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X-Ray Reflectivity analysis of SiO₂ nanochannels filled with water and ions: a new method for the determination of the spatial distribution of ions inside confined media

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Abstract

Chemical reactions occurring at the material–aqueous solution interface are controlled by an interfacial layer of a few nm where conceptual models such as the Electrical Double or Triple Layer models can be applied. These models describing the spatial distribution of ions in term of perpendicular distance from the planar surface and ignoring topography or structure parallel to the surface are not validated in confined media. In order to investigate the critical dimensions of these models, our first approach was to use a model system consisting of two parallel plane surfaces of SiO₂ spaced of 5 nm (nanochannels) filled with salt solutions XCl₂ (X = Ca²⁺, Mg²⁺, Ba²⁺). These filled nanochannels were characterized using hard X-Ray reflectivity for the determination of electron density profiles perpendicular to the surface. From these results, the surface densities of adsorbed ions at SiO₂ surface were calculated and the solution density inside the nanochannels was determined. This method opens new perspectives to a better understanding of water and ion distribution inside nanoconfined media.

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Keywords: Confined media; adsorption kinetics; X-Ray Reflectivity; Electric Double Layer

1. Introduction

Prediction of material behaviour regarding the interactions with water is interesting for geochemistry and requires the use of modelling. Thermodynamic models and rate laws integrated in computer programs (PHREEQC,

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JChess...) used to predict materials dissolution kinetics and phase transformation integrate data obtained from experiments performed in diluted media. Due to the fact that most of the materials in these domains are nanoporous filled of water and ions (clay materials, secondary minerals formed from rocks, alteration layer of glasses...) and the validity of these models and rate laws are still not proven yet, thus, prediction can be defective¹. The strong interaction between water and the surface in confined media are not considered in such calculations. Furthermore, it is also expected that nanoconfined water molecules are strongly influenced by the presence of ions through sorption processes with the surface. The ion ability to be solvated also modifies the electrostatic interactions in the system. These are really important since they strongly impact the hydrolysis rate of materials^{2,3}. In this context, the first step to adjust these models is the investigation of the Electric Double/Triple Layer models (EDL/ETL), which represents the charge distribution in the proximity of a charged surface in aqueous solution. The well-established concept for description of these adsorbed ions is called Stern layer concept, which combines the former pioneering approaches of Gouy and Chapman. In this case the layers are characterized by a static and a diffusive layer of ions⁴.

Before adjusting the models in confined media having the critical size known to modify the properties of aqueous solution in such media, 3 nm typically, we started to investigate the ion distributions at SiO₂ surface in 5 nm confined media. To reach this goal, we used a SiO₂ model system consisting in two parallel plane surfaces spaced of 5 nm (nanochannels) filled of electrolyte solution XCl₂ (X = Ba, Ca, Mg). To characterize the ion distribution we have used X-ray reflectivity, technique particularly interesting since it allows the determination of electron density profiles perpendicular to the surface⁵. Such method should lead to a better understanding of water characteristics confined in environments less than 5 nm can also help to adjust standard values such as viscosity and surface tension within nanoscale environment.

2. Materials and methods

The model systems used in the following section were elaborated at the Institute of Nanotechnology, Twente, Netherlands, and are described in Figure 1 (b) and (c). Nanochannels were placed in experimental set-up dedicated to the X-ray reflectivity measurement of samples as described in Fig. 1. At both sides of this cube two compartments were screwed providing at the one side, a constant supply of solution and an empty one at the other side. Hard X-ray reflectivity measurements at 27 keV ($\lambda = 0.4592 \text{ \AA}$) were performed at the ESRF BM32 beamline to limit the absorption of X-rays through sample crossing. Two types of experiments were performed. In the first experiment, the filling kinetics of nanochannels dried at 250°C under vacuum during 2 hours with a BaCl₂ solution at 1 M was investigated in order to determine the time required to reach the equilibrium. In the second experiment, samples were analyzed after their immersion during 24 hours in water and in solutions of CaCl₂ and MgCl₂ first at 0.1 M and then at 1 M. The pH(20°C) of the electrolyte solutions were comprised between 5.2 and 5.7.

From, X-ray reflectivity curves electron density profiles were extracted directly by inverse Fourier transform assuming the symmetry of the profile. The reflectivity curves were plotted in the standard I, q^4 vs. q ($q = 4\pi\sin(\theta)/\lambda$ with the θ incident angle) mode to remove the Fresnel decay with q the wave vector transfer and display large fringes in reciprocal space associated to gaps. These profiles were described using a classical rectangular box model, i.e. the interfacial bonding region having a constant density. The transition between the different layers is described by a standard rough interface model with a Gaussian statistics, i.e. using an error function profile.

