Programa de Pós-Graduação em Química
Universidade Federal de Pernambuco
Departamento de Química Fundamental, CCEN

Seleção 2020/I

Número de Inscrição

Instruções (LEIA ATENTAMENTE)

1. **Você está recebendo um caderno de prova que contém 5 páginas numeradas de 1 a 5. Qualquer irregularidade solicite imediatamente assistência a quem estiver aplicando a prova. Não serão aceitas reclamações sobre este assunto após 5 minutos de iniciada a prova.**
2. **Anote o seu número de inscrição no local apropriado no cabeçalho de cada folha.**
3. **As folhas contêm um texto em Inglês, seguido de 10 questões baseadas no texto.**
4. **A folha 5 contém uma tabela para ser preenchida com as respostas. Todas as respostas devem estar somente nesta tabela e somente ela será considerada para avaliação.**
5. **As provas de química e inglês têm, juntas, duração máxima de 4 horas.**
6. **Ao concluir, devolva as 5 páginas a quem estiver aplicando a prova.**
7. **Será permitida consulta somente a dicionários em papel. O uso de qualquer equipamento eletrônico de consulta/comunicação está proibido.**

Read carefully the following article, then answer the questions according to the instructions.

Water's wafer-thin surface

Pavel Jungwirth, *Nature* 474, (**2011**) 168–169. DOI: 10.1038/474168a.

The next time you drink a glass of water, take a moment to consider the surface of the liquid. It might surprise you to learn that the molecular structure of this seemingly unremarkable air–water interface has long been the subject of controversial theories. Recently, Stiopkin et al. weigh into the debate by reporting the results of spectroscopic and theoretical studies of this interface. Their findings strongly contradict the recurring idea that external interfaces with water, or compounds dissolved in it, can generate long-range molecular order in the liquid.

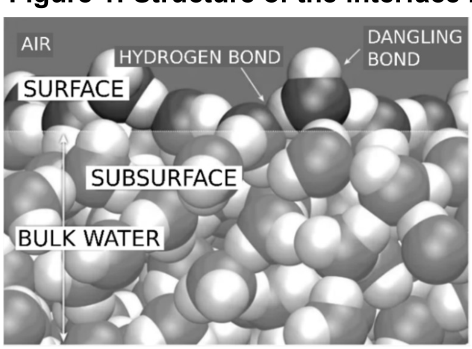
There have been two popular, mutually interconnected misconceptions about liquid water. According to the first, water can 'remember', for extended periods of time, patterns imposed on it by the environment or by solute molecules. This idea, among others, lent credence to a central tenet of homeopathy: that solutions of compounds could maintain biological activity even when repeatedly diluted to such an extent that effectively no molecules of those compounds remained in solution. But the 'memory of water' effect is not reproducible and the idea is now scientifically unacceptable — although this doesn't yet seem to have affected the commercial success of homeopathy.

The second misconception is that long-range order across hundreds or even thousands of molecular layers can exist in liquid water. An early incarnation of this idea was the report of polywater — a syrupy liquid apparently produced when water was repeatedly forced through capillary tubes, and which was thought to be polymerized water. As with the 'memory of water', the existence of polywater has been debunked, but similar ideas have proven to be more durable in the scientific literature. Indeed, there has been a renaissance of the notion that long-range order can be imposed on water by an interface of the liquid with air or with another immiscible liquid, or by an interface with a solid such as the containing vessel. Moreover, the dust has been blown off the picture of bulk water as a mixture of regions of two distinct liquid forms, a concept first proposed heuristically by Wilhelm Röntgen more than a century ago. In the most recent variant of this idea, robust X-ray scattering data for liquid water have been fitted into a microscopic version of Röntgen's elderly model. And, in keeping with the theory that liquid water is structured by surfaces, it has been proposed that long-range water patterning occurs around proteins and other biomolecules. This in turn has led to the enigmatic concept of 'cellular water' — the idea that all water molecules in cells are ordered, and that this order is crucial for biological function.

Stiopkin et al. have therefore performed a valuable service by looking in great detail and with little prejudice at the structure of an archetypal aqueous interface, that between water and air. They posed a seemingly simple question: how thick is this interface? In other words, how deep into bulk water does the patterning imposed by the surface propagate? In fact, for liquid water, with its highly dynamical and volatile surface, this is a difficult question to answer.

The authors succeeded by applying a combination of two state-of-the-art techniques, which they also helped to develop. The first was experimental: they used a sensitive version of surface-selective vibrational spectroscopy to study oxygen–hydrogen bonds in water that stick out into the air, and that are therefore not hydrogen-bonded to another water molecule. (Actually, for technical reasons, they studied oxygen–deuterium bonds of water molecules isotopically labelled once or twice with deuterium.) Such free or dangling bonds (Fig. 1) exist only at the surface and can thus be used as sensitive 'antennas' for detecting interactions of surface water molecules with molecules in the underlying subsurface water layer.

