

Água em superfícies e interfaces

Comportamentos inesperados

- <http://vimeo.com/7294988#signin>

Água junto de superfícies

- <http://faculty.washington.edu/ghp/researchthemes/water-science>
- Liquid crystal state in the exclusion zone

Near hydrophilic surfaces, water exists in a liquid crystal state.[38][39] This liquid crystal state has the following properties:[40]

 - the water molecules are constrained in movement (as shown by nuclear magnetic resonance imagery)
 - it is more stable (as shown by infrared radiation imagery)
 - it has a negative charge (as shown by a test of its electric potential)
 - it absorbs at 270 nm (as shown by light absorption imagery)
 - it is more viscous than liquid water (as shown by falling ball viscometry)
 - the molecules are aligned (as shown by polarizing microscopy)

Gerald Pollack speculated that this liquid crystal zone remained relatively unexplored recently, despite extensive writing on this topic up through 1949, because of the polywater and water memory debacles.[40]

Um assunto muito amplo

- Faraday Discussion 141: Water - From Interfaces to the Bulk

Heriot-Watt University, Edinburgh, United Kingdom (2008)

Faraday Discussion 141 was organised by the RSC Faraday Division. The conference was attended by 137 delegates from 21 countries around the world.

...was ...the aim of achieving a unification views towards the goal of **understanding the microscopic structure and behaviour of condensed phases of water at interfaces and progressing into the bulk**. ...experimental and theoretical scientists from diverse disciplines that traditionally do not interact; the gas phase clusters community, the surface science community and the condensed (liquid) phase community.

Efeito de sais sobre γ

- It is generally found, for example, that the addition of inorganic electrolyte to water results in an increase in the surface tension of the solution, although the effect is not dramatic and requires rather high salt concentrations to become significant (Fig. 8.6).
- The relative effectiveness of ions at increasing the surface tension of water generally follows the Hofmeister series: $\text{Li} > \text{Na} > \text{K}$, and $\text{F} > \text{Cl} > \text{Br} > \text{I}$, indicating that the effect results from a structuring of the water molecules at the surface due to solvation phenomena.
- *Drew Myers, Surfaces, Interfaces, and Colloids: Principles and Applications, 2nd Ed. (1999)*

Efeito de sais sobre a solubilidade do benzeno

- A ordem de efetividade de ânions na insolubilização (salting-out) de benzeno é $\text{SO}_4^{2-} > \text{OH}^-$, $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{I}^-$, e a ordem dos cátions é $\text{Ba}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Li}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Cs}^+ > \text{H}^+$.
- Os sais que causam salting-in contêm ions grandes (hidratados) e monovalentes, como $(\text{CH}_3)_4\text{NBr}$.
- Em geral, íons divalentes são mais efetivos em salting out que ions monovalentes, e íons com raios (hidratados) pequenos são mais efetivos que íons grandes.

Protein association in salt solutions

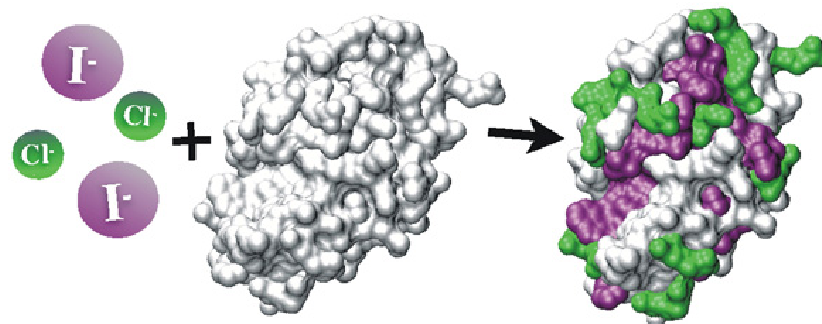
120 years after Franz Hofmeister (at the Pharmacological Institute in Prague) ordered salt ions according to their ability to salt-out proteins, the present molecular dynamics simulations provide a key to the molecular understanding of the lyotropic (Hofmeister) series.

Ion ordering is due to a multitude of different effects rather than due to a single one. ...association of lysozyme molecules we ... observed at least two such effects. ...direct interaction of aqueous anions with positively charged amino acid residues and the affinity of these anions for hydrophobic patches...

