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Ionic specificity of adsorption on silica surfaces : an analysis with molecular dynamics and potential of mean force



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Mesoporous silicas are ideal material for retention of actinides and fission products. The efficiency of retention depends on selectivity. Selectivity of surface ion adsorption in contact with ions and water depends on the interplay between partial dehydration and adsorption, two high terms which can almost cancel each other. As a result, selectivity is difficult to predict. Ions interact with charged surfaces. When the surface charge is not in contact with the solvent, such as in substituted clays, the ion surface interaction is weak. In the case of silica, naked surface charges result from silanol deprotonation. The interaction is very high and specific. We tackle this point with two "limiting" ions (Cs⁺ and Li⁺) and two "limiting" charges on surfaces. We present potential of mean force (PMF) profiles based on molecular dynamics (MD) simulations.

Molecular dynamics simulations

MD simulations use periodic boundaries, SPCE water, Dang parameters for ions, Berendz thermostat. All runs last 3ns, with 1ns for equilibration. Each surface owns a single charge on oxygen atom. Hydrophilicity increases with increasing number of silanols, namely 1, 29 and 57 2.852²nm². All surfaces amorphous and charge defect free.

Silica surfaces of increasing hydrophilicity, with a single punctual charge (pink)

PMF: Umbrella Sampling

The PMF results from the analysis of statistical distribution under external (harmonic) constraints. It is the free energy versus distance profile. (Kumar, JCompChem 1992, Souaille, CompPhysComm 2001)
With Li⁺-O interaction, very high harmonic constraints are required.

Time for binding or unbinding: mean first passage time (MFPT)

What is the required time for a MD run so that it is representative of equilibrium? It is good that the run lasts « a few » times the slower process in the model. In the present case, that means « 10 » times for an ion to bind and unbinding.

We consider the case of an ion confined between two walls. The average time for unbinding is approximately the time needed to come from contact ion pair (CIP) over the first barrier. The average time for binding is approximately the time needed to come from the pore center to the CIP position. The ion wall PMF is symmetrized

The average time for going from an initial position beyond fixed limits is called the mean first passage time (MFPT). It results from an analysis of diffusion under an external field, namely the PMF. For two absorbing barriers, the MFPT is

$$\tau_{\text{un}}(x) = \frac{1}{D_1} \int_x^{\infty} dq e^{-\frac{U(q)}{kT}} \int_{x_1}^q ds e^{-\frac{U(s)}{kT}}$$

For one absorbing barrier, with $t = \int_0^x dq e^{-\frac{U(q)}{kT}}$

$$\tau_{\text{un}}(x) = \int_x^{\infty} dq e^{-\frac{U(q)}{kT}} \left[\left(\frac{1}{D} \int_{x_1}^q e^{-\frac{U(s)}{kT}} ds \right) - \left(\frac{1}{D} \int_{x_1}^x e^{-\frac{U(s)}{kT}} ds \right) \right]$$

Association constants

We consider the adsorption reaction :

$$Li_{aq}^+ + O_C^{-q} \rightleftharpoons LiOc^{1-q}$$

O_c, surface oxygen. Association constants for this reaction can be estimated in a Bjerrum-like model, U^{eff} being the PMF

$$K_D(d) = \int_0^d dr 2\pi r^2 e^{-\beta U^{eff}}$$

Results: PMF profiles

Legend:

- 1 OH (blue)
- 29 OH (purple)
- 57 OH (green)
- Coulomb term (red)

Reduced charge (-1 e on oxygen)

Full charge (-1.5 e on oxygen)

Lithium ↑ Cesium ↑

Results: association constants and mean first passage times

ion	silanols	charge	Log(K _D)	Log(MFPT) center	Log(MFPT) bonded
Li	1	-1.0	7.5	0.98	7.1
Li	29	-1.0	8.1	0.97	7.6
Li	57	-1.0	8.7	0.98	8.2
Cs	1	-1.0	2.7	-1.2	1.3
Cs	29	-1.0	2.4	-1.1	1.4
Cs	57	-1.0	2.3	-1.6	1.6
Li	1	-1.5	20.9	-1.6	19.7
Li	29	-1.5	20.5	-1.2	19.6
Li	57	-1.5	22.6	-1.1	20.7
Cs	1	-1.5	5.1	-1.1	3.2
Cs	29	-1.5	5.0	-1.2	3.3
Cs	57	-1.5	3.8	0.89	3.6

MFPT bonded: average time for CIP to dissociate, (beyond the x₁ or x₂). MFPT center: average time for an ion at the center to associate (beyond x₁ or x₂). MFPT in ns. K_D in L/mol^l. MFPT are large compared to typical MD run durations.

The adsorption is quantitative, even for Cesium with a reduced charge.

- PMF profile are ion specific. The interaction is much stronger with Li⁺. This is an electrostatic size effect.
- PMF profile show the positions of CIP, SSIP. A third minimum can be distinguished.
- For US, the ion is monitored on top of a charged oxygen, with an harmonic constant on the surface/ion angle, keeping it close to 90°. A constraint close to 45° does not change appreciably the profile.
- There is an activation energy also for binding. This indicates that published MD runs can show out of equilibrium free ions.
- Increasing hydrophilicity impacts ion binding. The impact is ion specific. Higher hydrophilicity increases Li⁺ adsorption.

Conclusions

- PMF can be estimated for ion surface interaction
- Hydrophilicity has an impact on ion adsorption. This impact is ion specific.
- Ion adsorption is very strong with naked charges, often making MD dynamics simulations out of reach. This is in contrast with systems including buried charges (clays). Mesoscopic simulations are required. Many published MD results are questionable.
- Modelling potential of mean forces for ion silica surfaces interactions, to be published.
- Hydrophobic transition in porous amorphous silica, B. Siboulet B. Coasne, J.-F. Dufrière, P. Turq, Journal of Physical Chemistry, 115, 2011