1730
2	0.418687	0.498444	0.082869	1.944288	1.691602	21.3098
3	0.451151	0.432511	0.116338	1.753335	1.385893	14.8312
5	0.474646	0.355205	0.170148	1.551184	0.976557	9.88726
10	0.473557	0.281507	0.244936	1.387656	0.430056	6.80548
20	0.464330	0.258677	0.276993	1.349979	0.080625	6.08802
30	0.463508	0.257438	0.279054	1.348675	0.014730	6.05271
∞	0.463485	0.257342	0.279173	1.348630	0	6.04977
$\sigma_s = -1$ μeq/m^2; [Cl$^-$] = 1 M; R_{Ca} = 1; [Na$^+$] = 0.5 M; [Ca^{2+}] = 0.25 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.121676	0.836859	0.041465	1.855797	1.726075	42.2871
2	0.152236	0.772621	0.075143	1.563458	1.314237	22.4886
3	0.168918	0.727716	0.103366	1.418672	1.059592	16.0156
5	0.185415	0.667836	0.146748	1.277846	0.727052	11.0674
10	0.195413	0.602460	0.202127	1.179214	0.300673	8.00385
20	0.196184	0.581432	0.222384	1.160921	0.049434	7.33090
30	0.196145	0.580473	0.223382	1.160450	0.007900	7.30415
∞	0.196143	0.580437	0.223421	1.160438	0	7.30317
$\sigma_s = -1$ μeq/m^2; [Cl$^-$] = 1 M; R_{Ca} = 10; [Na$^+$] = 0.2 M; [Ca^{2+}] = 0.4 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.038984	0.921238	0.0397777	1.675211	1.545779	43.2548
2	0.049090	0.880012	0.0708980	1.404928	1.157221	23.4006
3	0.054756	0.848913	0.0963311	1.275901	0.920678	16.8997
5	0.060603	0.805168	0.134229	1.156187	0.617085	11.9330
10	0.064619	0.755748	0.179633	1.079524	0.241447	8.89718
20	0.065211	0.740444	0.194345	1.067307	0.035621	8.27059
30	0.065219	0.739845	0.194936	1.067056	0.005112	8.24939
∞	0.065219	0.739826	0.194955	1.067051	0	8.24876
$\sigma_s = -1$ μeq/m^2; [Cl$^-$] = 1 M; $R_{Ca} \to \infty$; [Na$^+$] → 0 M; [Ca^{2+}] = 0.5 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.174680×[Na$^+$]	0.961143	0.0388567	1.588873	1.459585	43.8615
2	0.220266×[Na$^+$]	0.931389	0.0686108	1.328826	1.081899	23.9665
3	0.246004×[Na$^+$]	0.907425	0.0925749	1.207066	0.853858	17.4466
5	0.272857×[Na$^+$]	0.872370	0.127630	1.096940	0.564016	12.4696
10	0.291823×[Na$^+$]	0.831971	0.168029	1.029855	0.213040	9.45786
20	0.294866×[Na$^+$]	0.819838	0.180162	1.020077	0.029323	8.86320
30	0.294922×[Na$^+$]	0.819410	0.180590	1.019902	0.003929	8.84519
∞	0.294923×[Na$^+$]	0.819398	0.180602	1.019899	0	8.84471

Tab. A2. Surface charge $\sigma_s = -1$ μeq/m^2 and chloride concentration [Cl$^-$] = 0.1 M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s, and mid-plane, y_m, potentials, and exchange constant $K(Ca/Na)_{AS}$ at various distances, h, between charged surfaces.