The former interactions are stronger for chloride than for iodide, the opposite is true for the latter effect. ... a subtle balance between these (and also other) forces. In the present case, the hydrophobic effect of iodide wins over the ion-pairing effect of chloride, which results in a stronger lysozyme-lysozyme association in aqueous NaI than NaCl..

http://www.uochb.cz/web/document/cms_library/751.jpg

Jungwirth, JACS (2008)



HOFMEISTER SERIES

Cations

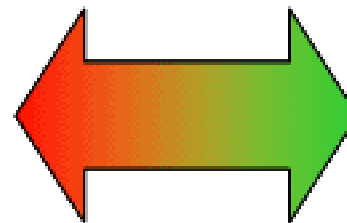
NH_4^+ K^+ Na^+ Li^+ Mg^{2+} Ca^{2+} guanidinium⁺



SO_4^{2-} HPO_4^{2-} acetate⁻ citrate⁻ Cl^- NO_3^- ClO_3^- F^- ClO_4^- SCN^-

Anions

↑ surface tension
harder to make cavity
↓ solubility hydrocarbons
Salt out (aggregate)
↓ protein denaturation
↑ protein stability



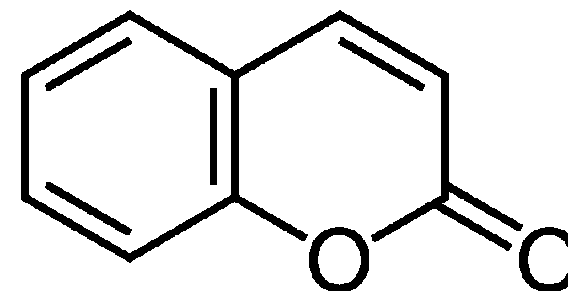
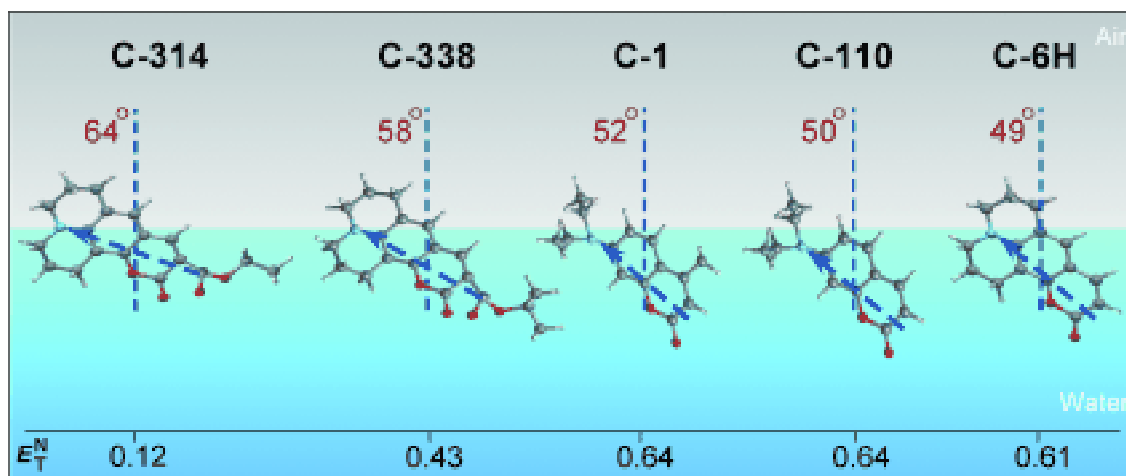
↓ surface tension
easier to make cavity
↑ solubility hydrocarbons
Salt in (solubilize)
↑ protein denaturation
↓ protein stability

<http://employees.csbsju.edu/hjakubowski/classes/ch331/protstructure/hofmeister.gif>

Cumarinas em interfaces

- Tahara and colleagues found that the spectra of all five coumarin dyes at the air/water interface resembled a cross between the bulk spectra of coumarin in polar water and non-polar hexane. This is because the dye molecules were positioned partly in the polar water and partly in the non-polar air at the interface. ... the closeness of the spectra to either the spectrum in water or in hexane changed depending on the precise structure of each coumarin dye.??...even molecules having similar structures experience substantially different polarity at the air/water interface.??...different molecules were positioned at slightly different angles at the interface of air and water so have different sections of their structures submerged and are, consequently, in quantitatively different surroundings.
- <http://www.rikenresearch.riken.jp/eng/research/6068>

