

# Supplemental Material for “Coulombic surface-ion interactions induce non-linear and chemistry-specific charging kinetics”

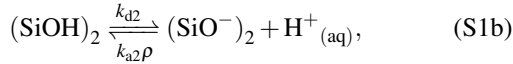
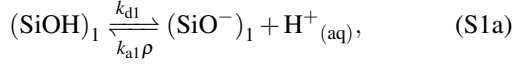
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## I. WHEN CAN MULTIPLE REACTIONS BE DESCRIBED BY SINGLE-REACTION KINETICS?

The single-reaction (one-pKa) charging reaction presented in this Letter is a simplified representation for many real liquid-solid interfaces, which often require multiple surface charging reactions for the reproduction of measured equilibrium Langmuir isotherms[1–4]. In this Supplemental Material we show that for a wide range of conditions a two-reaction model is well approximated by the single-reaction model presented in this Letter. For simplicity we will consider a two-reaction (two-pKa) system with two distinct surface-sites labeled  $(\text{SiOH})_1$  and  $(\text{SiOH})_2$ , charged by similar desorptive surface reactions but with different ad- and desorption rates



and hence the sites have different equilibrium areal densities  $\sigma_{\text{eq},1} \neq \sigma_{\text{eq},2}$  if the site densities  $\Gamma_i$  or equilibrium constants  $K_i = k_{a,i}\rho/k_{d,i}$  are unequal. The Langmuir equation describing their charging kinetics is

$$\partial_t \sigma_1 = k_{d1}(\Gamma_1 - \sigma_1) - k_{a1}\rho(\sigma_e)\sigma_1, \quad (\text{S2a})$$

$$\partial_t \sigma_2 = k_{d2}(\Gamma_2 - \sigma_2) - k_{a2}\rho(\sigma_e)\sigma_2, \quad (\text{S2b})$$

with the resulting areal charge density  $\sigma_e = \sigma_1 + \sigma_2$  coupling the two reactions. As both reactions have the same reactive ion ( $\text{H}^+$ ) a concentration change  $\Delta\rho$  at the surface would cause the equilibrium to shift for both reactions, and the equilibration kinetics resulting after this concentration shift would in principle need to be described by the two coupled non-linear differential equations (S2a) and (S2b) as they are coupled by the Gouy-Chapman “closure”, given by Eq. (3) in the Letter. However, here we show that if the two reactions have dissimilar equilibrium constants  $K_i$  or site densities  $\Gamma_i$  one of the two differential equations can almost always be neglected, as when the equilibrium constants differ so does the shift in equilibrium charge density  $\Delta\sigma_i = \sigma_{\text{eq},i}(\rho + \Delta\rho) - \sigma_{\text{eq},i}(\rho)$  for a given concentration shock  $\Delta\rho$ . When the difference in equilibrium charge densities of the two sites is very unequal (either  $\Delta\sigma_1 \gg \Delta\sigma_2$  or  $\Delta\sigma_1 \ll \Delta\sigma_2$ ) the change in surface charge can be described using a single reaction model (as  $\partial_t \sigma_e \simeq \partial_t \sigma_1$  or  $\partial_t \sigma_e \simeq \partial_t \sigma_2$ ). Solving for the coupled-Langmuir kinetics Eq. (2) in steady-state,  $\partial_t \sigma_i = 0$ , we find for  $\sigma_{i,\text{eq}} \ll \Gamma_i$  that the relative change in the equilibrium surface charge  $\Delta\sigma_i/\Delta\sigma_2 \propto (\Gamma_1 K_1)/(\Gamma_2 K_2)$  while for nearly saturated