σ = – 1 μeq/m^2; [Cl$^-$] = 0.1 M; $R_{Ca} \to 0$; [Na$^+$] = 0.1 M; [Ca^{2+}] → 0 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.995025	4000.64×[Ca^{2+}]	0.00497496	5.386131	5.253867	40.0654
2	0.990101	2012.56×[Ca^{2+}]	0.00989942	4.776295	4.517538	20.1276
3	0.985228	1351.70×[Ca^{2+}]	0.0147722	4.449953	4.070152	13.5200
5	0.975645	829.140×[Ca^{2+}]	0.0243553	4.085969	3.479205	8.29627
10	0.952756	451.823×[Ca^{2+}]	0.0472441	3.705018	2.606386	4.52768
20	0.912869	284.635×[Ca^{2+}]	0.0871310	3.476097	1.632609	2.86378
30	0.882965	241.159×[Ca^{2+}]	0.117035	3.407825	1.039664	2.43499
50	0.852861	219.616×[Ca^{2+}]	0.147139	3.373399	0.397639	2.22558
∞	0.843426	215.939×[Ca^{2+}]	0.156574	3.367886	0	2.19070
σ = – 1 μeq/m^2; [Cl$^-$] = 0.1 M; R_{Ca} = 0.1; [Na$^+$] = 0.0980762 M; [Ca^{2+}] = 0.000961894 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.385273	0.609790	0.00493706	4.463437	4.332951	40.0741
2	0.489282	0.500915	0.00980239	4.097727	3.844570	20.1329
3	0.552012	0.433382	0.0146060	3.895865	3.526518	13.5208
5	0.626382	0.349587	0.0240304	3.664466	3.079197	8.28647
10	0.702858	0.250711	0.0464312	3.412675	2.363316	4.49215
20	0.731173	0.183801	0.0850261	3.253785	1.502613	2.79476
30	0.724564	0.162010	0.113426	3.204712	0.958767	2.35039
50	0.708562	0.150219	0.141219	3.179729	0.364870	2.13146
∞	0.702286	0.148106	0.149607	3.175780	0	2.09460
σ = – 1 μeq/m^2; [Cl$^-$] = 0.1 M; R_{Ca} = 1; [Na$^+$] = 0.0854102 M; [Ca^{2+}] = 0.00729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.141746	0.853400	0.00485355	3.618570	3.488680	40.1284
2	0.191002	0.799429	0.00956964	3.317565	3.067626	20.1868
3	0.224976	0.760842	0.0141827	3.161758	2.799918	13.5722
5	0.271872	0.704998	0.0231300	2.994976	2.430044	8.32922
10	0.335592	0.620507	0.0439002	2.831703	1.848573	4.50386
20	0.381401	0.540658	0.0779413	2.740699	1.157527	2.75083
30	0.392202	0.506589	0.101209	2.715007	0.725152	2.27566
50	0.392923	0.485293	0.121783	2.702863	0.265631	2.03711
∞	0.391651	0.481153	0.127196	2.701139	0	1.99653
σ = – 1 μeq/m^2; [Cl$^-$] = 0.1 M; R_{Ca} = 10; [Na$^+$] = 0.05 M; [Ca^{2+}] = 0.025 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.0462362	0.949021	0.00474314	3.056468	2.926953	40.2670
2	0.0630963	0.927642	0.00926180	2.777175	2,528623	20.3244
3	0.0750272	0.911351	0.0136217	2.637166	2.278766	13.7091
5	0.0919799	0.886089	0.0219310	2.493269	1.938526	8.46457
10	0.116249	0.843250	0.0405017	2.363116	1.418332	4.63447
20	0.135639	0.795853	0.0685080	2.300023	0.833145	2.87596
30	0.141524	0.773039	0.0854370	2.285008	0.492973	2.40315
50	0.143622	0.758206	0.0981714	2.279044	0.163501	2.17385
∞	0.143724	0.755460	0.100817	2.278383	0	2.13831
σ = – 1 μeq/m^2; [Cl$^-$] = 0.1 M; $R_{Ca} \to \infty$; [Na$^+$] → 0 M; [Ca^{2+}] = 0.05 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.656700×[Na$^+$]	0.995354	0.00464572	2.734847	2.605470	40.4506
2	0.897719×[Na$^+$]	0.991008	0.00899237	2.465616	2.217778	20.5037
3	1.06878×[Na$^+$]	0.986866	0.0131337	2.332968	1.976378	13.8862
5	1.31242×[Na$^+$]	0.979102	0.0208979	2.199713	1.650480	8.64060
10	1.66170×[Na$^+$]	0.962366	0.0376335	2.084804	1.161663	4.81513
20	1.94054×[Na$^+$]	0.939095	0.0609046	2.034269	0.636486	3.07674
30	2.02635×[Na$^+$]	0.926660	0.0733402	2.023878	0.352571	2.62598
50	2.05994×[Na$^+$]	0.918719	0.0812815	2.020396	0.103530	2.42344
∞	2.06295×[Na$^+$]	0.917449	0.0825509	2.020102	0	2.39717

Tab. A3. Surface charge σ_s = – 1 μeq/m^2 and chloride concentration [Cl$^-$] = 0.01 M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s , and mid-plane, y_m , potentials, and exchange constant K(Ca/Na)$_{AS}$ at various distances, h, between charged surfaces.

