

A New Monte Carlo Method for the Titration of Molecules and Minerals

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Abstract. The charge state of molecules and solid/liquid interfaces is of paramount importance in the understanding of the reactivity and the physico-chemical properties of many systems. In this work, we propose a new Monte Carlo method in the grand canonical ensemble using the primitive model, which allows us to simulate the titration behavior of molecules or solids at constant pH. The method is applied to the charging process of colloidal silica particles dispersed in a mono-valent salt solution of various concentrations and pH. An excellent agreement is found between experimental and simulated results.

For the sake of simplicity we shall consider a planar solid/liquid interface. The solid surface is defined by explicit titratable sites distributed on a square lattice with the same intrinsic dissociation constant K_0 . The liquid phase is described by the so called primitive model (PM) where the ions are charged hard spheres embedded in a dielectric continuum that represent the solvent (for more details see [1]). The titration can be depicted in the usual way,



from which the intrinsic dissociation constant can be expressed,

$$K_0 = \frac{a_H a_A}{a_{HA}} \quad (2)$$

where a is the activity. The ordinary procedure to conduct a titration simulation [2] consist in many attempts of deprotonation and protonation where the trial energy for these latter and a particular surface group can be expressed as

$$\Delta U = \Delta U^{el} \pm kT \ln 10. (pH - pK_0) \quad (3)$$

where ΔU^{el} is the change in electrostatic energy when a site is protonated or deprotonated. The proton is implicitly treated through the constant pH. For this purpose a negative charge is assigned to a titrating site when it is deprotonated and vice versa. In order to satisfy the electroneutrality of the system a positive or negative ion is added/removed from the simulation cell according to the state of the surface site. From this we immediately note that the procedure is wrong by an energy corresponding to the use of the free positive or negative charge. Below a new method, called grand canonical titration (GCT), is proposed to correct for this error.

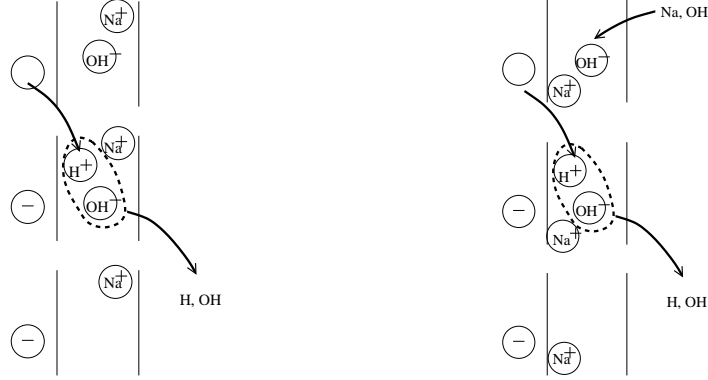


Fig. 1. Illustration of the ionisation procedure by: a) the deletion of an anion, here OH^- ; b) by the addition of a cation, here Na^+ .

Grand canonical titration

In this section the two possible GCT procedures for a surface next to an electrolyte solution are described. That is, the deletion of an anion (DAP), B^- , or the addition of a cation (ACP), A^+ , when a site is ionised. Similar methods for multivalent ions can be easily extrapolated from this work.

Deletion of an anion

In the case of DAP the ionisation of a surface site can be written as two steps. That is, the deprotonation of the surface and the exchange of the ion couple (H^+ , B^-) with the bulk. This is illustrated in Figure 1-a. The corresponding Boltzmann factor of the trial energy can be expressed as,

$$\exp(-\beta\Delta U) = \frac{N_B}{V} \exp(-\beta\mu_B) \exp(-\beta\Delta U^{el}) \exp\{+\ln 10(pH - pK_0)\} \quad (4)$$

where μ represents the chemical potential of the considered ion. A similar expression can be found for protonation as,

$$\exp(-\beta\Delta U) = \frac{V}{N_B + 1} \exp(+\beta\mu_B) \exp(-\beta\Delta U^{el}) \exp\{-\ln 10(pH - pK_0)\} \quad (5)$$

In these two equations, one can remark that only a prefactor involving the anion, B^- , appears since the energy of the proton is already taken into account through their last exponential term.