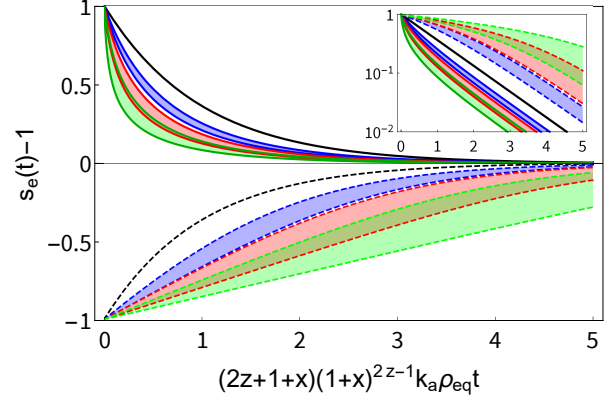


Figure S1. Replotting of Fig.1(a) showing charge relaxation for ion valencies  $z = 0, 1, 2, 3$  (respectively black, blue, red, green) calculated with curves not originating from Eq. (4) in the main Letter but instead plotted using Eq. (S5) with dimensionless static background-charge  $x \in [0, 1]$ . The outermost curves with  $x = 0$  revert exactly to those described by Eq. (4) in the main Letter, while curves with  $x = 1$  lie significantly closer to the black curve showing single-exponential relaxation, with intermediate  $x$  lying in the shaded region. Note that the near-equilibrium decay rate has changed from  $(2z + 1)k_a\rho_{\text{eq}}$  to  $(z + 1 + x)(1 + x)^{2z-1}k_a\rho_{\text{eq}}$  which for  $z = 3$  and  $x = 1$  yields a factor 32 difference in the near-equilibrium decay rate. In general however for small  $x$  the charging kinetics is well described by the single reaction of Eq. (4) in the main Letter.

surfaces with  $\sigma_{\text{eq}} \approx \Gamma$  the relative shift scales as  $\Delta\sigma_1/\Delta\sigma_2 \propto (\Gamma_1 K_2)/(\Gamma_2 K_1)$ . As long as  $\Delta\sigma_1/\Delta\sigma_2$  deviates significantly from unity, the shift in one of the two equilibrium-densities can be neglected for the shift in the total charge density. To find an explicit maximum bound for which this approximation is valid we calculate the maximum concentration shock  $\Delta\rho_m \in \rho[-1, \infty]$  for which this approximation holds by solving for  $\Delta\sigma_1/\Delta\sigma_2 = 1$ . This has a trivial solution  $\Delta\rho = 0$  when  $\Gamma_1 = \Gamma_2$  and  $K_1 = K_2$  and a non-trivial solution

$$\frac{\Delta\rho_m}{\rho} = \frac{1}{K_1 K_2 \rho^2} \frac{\Gamma_1 K_1 \rho - \Gamma_2 K_2 \rho}{\Gamma_2 (1 + K_1 \rho) - \Gamma_1 (1 + K_2 \rho)} \frac{\Gamma_1 (2 + K_2 \rho) - \Gamma_2 (2 + K_1 \rho)}{\Gamma_1 (1 + K_2 \rho) - \Gamma_2 (1 + K_1 \rho)}, \quad (\text{S3})$$

which simplifies to  $\Delta\rho_m/\rho = (K_1 K_2 \rho^2)^{-1} - 1$  in the case that  $\Gamma_1 \simeq \Gamma_2$ . In general, the range of validity of Eq. (S3) is large when  $K_1$  and  $K_2$  are very unequal, except close to a concentration where  $\rho^2 K_1 K_2 = 1$  where  $\Delta\rho_m$  tends to zero. Interestingly, in this case the charge density is exactly half-occupied  $\sigma_e = (\Gamma_1 + \Gamma_2)/2$ , which is rare for most

experimental conditions. For all other concentrations  $\rho$  a very large range  $\Delta\rho_m/\rho$  of concentration shocks remains over which a two-reaction system essentially equilibrates through a single charging reaction. However, while the dynamics will be governed by a single reaction, there will be a static background charge due to which  $\sigma_1 \neq \sigma_e$  such that the single reaction is still not exactly equal to the single-reaction kinetics in the Letter. That the deviation from the single-reaction kinetics in the Letter due to this static background charge is minor will be shown in the next paragraph.