σ = – 1 μeq/m^2; [Cl$^-$] = 0.01 M; $R_{Ca} \to 0$; [Na$^+$] = 0.01 M; [Ca^{2+}] → 0 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	K(Ca/Na)$_{AS}$
1	0.999500	400634×[Ca^{2+}]	0.000499750	7.688691	7.556427	40.0634
2	0.999001	201236×[Ca^{2+}]	0.000998994	7.078781	6.820022	20.1236
3	0.998502	135139×[Ca^{2+}]	0.00149772	6.752317	6.372507	13.5139
5	0.997506	82858.5×[Ca^{2+}]	0.00249355	6.387951	5.781113	8.28590
10	0.995028	45045.6×[Ca^{2+}]	0.00497236	6.005305	4.905674	4.50466
20	0.990131	28061.6×[Ca^{2+}]	0.00986914	5.770378	3.914543	2.80636
30	0.985348	23325.5×[Ca^{2+}]	0.0148525	5.693675	3.274599	2.33284
50	0.976280	20279.3×[Ca^{2+}]	0.0237195	5.641061	2.412300	2.02840
∞	0.942883	18418.9×[Ca^{2+}]	0.0571169	5.607684	0	1.84303
σ = – 1 μeq/m^2; [Cl$^-$] = 0.01 M; R_{Ca} = 0.1; [Na$^+$] = 0.00998008 M; [Ca^{2+}] = 0.00000996020 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	K(Ca/Na)$_{AS}$
1	0.389662	0.609838	0.000499360	6.748552	6.618065	40.0616
2	0.498027	0.500975	0.000997989	6.382753	6.129591	20.1176
3	0.565072	0.433432	0.00149599	6.180758	5.811388	13.5028
5	0.647941	0.349569	0.00249013	5.948969	5.363567	8.26310
10	0.744741	0.250295	0.00496357	5.695575	4.644787	4.45349
20	0.808384	0.181771	0.00984487	5.531336	3.765050	2.71545
30	0.827894	0.157499	0.0146064	5.474988	3.170793	2.21947
50	0.836401	0.139988	0.0236111	5.434910	2.349137	1.89354
∞	0.815423	0.128245	0.056332	5.408488	0	1.68945
σ = – 1 μeq/m^2; [Cl$^-$] = 0.01 M; R_{Ca} = 1; [Na$^+$] = 0.00980762 M; [Ca^{2+}] = 0.0000961894 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	K(Ca/Na)$_{AS}$
1	0.145515	0.853987	0.000498318	5.782699	5.652907	40.0616
2	0.198515	0.800490	0.000995057	5.481641	5,231689	20.1150
3	0.236207	0.762303	0.00149061	5.325629	4.963739	13.4958
5	0.290452	0.707069	0.00247850	5.158317	4.593119	8.24334
10	0.371921	0.623150	0.00492965	4.993232	4.007623	4.39076
20	0.449403	0.540856	0.00974092	4.897315	3.292154	2.56855
30	0.484932	0.500667	0.0144013	4.865855	2.800074	2.01137
50	0.513379	0.463500	0.0231206	4.843192	2.098607	1.61454
∞	0.516645	0.430336	0.0530196	4.827384	0	1.33399
σ = – 1 μeq/m^2; [Cl$^-$] = 0.01 M; R_{Ca} = 10; [Na$^+$] = 0.00854102 M; [Ca^{2+}] = 0.000729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	K(Ca/Na)$_{AS}$
1	0.0483028	0.951202	0.000495612	4.823482	4.693965	40.0665
2	0.0672166	0.931796	0.000987385	4.543953	4.295379	20.1189
3	0.0811876	0.917336	0.00147644	4.403641	4.045159	13.4978
5	0.102176	0.895376	0.00244749	4.259012	3.703836	8.23925
10	0.136226	0.858938	0.00483677	4.126636	3.178113	4.36367
20	0.173299	0.817254	0.00944667	4.058551	2.562443	2.48868
30	0.193508	0.792681	0.0138102	4.038687	2.155544	1.88542
50	0.213788	0.764522	0.0216905	4.025472	1.591909	1.42244
∞	0.227341	0.728017	0.0446421	4.017029	0	1.04227
σ = – 1 μeq/m^2; [Cl$^-$] = 0.01 M; $R_{Ca} \to \infty$; [Na$^+$] → 0 M; [Ca^{2+}] = 0.005 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	K(Ca/Na)$_{AS}$
1	2.18440×[Na$^+$]	0.999511	0.000488795	3.885969	3.756590	40.1000
2	3.05352×[Na$^+$]	0.999032	0.000968120	3.616435	3.368568	20.1520
3	3.70062×[Na$^+$]	0.998559	0.00144093	3.483400	3.126708	13.5302
5	4.68086×[Na$^+$]	0.997630	0.00237001	3.349271	2.799469	8.26948
10	6.29222×[Na$^+$]	0.995394	0.00460611	3.231860	2.304034	4.38590
20	8.08386×[Na$^+$]	0.991276	0.00872405	3.176384	1.744940	2.49331
30	9.08729×[Na$^+$]	0.987623	0.0123766	3.161893	1.393657	1.87609
50	10.1349×[Na$^+$]	0.981673	0.0183270	3.153388	0.939456	1.39642
∞	11.0368×[Na$^+$]	0.970333	0.0296669	3.149425	0	1.01990

Tab. A4. Surface charge σ_s = – 2 μeq/m^2 and chloride concentration [Cl^-] = 1 M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s , and mid-plane, y_m , potentials, and exchange constant $K(Ca/Na)_{AS}$ at various distances, h, between charged surfaces.