Cumarinas em interfaces



- Sen, S., Yamaguchi, S. & Tahara, T. Different molecules experience different polarities at the air/water interface. *Angewandte Chemie International Edition* 48, **6439–6442** (2009).
- Yamaguchi, S. & Tahara, T. Precise electronic $\chi(2)$ spectra of molecules adsorbed at an interface measured by multiplex sum frequency generation. *Journal of Physical Chemistry B* 108, **19079–19082** (2004)

Chaotropic substances and their effects on the mechanical strength of Portland cement-based material

Hebert Luis Rossetto; Milton Ferreira de Souza; Victor Carlos Pandolfelli
Materials Research (2008)

The ions follow the Hofmeister series (Figure 2b)...classify them according to their power of precipitating or solubilizing proteins.

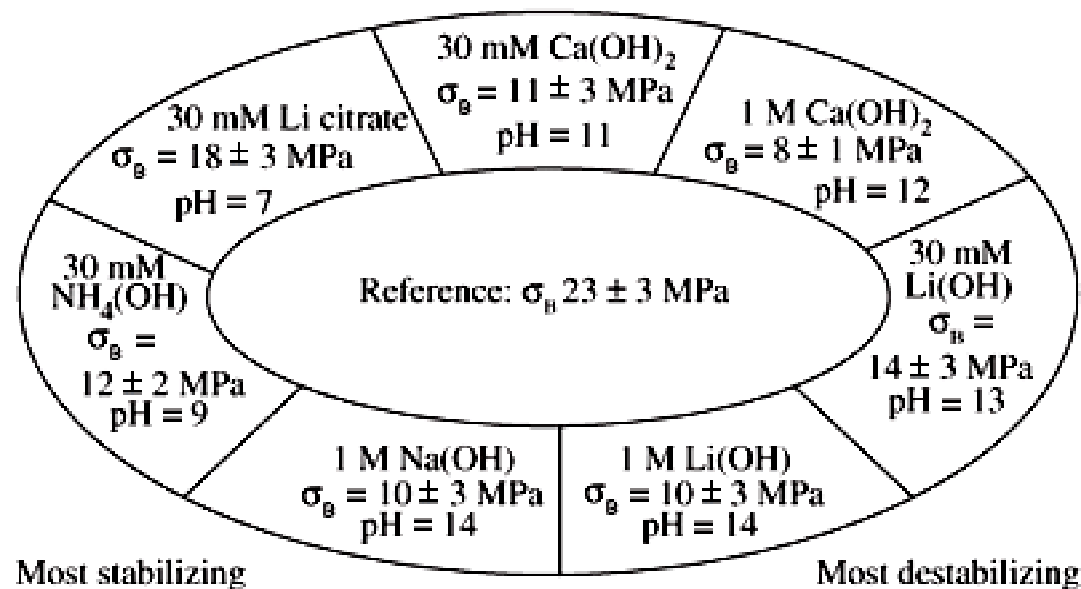
...also reflect the ions influence on the surrounding water molecules, ranging from stabilization (kosmotropes) to disruption (chaotropes).

...controversy ...about the mechanism ... an ion can disturb the water structure...it is generally accepted that salts have a disordering effect on the H-bonding network.

The chaotropic cations (such as Ca^{2+} , Li^+ , and Na^+) effect on the bending strength of cementitious plates followed the destabilizing sequence of $\text{Ca}^{2+} > \text{Li}^+ \approx \text{Na}^+$.

The lower the ion concentration, the less is the bending strength decrease. These chaotropic cations were all evaluated with the same chaotropic anion: OH^- .

...when a strong kosmotropic anion was used in the curing solution, such as for citrate, less severe reduction was imparted to the mechanical strength.



(a)

citrate³⁻ > sulfate²⁻ > phosphate²⁻ > OH⁻ > F⁻ > Cl⁻ > Br⁻ > I⁻ > NO₃⁻ > ClO₄⁻
 N(CH₃)₄⁺ > NH₄⁺ > Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺ > H⁺ > Ca²⁺ > Mg²⁺ > Al³⁺

← "KOSMOTROPES" [] [] [] [] "CHAOTROPES" →

(b)

Figure 2. a) Results for 3-point bending strength of cementitious plates cured in different ionic solutions compared to the reference sample (23 ± 3 MPa); and b) Hofmeister series¹⁰.