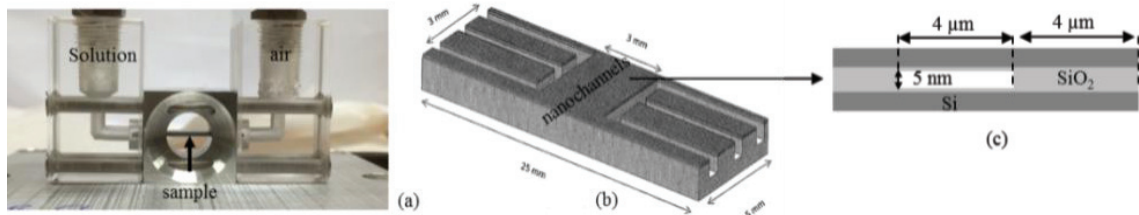


Fig. 1: (a) Patterned sample aligned inside sample holder, (b) structural design of sample, (c) cross section through the material visualizing the nanochannels.

3. Results and discussion

3.1 First experiments: Kinetics of filling of the nanochannels with a $BaCl_2$ solution at 1 M

The evolution of the X-ray reflectivity curves as a function of time during the filling of nanochannels with a solution of $BaCl_2$ 1 M is presented in Figure 2 (a). The results show some modifications of the width intensity of the fringes vs time until 18h50 highlighting an evolution of the densities inside the nanochannels and at the SiO_2 /solution interface. We attest that after 18h50 there is no evolution of the reflectivity signal showing that the equilibrium is reached. The associated electron density profiles presented in Fig.2 (b) present an increase of the density inside the nanochannels with the filling time. After 9h34, the density in the center of the nanochannels is equal to the one of the bulk water and the density at the SiO_2 surface exhibits a higher density than in the center. This could be explained by an adsorption process of Ba^{2+} ions after filling with electrolyte solution. After 18h50, the density in the center increases until a density close to the one of a bulk solution at $BaCl_2$ 1M.

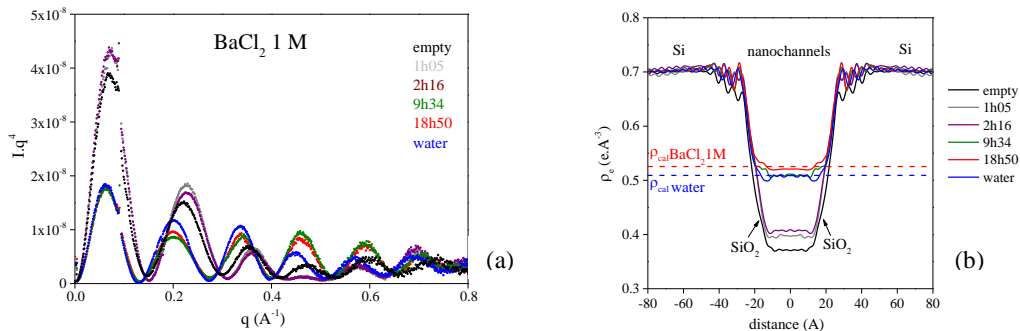


Fig. 2: (a) Reflectivity curves obtained from the kinetics of nanochannels filling with $BaCl_2$ solution at 1 M and (b) the associated electron density profiles.

3.2 Second experiments: Nanochannels filled of $CaCl_2$ and $MgCl_2$

The X-ray reflectivity curves are presented on the Fig.3 (a) show a shift of the fringes at high q characteristic of a modification of the SiO_2 /solution interface. The density profiles presented in Fig. 3(b) depict an electron density increase at the SiO_2 surface of the nanochannels for all solutions.

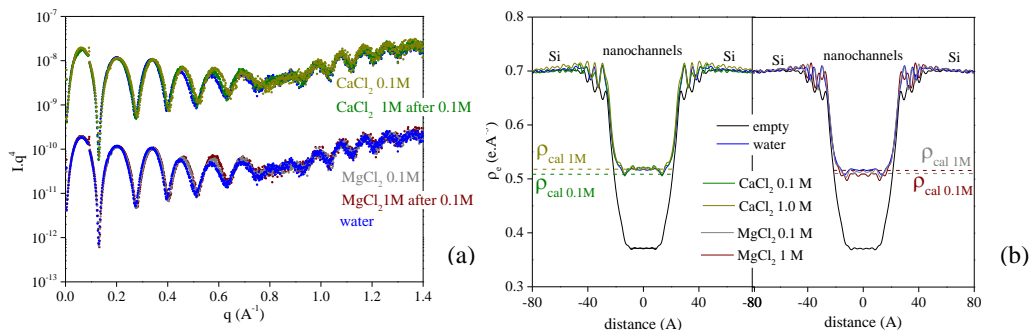


Fig. 3: (a) Reflectivity curves obtained from the measurements of nanochannels filled of $CaCl_2$ and $MgCl_2$ solution at 0.1 and then 1 M and (b) the associated electron density profiles.