σ = – 2 μeq/m^2; [Cl^-] = 1 M; R_{Ca} → 0, [Na^+] = 1 M, [Ca^{2+}] → 0 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.975628	80.5452×[Ca^{2+}]	0.0243717	3.860526	3.601780	80.5940
2	0.952547	41.0463×[Ca^{2+}]	0.0474528	3.323263	2.827727	41.1412
3	0.930840	28.1778×[Ca^{2+}]	0.0691602	3.060130	2.347652	28.3162
5	0.891965	18.3576×[Ca^{2+}]	0.108035	2.800588	1.707122	18.5737
10	0.824436	12.1572×[Ca^{2+}]	0.175564	2.598406	0.811815	12.5083
20	0.784664	10.6536×[Ca^{2+}]	0.215336	2.547114	0.166725	11.0843
∞	0.781163	10.5779×[Ca^{2+}]	0.218836	2.544916	0	11.0155
σ = – 2 μeq/m^2; [Cl^-] = 1 M; R_{Ca} = 0.1, [Na^+] = 0.854102 M, [Ca^{2+}] = 0.0729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.274795	0.702017	0.0231876	2.796618	2.545697	81.2776
2	0.345991	0.609607	0.0444020	2.520696	2.050099	41.7996
3	0.385382	0.550711	0.0639068	2.388874	1.722943	28.9320
5	0.424164	0.478078	0.0977581	2.262325	1.263650	19.1039
10	0.443993	0.403658	0.152349	2.168208	0.592744	12.9210
20	0.440671	0.378994	0.180335	2.146448	0.115052	11.4602
∞	0.439962	0.377634	0.182404	2.145674	0	11.3897
σ = – 2 μeq/m^2; [Cl^-] = 1 M; R_{Ca} = 1, [Na^+] = 0.5 M, [Ca^{2+}] = 0.25 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.093113	0.884862	0.0220251	2.299910	2.051034	82.6294
2	0.120471	0.838278	0.0412510	2.068545	1.607234	43.1429
3	0.136818	0.804881	0.0583011	1.966496	1.321722	30.2784
5	0.154730	0.758866	0.0864042	1.877351	0.933189	20.4730
10	0.167834	0.705451	0.126715	1.821140	0.402284	14.3838
20	0.169609	0.686919	0.143472	1.811073	0.067622	13.0247
∞	0.169601	0.686006	0.144393	1.810805	0	12.9683
σ = – 2 μeq/m^2; [Cl^-] = 1 M; R_{Ca} = 10, [Na^+] = 0.2 M, [Ca^{2+}] = 0.4 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.0297044	0.948917	0.0213789	2.102891	1.854725	83.6634
2	0.0385676	0.921911	0.0395213	1.885944	1.428262	44.1522
3	0.0439072	0.900838	0.0552546	1.793533	1.157309	31.2887
5	0.0498177	0.869830	0.0803524	1.716381	0.795205	21.5171
10	0.0542880	0.821966	0.113746	1.671891	0.321818	15.5519
20	0.0550271	0.819157	0.125816	1.665099	0.048314	14.3039
∞	0.0550391	0.818612	0.126349	1.664956	0	14.2598
σ = – 2 μeq/m^2; [Cl^-] = 1 M; R_{Ca} → ∞, [Na^+] → 0 M, [Ca^{2+}] = 0.5 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.132987×[Na^+]	0.978977	0.0210229	2.008908	1.761159	84.3202
2	0.172740×[Na^+]	0.961422	0.0385777	1.798627	1.342745	44.7875
3	0.196695×[Na^+]	0.946394	0.0536057	1.710637	1.078694	31.9232
5	0.223195×[Na^+]	0.922874	0.0771256	1.638901	0.729317	22.1747
10	0.243260×[Na^+]	0.892928	0.107072	1.599490	0.283983	16.2956
20	0.246670×[Na^+]	0.882974	0.117026	1.599490	0.039696	15.1200
∞	0.246734×[Na^+]	0.882591	0.117409	1.593899	0	15.0829

Tab. A5. Surface charge $\sigma_s = -2$ μeq/m^2 and chloride concentration $[Cl^-] = 0.1$ M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s, and mid-plane, y_m, potentials, and exchange constant $K(Ca/Na)_{AS}$ at various distances, h, between charged surfaces.