Água em superfícies metálicas

Our understanding of water adsorption and the wetting of metal surfaces has undergone a substantial revision since 2002, prompted by the availability of reliable structure calculations for water at surfaces, as well as new experiments against which to test structural models. This work has shown that water adsorption at metal surfaces is much more complex and sensitive to the individual surface than was perhaps believed previously.

Water adsorption and the wetting of metal surfaces

A. Hodgson, S. Haq; Surface Science Reports (2009)

STM

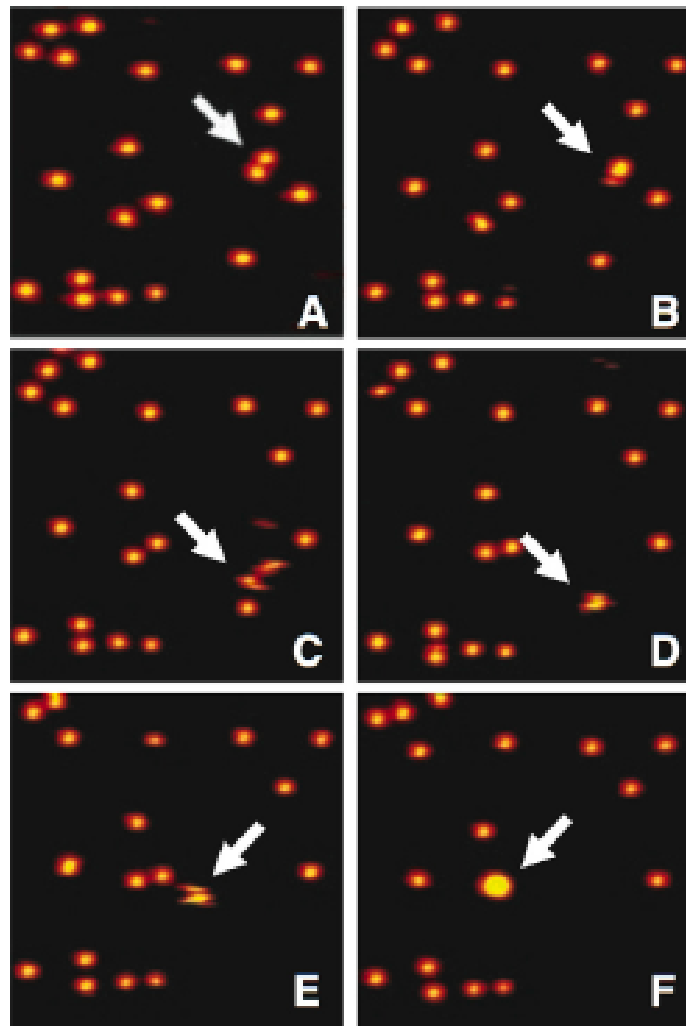


Fig. 3.10. STM images ($180 \times 180 \text{ \AA}^2$) showing water adsorbed on Pd(111). In A two monomers combine to form the dimer seen in B, which is mobile (C) and reacts to form larger clusters (D-F). Reproduced with permission from Ref. [96].
© 2002, American Association for the Advancement of Science.

