SARAH HOCINE

will present her Ph.D. dissertation

Adsorption of alkali cations and electrokinetic phenomena on charged silica surfaces

The defense will take place on **Thursday, September 28, 2017** at **1.30 pm**

in the ICSM Auditorium

In confined structures, such as mesoporous silica, the mobility of the cations and the surface/cations interactions are key phenomena. They drive adsorption properties, which control numerous applications, especially for extraction and separation. This modelling work describes equilibrium and transport interface properties that control ion exchange and ionic adsorption. The physical and chemical properties of adsorption processes of alkali cations at the surface of charged silica is studied thanks to a multiscale approach based on a molecular description. The systematic study of alkali series (Li^+, Na^+, K^+, and Cs^+) has been studied to that goal. The theoretical framework is McMillan-Mayer theory. The latter, which is known to be of fundamental significance for bulk solutions is found to be also relevant for confined media. The mean force potential of McMillan-Mayer between ions and surface sites has been calculated by Umbrella Sampling associated to the WHAM algorithm. The most important phenomenon we identified corresponds to the existence of Contact Ion Pairs (CIP) between the surface oxygen and the cations, without separating solvent molecules. The CIP correspond to the first minima in the potential curves if the associated energy is more than the thermal agitation ($k_B T$). For small ions (lithium) this surface complex is especially stable, adsorption constant and residence time being particularly high so that the direct molecular simulations are very difficult. A selectivity inversion has been observed between silanolates and siloxanes. Adsorption is different for kosmotropic ions (as Li^+) which has to be dehydrated to be adsorbed and chaotropic ions (as Cs^+) for which the solvent bound is weaker. Adsorption constants for sites of the same nature are not equal. The study of the electrokinetic phenomena (electro-osmosis and surface conductivity) has also been performed by comparing the classical descriptions (Poisson-Boltzmann, Smoluchowski, and Bikerman models) to molecular simulations. The traditional picture of the interface with several layers (inner and outer Helmholtz, Stern and Gouy-Chapman layers, shear plane) is found to be replaced by a simpler but more efficient model. For the ions, two domains are obtained: (i) CIPs, firmly bound to the surface that transmit the electrical force to the solid (and not the fluid) (ii) other ions that are globally free that transmit the electric force to the fluid. No space dependent viscosity or dielectric constant have been obtained. On the other hand, a decrease of ion mobility in the vicinity of the surface has been observed. This phenomenon can be quantitatively understood as a hydrodynamic effect that comes from the solid surface, which hinders the backflow of the solvent. This work allows a better characterization of charged glass-solution interfaces for separation science. It shows how molecular simulations can not only predict the parameters of macroscopic models (adsorption constant, transport coefficients), but also modify the latters in order to make them in agreement with molecular descriptions. Such a strategy can be extended to more complex systems, such as models of grafted surfaces.

Keywords: Modeling; Confined media; Hydration forces