σ = – 2 μeq/m^2; $[Cl^-]$ = 0.1 M; $R_{Ca} \to 0$, $[Na^+]$ = 0.1 M, $[Ca^{2+}] \to 0$ M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.997506	8049.46×$[Ca^{2+}]$	0.00249371	6.162496	5.903737	80.4951
2	0.995025	4093.94×$[Ca^{2+}]$	0.00497446	5.623426	5.127692	40.9404
3	0.992559	2800.56×$[Ca^{2+}]$	0.00744126	5.357381	4.643980	28.0071
5	0.987673	1802.12×$[Ca^{2+}]$	0.0123273	5.089137	3.989558	18.0236
10	0.975817	1123.33×$[Ca^{2+}]$	0.0241828	4.854538	2.999373	11.2382
20	0.954451	855.692×$[Ca^{2+}]$	0.0455491	4.744610	1.889202	8.56603
30	0.937593	793.300×$[Ca^{2+}]$	0.0624069	4.717300	1.215452	7.94548
50	0.919290	763.875×$[Ca^{2+}]$	0.0807096	4.704347	0.473937	7.65490
∞	0.913024	758.996×$[Ca^{2+}]$	0.0869755	4.702272	0	7.60735
σ = – 2 μeq/m^2; $[Cl^-]$ = 0.1 M; R_{Ca} = 0.1, $[Na^+]$ = 0.0980762 M, $[Ca^{2+}]$ = 0.000961894 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.293385	0.704136	0.00247917	4.959899	4.708926	80.4716
2	0.382457	0.612608	0.00493549	4.681831	4.210689	40.8471
3	0.438895	0.553733	0.00737167	4.547064	3.879042	27.8290
5	0.508834	0.478986	0.0121806	4.412893	3.403213	17.6696
10	0.585888	0.390352	0.0237594	4.295040	2.626067	10.5307
20	0.623142	0.332598	0.0442601	4.237029	1.683088	7.50522
30	0.625294	0.314723	0.0599829	4.221721	1.084458	6.74917
50	0.618423	0.305269	0.0763076	4.214302	0.419195	6.38220
∞	0.614838	0.303590	0.0815722	4.213129	0	6.32056
σ = – 2 μeq/m^2; $[Cl^-]$ = 0.1 M; R_{Ca} = 1, $[Na^+]$ = 0.0854102 M, $[Ca^{2+}]$ = 0.00729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.103315	0.894236	0.00244910	4.065555	3.816592	80.5178
2	0.140526	0.854625	0.00484984	3.831464	3.369295	40.8687
3	0.166333	0.826455	0.00721203	3.726060	3.078154	27.8118
5	0.201798	0.786378	0.0118241	3.629298	2.670036	17.5523
10	0.249124	0.728220	0.0226559	3.554078	2.026613	10.1490
20	0.282844	0.676348	0.0408074	3.521611	1.272099	6.76001
30	0.291444	0.654923	0.0536339	3.513693	0.802400	5.82691
50	0.292968	0.641548	0.0654839	3.510097	0.297130	5.34876
∞	0.292331	0.638922	0.0687465	3.509587	0	5.26599
σ = – 2 μeq/m^2; $[Cl^-]$ = 0.1 M; R_{Ca} = 10, $[Na^+]$ = 0.05 M, $[Ca^{2+}]$ = 0.025 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.0333921	0.964199	0.00240931	3.487444	3.239220	80.6562
2	0.0458131	0.949450	0.00473663	3.267495	2.808793	41.0010
3	0.0545680	0.938431	0.00700115	3.171551	2.531679	27.9343
5	0.0668173	0.921829	0.0113537	3.086847	2.148737	17.6486
10	0.0837347	0.895058	0.0212075	3.025585	1.563435	10.1763
20	0.0967309	0.866875	0.0363943	3.002231	0.917355	6.70080
30	0.100663	0.853478	0.0458588	2.997361	0.545182	5.73753
50	0.102114	0.844649	0.0532371	2.995492	0.182142	5.25744
∞	0.102196	0.842980	0.0548239	2.995286	0	5.18143
σ = – 2 μeq/m^2; $[Cl^-]$ = 0.1 M; $R_{Ca} \to \infty$, $[Na^+] \to 0$ M, $[Ca^{2+}]$ = 0.05 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	$-y_s$	$-y_m$	$K(Ca/Na)_{AS}$
1	0.473639×$[Na^+]$	0.997626	0.00237399	3.158335	2.910471	80.8454
2	0.650468× $[Na^+]$	0.995363	0.00463675	2.944922	2.487937	41.1879
3	0.775195×$[Na^+]$	0.993184	0.00681598	2.853329	2.217478	28.1196
5	0.949616×$[Na^+]$	0.989056	0.0109441	2.774128	1.846759	17.8316
10	1.18969×$[Na^+]$	0.980027	0.0199726	2.719167	1.291161	10.3601
20	1.37267×$[Na^+]$	0.967186	0.0328145	2.699913	0.705730	6.91380
30	1.42804×$[Na^+]$	0.960113	0.0398866	2.696405	0.392194	5.99233
50	1.44982×$[Na^+]$	0.955451	0.0445490	2.695265	0.115800	5.56765
∞	1.45178×$[Na^+]$	0.954683	0.0453171	2.695169	0	5.51143

Tab. A6. Surface charge $\sigma_s = -2$ μeq/m^2 and chloride concentration [Cl^-] = 0.01 M. Fractions of surface charge balanced by Na^+, Ca^{2+} and Cl^- ions, scaled surface, y_s , and mid-plane, y_m , potentials, and exchange constant $K(Ca/Na)_{AS}$ at various distances, h, between charged surfaces.