As the total surface charge density (in units of the elementary charge) is given by  $\sigma_e = \sigma_1 + \sigma_2$ , the Gouy-Chapman relation (Eq. (3) in the Letter) between the surface occupancy  $\sigma_1$  and concentration  $\rho$  for two reactions now reads

$$\rho(\sigma_1) = \left( \frac{z(\sigma_1 + \sigma_2)}{\sigma^*} + \sqrt{1 + \left( \frac{z(\sigma_1 + \sigma_2)}{\sigma^*} \right)^2} \right)^{2z}. \quad (\text{S4})$$

As discussed in the previous section we will now assume that  $\Delta\rho \ll \Delta\rho_m$  and without loss of generality we identify  $\sigma_{\text{eq},2}$  as the static-charge density ( $\Delta\sigma_1/\Delta\sigma_2 \gg 1$ ) from which follows  $\sigma_2 \simeq \sigma_{\text{eq},2}(\rho) \simeq \sigma_{\text{eq},2}(\rho + \Delta\rho) = \text{cnst}$ . The non-dimensional change in total surface charge will then be  $\partial_t s_e = \partial_t \sigma_e / \sigma_{\text{eq},e} \simeq \partial_t \sigma_1 / \sigma_{\text{eq},e}$  and when  $\sigma_{\text{eq},e} \gg \sigma^*$  by combining Eq. (S2a) and Eq. (S4) we find

$$-\partial_t s_e = k_{d1}(s_e - 1) + k_{a1}\rho_{\text{eq}}(s_e(s_e + x)^{2z} - (1 + x)^{2z}), \quad (\text{S5})$$

where the dimensionless static surface charge density  $x = \sigma_{\text{eq},2}/\sigma_{\text{eq},e} \in [0, 1]$  is the ratio of static charge  $\sigma_{\text{eq},2}(\rho + \Delta\rho)$  after the concentration shock. Interestingly, the near-equilibrium decay rate  $\tau_-$  is altered from  $(2z + 1)k_a\rho_{\text{eq}}$  to  $(2z + 1 + x)(1 + x)^{2z-1}k_a\rho_{\text{eq}}$  and hence the deviation from uncharged Langmuir kinetics becomes even larger if the background surface charge is included. Clearly both the timescale and dynamics revert back to the single-reaction kinetics of Eq. (4) in the Letter when  $x \ll 1$ . To check how much the dynamics is affected at intermediate  $x$  we replot Fig.1(a) in the Letter but now with Eq. (S5) with  $z = 0, 1, 2, 3$  (black, blue, red, green) and  $s = 1$  and  $s = -0.99$  instead of Eq. (4). The resulting shaded regions in Fig.S1 represent curves with different  $x \in [0, 1]$ . We observe that for increasing  $x$  the dynamics moves closer to single-exponential decay (black line), with this shift being more pronounced for increasing  $z$ . However, even for  $x = 1$  there is no over-dramatic difference from the single-reaction kinetics explored in the Letter and in many cases a two-reaction system is well approximated by the single-reaction model in the Letter. However one should be cautious when extracting the ion valency from dynamics around  $x \simeq 1$  as here the dynamics closely resembles that of a single ion with  $z - 1$ . We expect this may occur in processes such as the adsorption of heavy metal ions from ground water which occurs on pre-charged substrates [3]. Under these conditions surface charging can be readily described using Eq. (S5).

To summarize, here we have shown that the one-pKa charging reaction is a valid approximation for more complex sys-

tems, involving multiple charging reactions, when (i) the ratio of the equilibrium constant  $K_1/K_2$  is not close to unity and (ii) the concentration shock  $\Delta\rho$  is constrained within a range  $\Delta\rho_m$  which we show to be generally large.

## II. SURFACE CHARGING KINETICS FROM PRESSURE-JUMP EXPERIMENTS

While experimental investigations of surface charging kinetics are rare, several kinetic studies employing a pressure-jump technique exist [5, 6]. In such an experiment a mixture of colloidal particles and aqueous electrolytes is slowly pressurized to more than 1 MPa, thereby shifting the surface reactions at the colloidal surface to a high-pressure equilibrium. When this pressure is suddenly released, the solution pressure converges to atmospheric pressure in  $\simeq 0.1$  ms. After this jump, the colloidal surface charge must revert from its high-pressure equilibrium to its atmospheric equilibrium. The change in surface charge is measured indirectly, by using the solution conductance as a proxy for the surface charge. While it is unclear what the exact relation between charge and conductance is, a linear relation is often assumed [6].