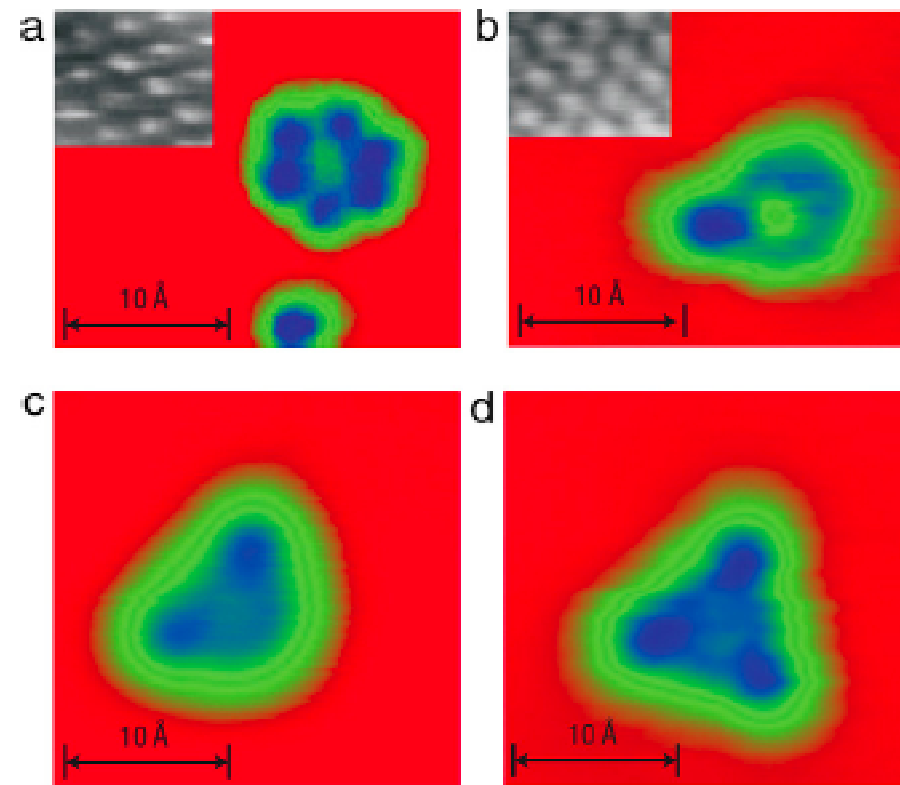


Fig. 3.14. High resolution STM images of adsorbed water clusters. (a) shows H_2O hexamer on Cu(111), the inset shows atomically resolved substrate. (b) D_2O heptamer on Ag(111). (c) D_2O octamer on Ag(111). (d) D_2O nonamer on Ag(111). Reproduced with permission from Ref. [102].
© 2007, Nature.