σ = – 2 μeq/m^2; [Cl^-] = 0.01 M; $R_{Ca} \to 0$, [Na^+] = 0.01 M, [Ca^{2+}] → 0 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	– y_s	– y_m	$K(Ca/Na)_{AS}$
1	0.999750	804941×[Ca^{2+}]	0.000249937	8.465075	8.206316	80.4941
2	0.999500	409384×[Ca^{2+}]	0.000499745	7.925987	7.430251	40.9384
3	0.999251	280039×[Ca^{2+}]	0.000749413	7.659912	6.946502	28.0039
5	0.998752	180177×[Ca^{2+}]	0.00124827	7.391578	6.291937	18.0178
10	0.997508	112231×[Ca^{2+}]	0.00249182	7.156592	5.300637	11.2231
20	0.995045	85215.0×[Ca^{2+}]	0.00495509	7.045302	4.180165	8.52160
30	0.992630	78585.5×[Ca^{2+}]	0.00736965	7.015991	3.472467	7.85870
50	0.988028	74690.8×[Ca^{2+}]	0.0119715	6.998365	2.541585	7.46932
∞	0.970523	72529.6×[Ca^{2+}]	0.0294767	6.988471	0	7.25356
σ = – 2 μeq/m^2; [Cl^-] = 0.01 M; R_{Ca} = 0.1, [Na^+] = 0.00998008 M, [Ca^{2+}] = 0.00000996020 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	– y_s	– y_m	$K(Ca/Na)_{AS}$
1	0.295583	0.704167	0.000249788	7.245041	6.994067	80.4607
2	0.386846	0.612655	0.000499344	6.966948	6.495800	40.8340
3	0.445466	0.553786	0.000748694	6.832147	6.164101	27.8137
5	0.519729	0.479024	0.00124675	6.697882	5.688072	17.6493
10	0.607303	0.390210	0.00248736	6.579688	4.909437	10.4942
20	0.663518	0.331541	0.00494095	6.520594	3.953666	7.42016
30	0.680510	0.312149	0.00734092	6.503786	3.315550	6.59801
50	0.689129	0.298972	0.0118994	6.493061	2.226415	6.08448
∞	0.680389	0.290722	0.0288892	6.486653	0	5.78098
σ = – 2 μeq/m^2; [Cl^-] = 0.01 M; R_{Ca} = 1, [Na^+] = 0.00980762 M, [Ca^{2+}] = 0.0000961894 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	– y_s	– y_m	$K(Ca/Na)_{AS}$
1	0.105202	0.894549	0.000249416	6.229835	5.980870	80.4530
2	0.144294	0.855208	0.000498276	5.995696	5.533513	40.7983
3	0.171976	0.827277	0.000746693	5.890233	5.242272	27.7353
5	0.211163	0.787594	0.00124224	5.793330	4.833796	17.4615
10	0.267583	0.729944	0.00247302	5.717679	4.187923	10.0130
20	0.317921	0.677186	0.00489279	5.684121	3.414973	6.50306
30	0.339940	0.652819	0.00724153	5.674912	2.894733	5.42153
50	0.357225	0.631124	0.0116509	5.668865	2.164095	4.64552
∞	0.360413	0.612518	0.0270685	5.664957	0	4.09406
σ = – 2 μeq/m^2; [Cl^-] = 0.01 M; R_{Ca} = 10, [Na^+] = 0.00854102 M, [Ca^{2+}] = 0.000729490 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	– y_s	– y_m	$K(Ca/Na)_{AS}$
1	0.0344270	0.965325	0.000248451	5.254543	5.006316	80.4551
2	0.0478796	0.951625	0.000495500	5.034517	4.575789	40.7900
3	0.0576623	0.941596	0.000741476	4.938480	4.298515	27.7104
5	0.0719538	0.926816	0.00123041	4.853569	3.915010	17.3931
10	0.0938641	0.903701	0.00243500	4.791738	3.326066	9.82112
20	0.116040	0.879197	0.00476274	4.767171	2.655569	6.09936
30	0.127563	0.865467	0.00697014	4.761110	2.224377	4.86061
50	0.138852	0.850179	0.0109692	4.757404	1.637821	3.87711
∞	0.146421	0.830771	0.0228077	4.755190	0	3.03053
σ = – 2 μeq/m^2; [Cl^-] = 0.01 M; $R_{Ca} \to \infty$, [Na^+] → 0 M, [Ca^{2+}] = 0.005 M						
h, Å	F_{Na}	F_{Ca}	F_{Cl}	– y_s	– y_m	$K(Ca/Na)_{AS}$
1	1.55174×[Na^+]	0.999754	0.000246015	4.309569	4.061701	80.4879
2	2.16468×[Na^+]	0.999511	0.000488511	4.096055	3.639034	40.8187
3	2.61264×[Na^+]	0.999272	0.000728362	4.004343	3.368366	27.7324
5	3.27048×[Na^+]	0.998799	0.00120075	3.924884	2.996922	17.3976
10	4.27048×[Na^+]	0.997660	0.00234035	3.869254	2.436783	9.77740
20	5.33962×[Na^+]	0.995557	0.00444342	3.848731	1.823273	5.97833
30	5.90115×[Na^+]	0.993687	0.00631305	3.844153	1.448489	4.68681
50	6.47364×[Na^+]	0.990629	0.00937068	3.841664	0.972597	3.64176
∞	6.96021×[Na^+]	0.984721	0.0152793	3.840569	0	2.77591