Of particular interest is a set of experiments where the adsorption of divalent transition metals such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Co}^{2+}$  onto  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ) particles is studied. Here the authors reject simplest adsorption mechanism, for  $\text{Cu}^{2+}$  given by



because this single-step reaction does not show single-exponential decay [5]. Their theoretical model used for analysis fixes the surface (zeta) potential, and hence they find that multiple reactions are needed to explain the observed charge equilibration [5–7]. While their analysis is valid for fixed surface potential, for a potential varying with surface charge we actually expect deviations from single-exponential decay, as shown by Eq. (4) in our Letter. The Langmuir-Gouy-Chapman dynamics of reaction (S5) with  $z = 2$  for surface potentials larger than 50 mV is given by

$$-\partial_t s_+ = k_a\rho_{\text{eq}}(s_+^{-3} - s_+^{-4}) + k_d(s_+ - s_+^{-4}). \quad (\text{S6})$$

To test whether the non-linear dynamics observed in the pressure-jump experiment are explained by Eq. (S6), we extract the experimental data from the relevant pressure-jump experiment for copper adsorption (Fig.1 in Ref. [5]). In this experiment it is found that the conductivity after the pressure jump decreases and reaches a constant value within 200 ms. In Fig.S2 we compare the experimental data (symbols) with equilibration expected from Eq. (S6) (black line), where we assume the experimentally common case where  $\sigma_{\text{eq}} \ll \Gamma$  and extract the reaction time  $\tau_+ = (5k_d)^{-1} \simeq 27$  ms from the single-exponential, late time, relaxation (green line). As the final equilibrium charge density is not measured in a

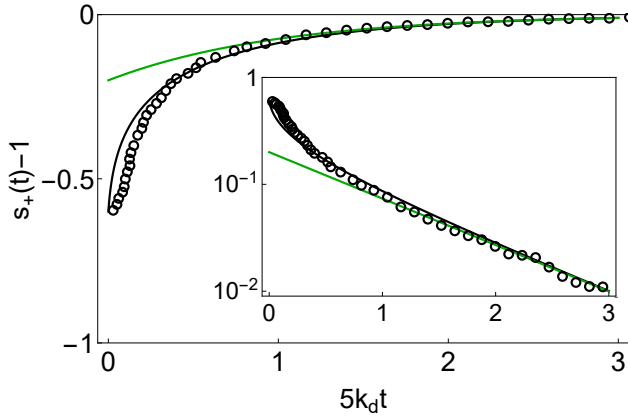


Figure S2. Comparison between experimental data from Fig.1 of Ref. [5] (symbols), single exponential decay (green) and non-linear dynamics (black, Eq. (S6)) with initial degree of undercharging  $s(0) - 1 = -0.6$ . The reaction time  $\tau_+ \simeq 27$  ms is fitted from the late time decay, yielding  $k_d^{-1} \simeq 135$  ms. Inset shows the same data in a semi-logarithmic representation.

pressure-jump experiment we use the degree of undercharging  $s(0) - 1 \simeq -0.6$  as a fit parameter, where we note that an undercharged surface naturally explains why conductivity decreases: during equilibration mobile copper ions are taken out of solution. It can be seen that the difference between the single exponential decay (green) and experimental data (symbols) is large, but that Eq. (S6) (black) can naturally explain a large part of the deviation from single-exponential decay, without needing to introduce a second reaction with a different timescale.

While further analysis is required to reinstate reaction mechanism (S5), our analysis shows the importance of taking Coulombic surface-ion interactions into account when considering kinetics. Not only do we show that non-linear decay is readily captured by our model, also the desorption time  $k_d^{-1}$  is five times slower than the late-time decay  $\tau_+$ , in this divalent case. Furthermore, we have demonstrated that chemical information can easily be extracted from a single equilibration curve, even when the initial degree of undercharging is unknown.

