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Specificity of ionic adsorption in silicas studied with molecular dynamics and potential of mean force



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INTRODUCTION

Context

- ✓ Radionuclides retention in glasses
- ✓ Decontamination of polluted soils and water
- ✓ Ion exchange in mesoporous oxides

Objectives

- ✓ Analyse the role of the cation on adsorption
- ✓ Determinate thermodynamic and kinetics properties of ions in contact with charged surfaces

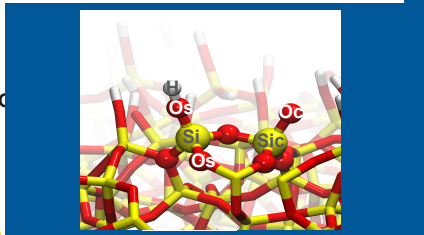


Fig.1: Snapshot from molecular dynamics showing the silica surface with atom types. [2]

01 BIASED MOLECULAR DYNAMICS

- ✓ DL_POLY
- ✓ Water model: SPC/E
- ✓ Simulation box: $2.8 \times 2.8 \times 5.0 \text{ nm}^3$
- ✓ Simulation time: 2 ns
- ✓ A single net charge on the surface (oxygen atom)
- ✓ Free energy profile vs. interatomic distance (PMF)
- ✓ Varying hydrophilicity: 1, 29 and 57 silanols
- ✓ Harmonic constraint at varying distances [3]

$$V = \frac{1}{2} k (r - r_0)^2$$

Stiffness constant \rightarrow Average distance

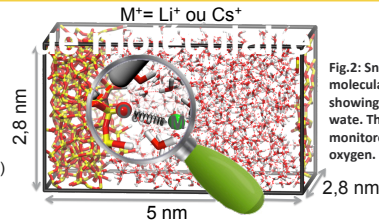


Fig.2: Snapshot of a molecular dynamic box showing ion interaction in water. The solvated ion is monitored on top of the oxygen.

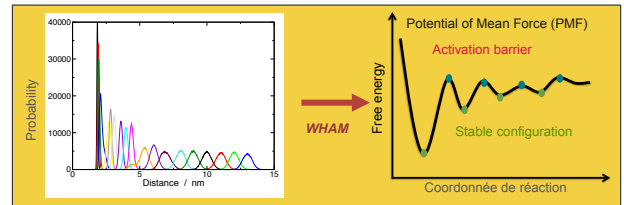


Fig.3: Histogram of probabilities vs. distance and free energy profile as produced by WHAM.

02 RESULTS

Association constants: two models for silica

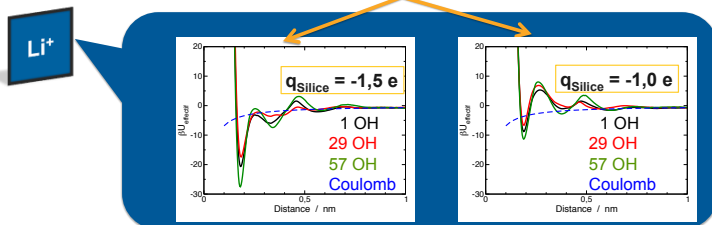


Fig.4 : Potential of Mean Force (PMF) for various surfaces (1 OH, 29 OH at 57 OH) in the case of Li^+ ion, vs. distance r and with $\epsilon_r = 78.4$ for the solvent.

Mean residence time : τ

τ_1 : Average mean time for the ion to leave the bonded position.

τ_2 : Average mean time for the ion to come to bonded position.

Ion	Charge on O_c	τ_1 (ns)	τ_2 (ns)	$\log K_D$ (L/mol)
Li	-1,0	1.6×10^{-7}	2.7×10^{-8}	0.15
	-1,5	1.1×10^{-6}	$1,8 \times 10^{-10}$	4.7

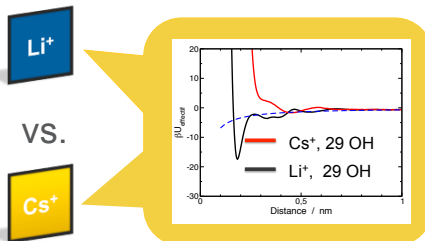
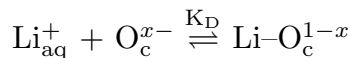


Fig.5 : Potential of Mean Force, for the Li^+ and Cs^+ , vs. the distance r , with $\epsilon_r = 78.4$ for the solvent.

We consider the following adsorption reaction:



The association constant can be calculated out of the free energy profile:

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

- ✓ The interaction is much stronger with Li^+ than with Cs^+ .
- ✓ Increasing hydrophilicity increases Li^+ adsorption.

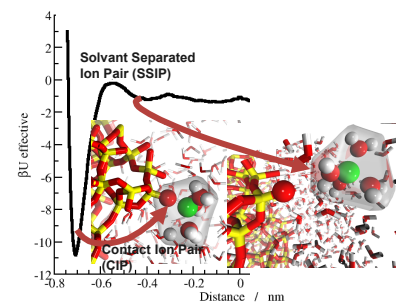


Fig.6 : In a Solvent Separated Ion pair, a single molecule is intercalated. This is the second minimum position.

03 CONCLUSIONS

- ✓ We developed a method which provides a quantitative analysis of solvated ion to charged surface analysis.
- ✓ PMF show oscillations similar to those observed between ions. The Lithium ion is more strongly bonded than the Cesium ion.
- ✓ Surface hydrophilicity increases Li^+ binding.
- ✓ Association constants are very high. This shows that modeling equilibria of such systems at the atomic level is problematic. [1]



Remerciements

In tribute to Professor Pierre Turq, deceased on 21st mai 2015.

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Références

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