APPENDIX B: Numerical integration of the Poisson-Boltzmann equation

The Poisson-Boltzmann equation for flat diffuse layer is:

$$d^2\varphi_x/dx^2 = -\rho_x/\varepsilon_o\varepsilon = -(1000F/\varepsilon_o\varepsilon)\Sigma z_i c_i \exp(-z_i F\varphi_x/RT) \quad \text{or} \quad (B1)$$

$$d^2y_x/dx^2 = -(1000F^2/RT\varepsilon_o\varepsilon)\Sigma z_i c_i \exp(-z_i y_x) \quad (B1a)$$

Here φ_x is potential (Volts), $y_x = F\varphi/RT$ is scaled potential, and ρ_x is charge density (C/m^3) at distance x (meters) from charged surface; ε_o is dielectric constant of free space (8.8542×10^{-12} F/m = $C\times V^{-1}\times m^{-1}$), ε is dielectric constant of medium (dimensionless; 78.47 for water at 25°C), z_i is charge of ion, c_i is molar concentration of ion in the bulk solution (moles per liter), 1000 is m^3-to-dm^3 conversion factor, 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).

Multiplying of both sides of Eq. (B1a) by $2dy_x$, one may obtain equality:

$$2dy_x\times d^2y_x/dx^2 = d(dy_x/dx)^2 = -(2000F^2/RT\varepsilon_o\varepsilon)\ \Sigma z_i c_i \exp(-z_i y_x)dy_x \quad (B2)$$

Integration of Eq. (B2) from $y_x = y_m$ (scaled potential at mid-plane between charged surfaces) to y_x gives relation:

$$dy_x/dx = -\operatorname{sgn}(y_x)\times(2000F^2/RT\varepsilon_o\varepsilon)^{0.5}\times[\Sigma c_i\{\exp(-z_i y_x) - \exp(-z_i y_m)\}]^{0.5} \quad \text{or} \quad (B3)$$

$$dy_x/d[x, Å] = -\operatorname{sgn}(y_x)\times(1/3.04)\times[\Sigma c_i\{\exp(-z_i y_x) - \exp(-z_i y_m)\}]^{0.5} \quad (B3a)$$

In the absence of overlap, scaled mid-plane potential in Eq. (B3) should be equated to zero.

In general case, surface charge is related with field strength $d\varphi_x/dx$ at interface (x = 0) as:

$$\sigma_s,\ C/m^2 = -\varepsilon_o\varepsilon(d\varphi_x/dx)_{x=0} = -(RT\varepsilon_o\varepsilon/F)\times(dy_x/dx)_{x=0} \quad (B4)$$

Substitution of Eq (B4) into Eq (B3) and scaling by $10^6/F$ μeq/C gives charge-potential relationship:

$$\sigma_s,\ \mu eq/m^2 = \operatorname{sgn}(\varphi_s)\times(10^6/F)\times(2000RT\varepsilon_o\varepsilon)^{0.5}\times[\Sigma c_i\{\exp(-z_i y_s) - \exp(-z_i y_m)\}]^{0.5} \quad \text{or} \quad (B5)$$

$$\sigma_s,\ \mu eq/m^2 = \operatorname{sgn}(\varphi_s)\times0.608\times[\Sigma c_i\{\exp(-z_i y_s) - \exp(-z_i y_m)\}]^{0.5} \quad (B5a)$$

In the absence of overlap, scaled mid-plane potential in Eq. (B5) should be equated to zero.

If values of scaled surface y_s and mid-plane y_m potential are known, the distance between charged surfaces may be calculated from Eq (B3):

$$[h, Å] = -2\times\operatorname{sgn}(y_s)\times3.04\int_{y=y_m}^{y=y_s}\{1/[\Sigma c_i\{\exp(-z_i y) - \exp(-z_i y_m)\}]^{0.5}\}dy \quad (B6)$$

Factor 2 in Eq. (B6) arises due to replacement of dx in Eq (B3) by dh = 2dx. At small $y-y_m$, numerical integration of Eq. (B6) is very uncertain. Relation, valid for $y - y_m \to 0$, may be deduced from (B6), applying approximation $\{\exp(-zy) - \exp(-zy_m)\} \approx -z(y - y_m)\exp(-zy_m)$:

$$\Delta[h, Å] \approx 4\times3.04\times|y-y_m|^{0.5}/|\Sigma z_i c_i \exp(-z_i y_m)|^{0.5} \quad (B7)$$

However, range of applicability of Eq (B7) is small. Better result may be obtained with use of modified Eq. (B7):

$$\Delta[h, Å] \approx 4\times3.04\times|y-y_m|/[\Sigma c_i\{\exp(-z_i y) - \exp(-z_i y_m)\}]^{0.5} \quad \text{(B8)}$$

For calculation of data in Tabs A1-A6, the following algorithm was applied.