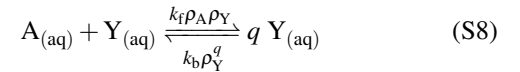
### III. SIMILARITY BETWEEN SURFACE CHARGING AND AUTOCATALYTIC KINETICS

Here we will show the similarity between classical autocatalytic kinetics and surface charging as described by Eq. (4) in the Letter. First we derive an approximate solution for this Chini differential Eq. (4) in the main text, by expanding it up to second order around  $s = 1$  obtaining a Bernoulli differential equation (Supplementary Ref.[8]). Solving this equation

by standard methods we obtain

$$s_{\pm}(t) - 1 = \frac{(s_{\pm}(0) - 1)e^{-t/\tau_{\pm}}}{1 \mp z(1 - e^{-t/\tau_{\pm}}) \left( s_{\pm}(0) - 1 \pm \frac{s_{\pm}(0) - 1}{(2z + 1)(k_d/k_a \rho_{\text{eq}})^{\pm 1} + 1} \right)}, \quad (\text{S7})$$

where  $\tau_{\pm}$  is given by Eq. (5) in the Letter. Our Eq. (S7) reverts to single exponential decay when  $(s_{\pm}(0) - 1)z \ll 1$ , and is valid only as long as  $\mp z(s_{\pm}(0) - 1) \gg -1$ . For most practical purposes Eq. (S7) is not of much use, however it is interesting to note that a similar solution exists for autocatalytic equations thereby substantiating the claim that surface charging is autocatalytic. To make this comparison explicit we consider the simplest possible autocatalytic reaction (Eq. (1a') from Ref.[9]),



where the aqueous reactant  $Y_{(\text{aq})}$  together with reactant  $A_{(\text{aq})}$  produces  $q$  copies of itself. The reaction is autocatalytic when the autocatalytic order  $q \geq 2$ . When the concentration  $\rho_A$  is constant the production rate of  $Y_{(\text{aq})}$  is given by the Chini differential equation

$$-\partial_t y = k_f \rho_A (y^q - y), \quad (\text{S9})$$

with  $y = \rho_Y / \rho_{Y,\text{eq}}$ , which already shows similarities to Eq. (4) in the Letter. To obtain a solvable Bernoulli equation we expand Eq. (S9) up to second order around  $x = 1$ , which has the solution

$$y(t) - 1 = \frac{(y(0) - 1)e^{-t/\tau_y}}{1 - \frac{q}{2}(y(0) - 1)(1 - e^{-t/\tau_y})}, \quad (\text{S10})$$

with  $\tau_y = (q - 1)k_f \rho_A$ . While Eq. (S10) is already very similar to Eq. (S7), the similarity becomes even more apparent when comparing the autocatalytic dynamics to the dynamics of an adsorptively charged surface with  $\sigma_{+, \text{eq}} \ll \Gamma$  (where  $k_d \gg k_a \rho_{\text{eq}}$ ) in which case Eq. (S7) simplifies to

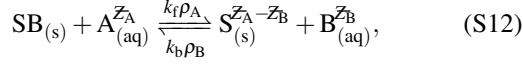
$$s_+(t) - 1 = \frac{(s_+(0) - 1)e^{-t/\tau_+}}{1 - z(s_+(0) - 1)(1 - e^{-t/\tau_+})}. \quad (\text{S11})$$

Comparing Eq. (S10) with Eq. (S11) we find the only difference is the definition of the timescale  $\tau_i$  and that the ion-valency  $z$  replaces the autocatalytic order  $q/2$ . This correspondence between the ion valency  $z$  and autocatalytic order  $q$  supports the interpretation that the Coulombic ion-surface interactions acts autocatalytically.