3.3 Electrolyte solution behaviour inside the nanochannels and determination of ions surface density

Regarding the first experiment, the electrolyte solution behavior inside the nanochannels can be described as follows. First of all, the density inside the nanochannels is close to the bulk water one until the saturation of the $Si-$

O⁻ site is reached. Thus, the ion adsorption can probably explain the depletion of the electrolyte solution inside the nanochannels. Afterwards, when the surface sites are saturated, the density of the solution in the center the nanochannels ($\rho_{eXRRCenter}$) increases until the density of the bulk electrolyte solution. The rate of the density increase is probably dependent on the ion diffusion coefficients in water (at 25°C $D_{Ba}=5.4 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, $D_{Ca}=5.5 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, $D_{Mg}=6.6 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) and higher than the auto-diffusion coefficient of water (at 25°C $D_{H_2O}=2.6 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$).

The surface densities of ions have been determined considering a surface negatively charged according to two approaches: (i) a monolayer of adsorbed X^{2+} (Helmoltz model, equation (1)) and (ii) a distribution of X^{2+} (Gibbs concept, integral of the X^{2+} excess at the surface, equation (2)). The results are presented in Table 1.

$$\Gamma_{ads} = \frac{\rho_{eXRRSurf} \cdot \phi_X}{Z_X} \quad (1)$$

with $\rho_{eXRRSurf}$ the electron density at the surface of SiO₂ (Fig. 2(b) and (b)), ϕ_X the ionic diameter ($\phi_{Ca^{2+}}=1.44 \text{ \AA}$, $\phi_{Mg^{2+}}=2.00 \text{ \AA}$, $\phi_{Ba^{2+}}=2.70 \text{ \AA}$ and $\phi_{H_3O^+}=2.70 \text{ \AA}$) and Z_X the atomic number of X.

$$\Gamma_{ads} = \frac{\int_0^l (\rho_{eXRR} - \rho_{eXRRCenter}) dz}{Z_X} \quad (2)$$

with $\rho_{eXRRCenter}$ the electron density in the center of the filled nanochannels (Table 1) and l the distance considered for the X^{2+} distribution at the surface. The results from the equation (1) are about in the same order of magnitude than the one obtained at the equilibrium of the adsorption isotherms in ordered mesoporous silica SBA-15 having a pore size of 4.7 nm. However, these results are ten times higher than the ones obtained from the equation (2).

Table 1. Calculated electron densities $\rho_{ecalSol}$ of solution and $\rho_{ecalSample}$ inside the sample, and electron densities determined from the electron density profiles $\rho_{eXRRCenter}$ in the center of the filled nanochannels and $\rho_{eXRRSurf}$ at the surface of SiO₂. $\rho_{ecalSample}$ have been calculated with a $\rho_{eSiO_2} = 0.628 \text{ e} \cdot \text{\AA}^{-3}$ and $\rho_e = 0.372 \text{ e} \cdot \text{\AA}^{-3}$ measured inside the empty sample.

Aqueous solution	$\rho_{ecalSol}$ (e.Å ⁻³)	$\rho_{ecalSample}$ (e.Å ⁻³)	$\rho_{eXRRCenter}$ (e.Å ⁻³)	$\rho_{eXRRSurf}$ (e.Å ⁻³)	Γ_{ads} (equation 1) (X ²⁺ /nm ²)	Γ_{ads} (equation 2) (X ²⁺ /nm ²)
water	0.334	0.508	0.508	0.516	8.7	8.3
BaCl ₂ 1 M	0.378	0.526	0.521	0.533	1.9	0.2
CaCl ₂ 0.1 M	0.336	0.509	0.520	0.525	3.8	0.3
CaCl ₂ 1 M	0.358	0.518	0.520	0.531	3.9	0.3
MgCl ₂ 0.1 M	0.336	0.509	0.515	0.526	4.5	0.6
MgCl ₂ 1 M	0.355	0.516	0.508	0.524	4.5	0.6

4. Conclusion and outlook

The X-Ray reflectivity measurements of nanochannels filled with electrolyte solution allowed the determination of the electron density profiles inside a confined media. From these profiles the surface density of ions adsorbed at SiO₂ surface and the density of the electrolyte inside the nanochannels were determined. Nevertheless, it is necessary to study the effect of the size of the confinement decreasing the size of nanochannels. Thus, the oncoming experiments will be carried out in nanochannels of 2 and 3 nm. We are expecting to determine the electron density profiles and then calculate the potential in a SiO₂ confined media in order to investigate the critical dimensions of the EDL-TDL models validity.

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