Figure 1: Structure of the interface between liquid water and air.



This image, taken from a classical molecular-dynamics simulation, reveals the features of liquid water at an air–water interface. Most water molecules form hydrogen bonds to each other, but some at the surface do not (these are known as dangling bonds). Stiopkin *et al*. report evidence that the surface has a depth of only one layer of molecules, contradicting theories that interfaces with water impose long-range order deep into the bulk liquid.

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The surface layer of water molecules thus sits atop a subsurface layer, the properties of which approach those of bulk water.

Stiopkin and colleagues' second approach was to perform sophisticated and accurate calculations to model the vibrations of water molecules in the liquid. This allowed them to compare the strength of hydrogen bonds between water molecules in the interfacial layer and in the bulk. They also used an old but neat trick, known as isotopic dilution, to disentangle the contributions of intramolecular and intermolecular couplings of individual water molecules to observed spectral shifts. This involved analysing a set of samples prepared by mixing together varying fractions of ordinary water (H_2O) and doubly deuterated water (D_2O).

By now, the reader may be waiting impatiently for the great news concerning amazing structural patterns discovered at the surface of water. If so, the reader will be disappointed — Stiopkin *et al*. found that the surface does not have a long-range impact on water and that the strength of interactions of surface water molecules with those in the subsurface layer is comparable to that between water molecules in the bulk. This means that only the surface layer is distinctly different in structure from the rest of the liquid, and that the water surface has the thickness of just one layer of water molecules, which is about 0.3 nanometers.

Other studies have shown that the surface thickness of water may be extended by more complex interfaces (such as charged ones) or by solutes, but not to more than a small number of water layers. When taken together with those previous studies, the main message of Stiopkin and colleagues' findings is that the old models of long-range patterning in liquid water and their newer incarnations are not substantiated. The fact that these models are not always perceived merely as historical curiosities warrants broad attention to the present work. The authors' findings may seem to represent a 'negative' result. But by offering a sober view of the fascinating and important — but by no means magical — properties of liquid water, they should have a most welcome, positive effect.

For questions 1-5, choose only one answer.

1) Concerning the article above, it can be said that:

(a) No new studies on the structure of water at interfaces have been released.

(b) Scientists started to study water structure just recently.

(c) Homeopathy has scientific basis.

(d) Stiopkin’s results do not show long-range effects of interfaces upon water structure.

(e) Water at interfaces is indistinguishable from bulk water.

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2) The most common misconceptions about liquid water are:
   (a) There is a “memory of water” effect and water is ordered across thousands of molecular layers.
   (b) Syrup is not made of water and water structure can be studied.
   (c) Water structure can be studied experimentally and theoretically.
   (d) The existence of “polywater” has not been debunked and “cellular water” is not a scientific consensus.
   (e) Hydrogen bonds are formed between water molecules in the bulk, instead of dangling bonds.

3) Concerning the experiments cited in this article:
   (a) A “water memory test” was performed by Stiopkin.
   (b) X-ray scattering experiments were performed by Röntgen.
   (c) Pavel Jungwirth performed state-of-the-art experiments.
   (d) Pavel Jungwirth performed isotopic dilution experiments.
   (e) Stiopkin and co-workers performed surface-selective vibrational spectroscopy experiments.

4) According to the article, it can be said the following about the effect of interfaces upon water:
   (a) Neutral interfaces affect water across several hundreds of molecular layers.
   (b) Water molecules inside cells are unique and fully ordered.
   (c) The air/water interface does not induce long-range effects upon water’s structure.
   (d) The thickness of the water layer at charged interfaces is 0.3 nanometers.
   (e) The thickness of the water layer does not depend upon interface’s charge.

5) The expression “state-of-the-art techniques”, used in the text, means:
   (a) A combination of scientific and artistic experiments.
   (b) The most advanced experiments and models currently available.
   (c) Modern artistic graphical representations of molecular systems.
   (d) Old apparatuses and experimental set-ups.
   (e) Techniques performed by artists.

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For questions 6-10, according to the article assign true (T) or false (F) to the following statements.

6. “Water memory” effect is a valid and accepted scientific concept.
7. The structure of water at interfaces is still being studied.
8. The pictures at Röntgen’s laboratory had dust.
9. Jungwirth says water has no magical properties.
10. Sensitive “antennas” can be used to study bulk water.

Answers for questions 1-5

Question	(a)	(b)	(c)	(d)	(e)
1					
2					
3					
4					
5					

Answers for questions 6-10

Question	True (T)	False (F)
6		
7		
8		
9		
10		