### IV. CHARGING DYNAMICS OF ION DISPLACEMENT REACTIONS

Here we will generalize the derivation of Eq. (4) in the main text from single-ion reactions to two-ion reaction also known

as ion-displacement reactions, yielding Eq. (7) in the main text. We will consider a general form for the single-step ion-displacement reaction where an aqueous ion  $A_{(aq)}^{Z_A}$  displaces from the (uncharged) surface group  $SB_{(s)}$  the ion  $B_{(aq)}^{Z_B}$ , leaving a charged surface site  $SA_{(s)}^{Z_A-Z_B}$  combining into the reaction



where  $Z_A$  and  $Z_B$  are the valencies of ad- and desorbing ions A and B respectively, which contrary to the ion-valency  $z_i$  in the main text is here not considered to be strictly positive as the total charge difference between A and B is important. The resulting charge of the surface groups is given by  $Z_S = Z_A - Z_B$ , such that the surface charge is  $e\sigma Z_S$ . As in the main text, the charging dynamics will be described by Langmuir kinetics, which assumes identical and independent surface sites such that

$$\partial_t \sigma = k_A \rho_A(\sigma)(\Gamma - \sigma) - k_B \rho_B(\sigma)\sigma. \quad (S13)$$

Note that now both terms contain the non-trivial  $\rho(\sigma)$  dependence, which allows for sigmoidal equilibration as discussed

in the Letter. For  $\rho(\sigma)$  we use the Gouy-Chapman expression

$$\rho_i(\sigma) = \rho_{b,i} \left( \frac{z_S \sigma}{\sigma^*} + \sqrt{1 + \left( \frac{z_S \sigma}{\sigma^*} \right)^2} \right)^{\pm 2z_i}, \quad (S14)$$

where  $z_i = |Z_i|$ . The exponent for  $\rho_i$  is positive when  $Z_i Z_S < 0$  and negative when  $Z_i Z_S > 0$ . When  $Z_i Z_S = 0$  the dynamics revert to the single-ion charging reaction in the main text. In the high charge limit  $|\phi_{eq}| > 2$  (when  $z_S \sigma_{eq} / \sigma^* > 1$ ) we find

$$-\partial_t s = k_A \rho_{A,eq}(s^{1+2z_A} - s^{\pm 2z_A}) + k_B \rho_{B,eq}(s^{1+2z_B} - s^{\pm 2z_B}), \quad (S15)$$

where the  $\pm$  sign in front of  $z_i$  is negative when  $Z_i Z_S > 0$  and positive when  $Z_i Z_S < 0$ . Substituting  $Z_A = +2$  and  $Z_B = +1$  (hence  $Z_S = +1$ ) we find Eq. (7a) in the main text, while substituting  $Z_A = -1$  and  $Z_B = -2$  (hence  $Z_S = +1$ ) yields Eq. (7b). Furthermore, for  $Z_A = 0$  this equation reverts to desorptive charging and for  $Z_B = 0$  this equation reverts to adsorptive charging as described in the Letter. The presented derivation can be naturally extended to single-step reactions involving an arbitrary number of charged species.

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- [1] W. Van Riemsdijk, J. De Wit, L. Koopal, and G. Bolt, *Journal of colloid and interface science* **116**, 511 (1987).
- [2] T. Hiemstra, W. H. Van Riemsdijk, and G. Bolt, *Journal of colloid and interface science* **133**, 91 (1989).
- [3] M. Kosmulski, *Chemical properties of material surfaces*, Vol. 102 (CRC press, 2001).
- [4] M. Borkovec, B. Jönsson, and G. J. Koper, in *Surface and colloid science* (Springer, 2001) pp. 99–339.
- [5] K. Hachiya, M. Sasaki, T. Ikeda, N. Mikami, and T. Yasunaga, *The Journal of Physical Chemistry* **88**, 27 (1984).
- [6] D. L. Sparks, *Kinetics of soil chemical processes* (Academic Press, 2013).
- [7] C. Bernasconi, *Relaxation Kinetics* (Academic Press San Diego, 1976).
- [8] G. Teschl, *Ordinary differential equations and dynamical systems*, Vol. 140 (American Mathematical Soc., 2012).
- [9] P. Schuster, *Monatshefte für Chemie-Chemical Monthly* **150**, 763 (2019).