Input data: Cl, R_{Ca}, [σ_s, μeq/m^2], y_s
Apply: $y_m = 0$
Calculate: $Na = \{(0.25 + 2R_{Ca}Cl)^{0.5} - 0.5\}/2R_{Ca}$; $Ca = \{Cl - Na\}/2$
$Sigma = 0.608sgn(y_s)\{[Na^+](\exp(-y_s)-1)+[Ca^{2+}](\exp(-2y_s)-1)+[Cl^-](\exp(y_s)-1)\}^{0.5}$
IF ABS(Sigma)<ABS[σ_s , μeq/m^2] OR $y_s\times$[σ_s , μeq/m^2]<0 THEN PRINT: "Wrong data": END

(Cycle 1)
Calculate:
$Sigma=0.608sgn(y_s)\{Na(\exp(-y_s)-\exp(-y_m))+Ca(\exp(-2y_s)-\exp(-2y_m))+Cl(\exp(y_s)-\exp(y_m))\}^{0.5}$
If ABS{Sigma/[σ_s , μeq/m^2] – 1}>10^{-12} THEN:
Calculate $y_m = y_m + 0.05\times sign(y_s)\times\ln(Sigma/[\sigma_s , μeq/m^2])$ AND repeat Cycle 1
(End of Cycle 1)

Calculate:
$dY = (y_s-y_m)/1000000$; $deltaY = 10\times dY$; $y = y_m + deltaY$; $y_{av} = y_m + 0.5\times deltaY$
$h = 12.16\times|deltaY|/\{Na(\exp(-y)-\exp(-y_m))+Ca(\exp(-2y)-\exp(-2y_m))+Cl(\exp(y)-\exp(-y_m))\}^{0.5}$
$DNa = 0.05\times Na\times h\times[\exp\{-y\}+ 4\exp\{-y_{av}\}+ \exp\{-y_m\} - 6]/6$
$DCa = 0.05\times Ca\times h\times[\exp\{-2y\}+ 4\exp\{-2y_{av}\}+ \exp\{-2y_m\} - 6]/6$
$DCl = 0.05\times Cl\times h\times[\exp\{y\}+ 4\exp\{y_{av}\}+ \exp\{y_m\} - 6]/6$

(Cycle 2)
FOR n = 11 TO 1000000 STEP 1
Calculate: $y_{n-1} = y_m + (n-1)\times dY$; $y_{av} = y_m + (n-0.5)\times dY$; $y_n = y_m + n\times dY$
$f_{n-1} = 1/\{Na(\exp(-y_{n-1})-\exp(-y_m))+Ca(\exp(-2y_{n-1})-\exp(-2y_m))+Cl(\exp(y_{n-1})-\exp(-y_m))\}^{0.5}$
$f_{av} = 1/\{Na(\exp(-y_{av})-\exp(-y_m))+Ca(\exp(-2y_{av})-\exp(-2y_m))+Cl(\exp(y_{av})-\exp(-y_m))\}^{0.5}$
$f_n = 1/\{Na(\exp(-y_n)-\exp(-y_m))+Ca(\exp(-2y_n)-\exp(-2y_m))+Cl(\exp(y_n)-\exp(-y_m))\}^{0.5}$
$f_{tot} = (f_{n-1} +4f_{av}+f_n)/6$
$h = h + 6.08\times dY\times f_{tot}$
$DNa = DNa + 0.05\times Na\times(6.08\times dY\times f_{tot})\times[\exp\{-y_{n-1}\}+ 4\exp\{-y_{av}\}+ \exp\{-y_n\} - 6]/6$
$DCa = DCa + 0.05\times Ca\times(6.08\times dY\times f_{tot})\times [\exp\{-2y_{n-1}\}+ 4\exp\{-2y_{av}\}+ \exp\{-2y_n\} - 6]/6$
$DCl = DCl + 0.05\times Cl\times(6.08\times dY\times f_{tot})\times [\exp\{y_{n-1}\}+ 4\exp\{y_{av}\}+ \exp\{y_n\} - 6]/6$
NEXT n
(End of Cycle 2)

Calculate: $Kex = 2\{DCa - Ca\times DCl/Cl\}\times[\sigma_s, μeq/m^2]/\{DNa - Na\times DCl/Cl\}^2/R_{Ca}$
$FNa = -DNa/[\sigma_s, μeq/m^2]$; $FCa = -2\times DCa/[\sigma_s, μeq/m^2]$; $FCl = DCl/[\sigma_s, μeq/m^2]$

PRINT "h =" h; "y_s =" y_s; "y_m =" y_m; "FNa =" FNa; "FCa =" FCa; "FCl =" FCl; "Kex =" Kex
END (End of program)

To obtain results at round values of distance between charged planes (h, Å) the input value of scaled surface potential, y_s , was varied manually. Initial 10 steps of integration were approximated by Eq. (B8). Double accuracy (16 digits) was applied.