Addition of a cation

In the case of ACP, the ionisation of a surface site can be described in three steps, see Fig. 1-b. That is, the addition of the ion couple (A^+ , OH^-), the deprotonation and the exchange of the ion couple (H^+ , B^-) with the bulk. The corresponding Boltzmann factor of the trial energy can be expressed as,

$$\exp(-\beta\Delta U) = \frac{V}{N_A + 1} \frac{V}{N_B + 1} \exp(\beta\mu_{AB}) \quad (6)$$

$$\frac{N_B + 1}{V} \exp(-\beta\mu_B) \exp(-\beta\Delta U^{el}) \exp\{+\ln 10(pH - pK_0)\}$$

After some simplifications this equation can be rewritten as,

$$\exp(-\beta\Delta U) = \frac{V}{N_A + 1} \exp(+\beta\mu_A) \exp(-\beta\Delta U^{el}) \exp\{+\ln 10(pH - pK_0)\} \quad (7)$$

and for protonation,

$$\exp(-\beta\Delta U) = \frac{N_A}{V} \exp(-\beta\mu_A) \exp(-\beta\Delta U^{el}) \exp\{-\ln 10(pH - pK_0)\} \quad (8)$$

Results & discussion

As an example, Fig. 2 presents the simulated ionisation fraction (α) for a surface next to a 20 mM CaX_2 solution as a function of pH. The surface sites are chosen to be points with a density of 4.8 /nm² and pK_0 is set to 9.8. The ionisation fraction is obtained through the ordinary procedures and the corresponding GCT methods. It should be note that in the case of addition of calcium, an attempt is made to simultaneously deprotonate two sites selected at random. One can immediately notice that both GCT procedure, addition of Ca^{2+} and deletion of X^- , gives exactly the same results illustrating the self-consistency of our new method. Interestingly, it can be seen that for this pH range, DAP slightly underestimates α while CAP largely overestimates it. The opposite takes place, not shown here, for pH values lower than the pK_0 . This is simply explained by the large excess density of the counter-ions near the charged wall, see Eq. (5-9).

On Fig. 3 the simulated and experimental surface charge density against pH for various ionic strength of silica particles next to a 1-1 salt solution is presented. Experimental details are given in ref. [3]. For simulations, the surface site density and the pK_0 is set to 4.8/nm² and 7.4, respectively. The site diameter is set equal to that of free charges, i.e. 0.4 nm. As expected, α increases with the ionic strength. Except for high salt concentration at the lowest pH values, the simulation predictions are in very good agreement with the experiments. This last result is particularly important in the field of colloid science as it shows

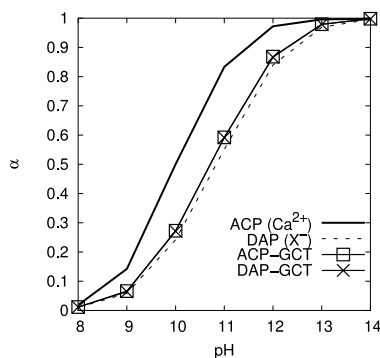


Fig. 2. Ionisation fraction for a surface next to a 20 mM CaX_2 solution varying the pH. The surface site density is set to $4.8/\text{nm}^2$ and pK_0 to 9.8. ACP: addition cation procedure; DAP: deletion anion procedure; GCT: gand canonical titration

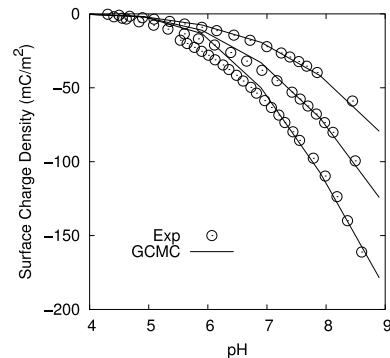


Fig. 3. Surface charge density of silica next to a sodium salt solution varying the pH and for increasing concentration: from top to bottom 10 mM, 100 mM, 1000 mM. empty circles: experiments; full curves: simulations.

that the *seven* parameters of the commonly used classical Stern model [4] can be reduced to two, namely the surface site density and pK_0 . In addition to simplicity, our approach appears to have a clearer physical basis.

References

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