TPD

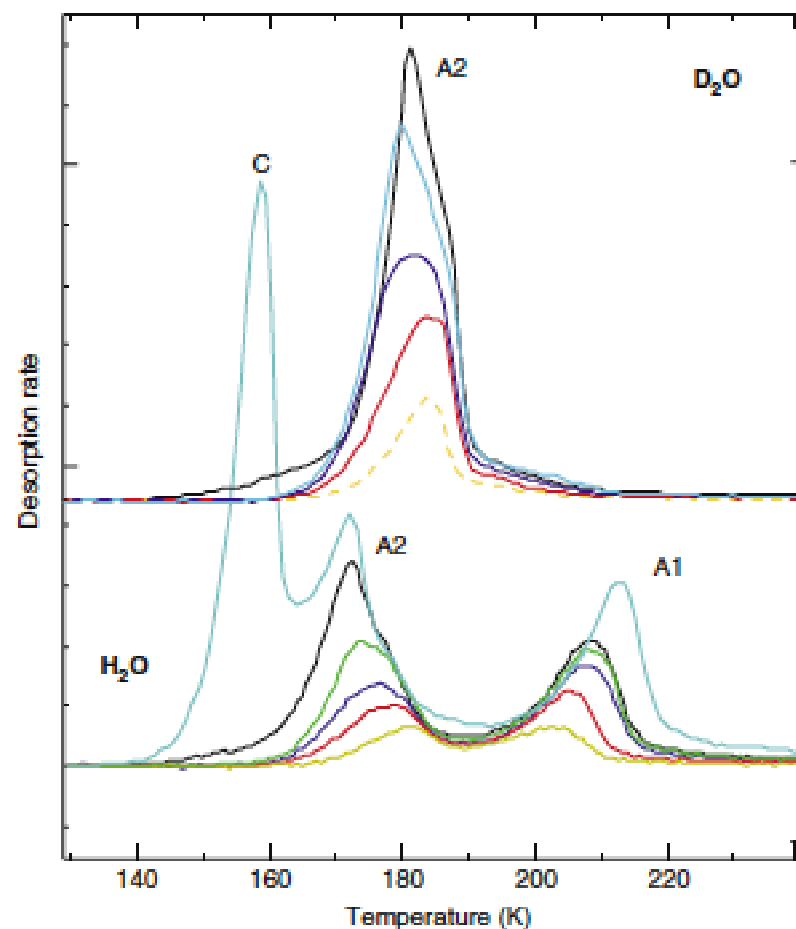
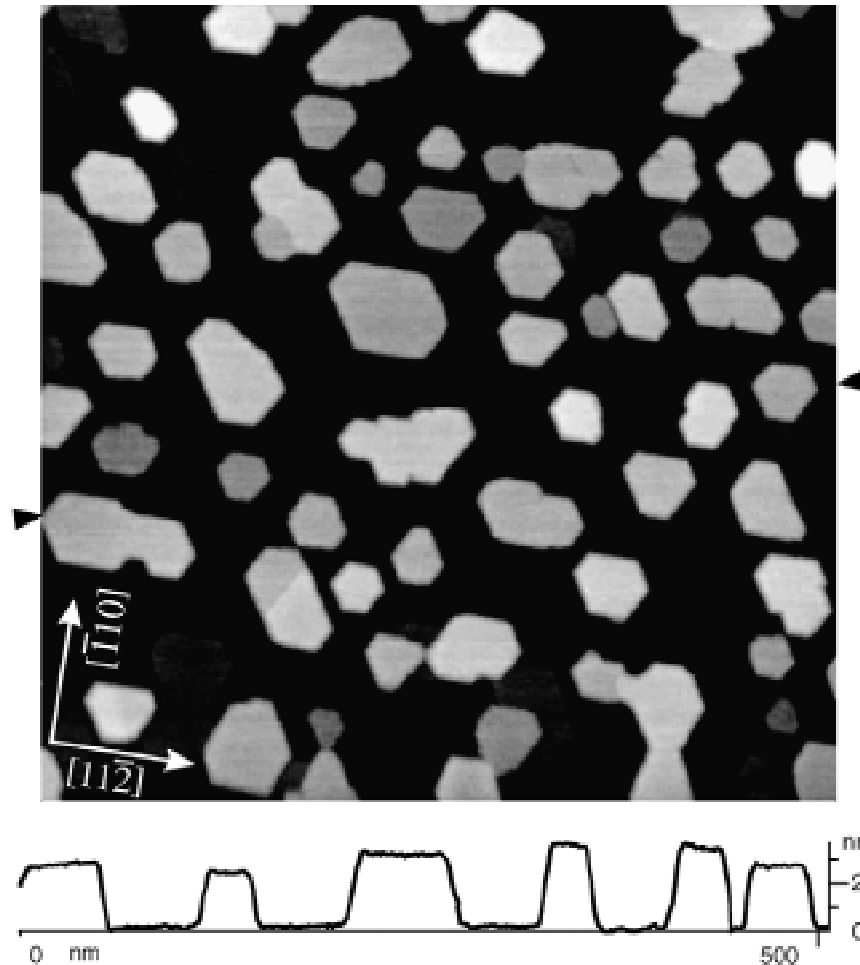


Fig. 4.2.1. Temperature programmed desorption of H_2O and D_2O adsorbed on $Ru(0001)$ recorded at a heating rate of 1 K s^{-1} . H_2O shows three peaks, a multilayer peak (C), a low temperature peak (A2) near 150 K, associated with H_2O decomposition/desorption and a second peak (A1) near 210 K associated with desorption from a partially dissociated phase. Adapted from Ref. [4,75].



Monocamada
+
nanocristais

Fig. 6.5. Surface topography of a crystalline ice-multilayer grown on Pt(111) ($500 \times 500 \text{ nm}^2$). The ice film consists of a monolayer of water and regular ice crystals of ca. 3 nm height. The cross section below the image was taken along the line connecting the two triangular markers. Reproduced with permission from Ref. [182].
© 2008, American Physical Society.

Água em interfaces

Qualquer superfície exposta à atmosfera
contem água adsorvida,
formando filmes ou ilhas,
contribuindo para várias das propriedades
superficiais.

Exercícios

Encontre na literatura um artigo que trate da adsorção da água em algum tipo de superfície.

Responda às perguntas:

- 1- Qual é a superfície estudada, qual é a sua composição e quais são suas características?
- 2- Quais são as características do fenômeno de adsorção da água nesta superfície.
- 3- Ocorre apenas adsorção ou também ocorre absorção da água?
- 4- A adsorção da água muda significativamente alguma propriedade da substância ou material considerado?
- 5- A adsorção da água afeta alguma aplicação desta substância ou material?