



Exclusion zone water is associated with material that exhibits proton diffusion but not birefringent properties

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ABSTRACT

The structural properties of water have been under investigation for decades but remain a subject of debate. A recent controversy has arisen with evidence suggesting that the region of water located at the interface with hydrophilic surfaces is highly structured and extends up to 500 μm . The supporting evidence for this claim is the physical exclusion of particulates resulting in an Exclusion Zone, or “EZ” and birefringence as seen through a polarized light microscope. Several studies have been undertaken to investigate alternate causes for the Exclusion Zone and these suggest that a flow of ions from the hydrophilic material is an alternate explanation. This study investigates both claims with particular emphasis on the presence of birefringence in the EZ. The findings indicate that any observed birefringence in EZ water is not due to a crystalline structuring of water but is rather an optical reflection phenomenon from the material at the water-surface interface.

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1. Introduction

It has been known for roughly a century [1] that liquids exhibit properties at the liquid-surface interface that differ from those of the bulk. In the review by Henniker it was noted that the molecules of liquids are aligned by the surface properties of an adjacent material. Henniker also proposed that the aligned layer of molecules then proceeds to affect the alignment of neighboring molecules, thus having a perpetuating effect for a considerable distance from the initiating surface. Of the liquids studied, water has undergone extensive investigations since its interfacial properties are of great importance to all life on Earth [2–4]. Due to the tendency of the interfacial region of water to remain in its aligned state it has been labelled “structured water” or “ordered water.” As this region of water is also associated with a water-surface interface it is also called “interfacial water.” The reported characteristic differences between interfacial water and bulk water include a higher viscosity at hydrophilic surfaces [5,6], greater reduction of spin-lattice (T_1) and spin-spin (T_2) magnetic relaxation times as probed by Nuclear

Magnetic Resonance [7,8], changes in density [9,10] and molecular ordering [11]. Understanding interfacial water has ramifications in many fields, particularly biology where water is recognized as a dynamic and active component of the inner workings of a cell [4,12–14]. Indeed Nuclear Magnetic Resonance is used to clinically detect cancer by determining the differences in spin relaxation times in cellular water [8,15,16].

It is understood that the unusual physical properties of water are derived from the ability of water molecules to bind tetrahedrally to each other to form a three-dimensional association even in the liquid state. Such “associated liquids” have the possibility of longer range ordering than non-associated liquids [17]. It has recently been proposed that water at hydrophilic interfaces not only exhibits long-range ordering but also mechanical force. This was demonstrated by the exclusion of micro particles and solutes to distances up to 500 μm from the surface, thereby earning the name “Exclusion Zone” water (or EZ water) [18–20]. It has been claimed that the properties of EZ water are the result of long-range ordering of the water molecules [18,19,21–23].

Polarized light microscopy (PLM) is a useful method for detecting long-range order and is often used to detect and identify crystalline structures in biological samples [24]. In this method samples are placed between two polarizing filters, one is fixed in

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place (polarizer) and the other is allowed to rotate (analyzer). The polarizer polarizes light which is then transmitted through the sample. The analyzer is set to block, or extinguish the polarized light from the polarizer; this is located after the sample in the light path. Any crystalline formations in the sample will further refract light as it passes through. It is this alternately refracted light that will be allowed through the analyzer. Many crystalline samples are birefringent, that is to say as light rays pass through the material it undergoes a double refraction. Each of the refracted rays are polarized perpendicular to each other [25]. A useful accessory of the polarized light microscope is the $\frac{1}{4}$ wave plate (located between the sample and the analyzer) which causes the birefringent rays to interfere with each other either destructively or constructively. This interference produces bright colors. Typically, the polarizer and analyzer are set up so that light is extinguished for all materials that are not birefringent.

A study by Bunkin et al. [26] investigating the properties of water close to a piece of Nafion showed anisotropic features which are described as “a set of light and dark fringes oriented in parallel to [the] Nafion interface.” The image in question is generated by passing a laser through two crossed polarizers in a fashion similar to that of polarized light microscopy. Pollack also claims to have evidence of crystalline order within the EZ as shown in his book “The Fourth Phase of Water: Beyond Solid, Liquid and Vapor” [27]. The image shown is a spear-shaped piece of Nafion, a sulfonated tetrafluoroethylene based fluoropolymer developed by DuPont, in a microsphere solution viewed through a polarized light microscope with the wave plate applied. The resulting image shows colors indicating birefringence close to the Nafion interface. These observations seem to give credence to the idea of long-range ordering of water molecules.

There are, however, several studies that suggest alternate reasons for the exclusion phenomena. It has been proposed that the EZ arises from chemotaxis of the microspheres in long-range diffusion gradients of OH[−] (or H⁺) and salt [28–31]. Indeed, Nafion does contain a very high concentration of exchangeable protons that diffuse readily into water [26]. Other materials have also been said to exhibit exclusion zones such as biological gels [19] and metals [20]. In each example ion diffusion may explain the EZ rather than long-range ordering of water molecules. In the case of metals, oxidation was evident - suggesting ion exchange occurred [20]. In this case, to address the possibility of repulsion by like charges driving the EZ, different types of functionalized microspheres (positively and negatively charged) were used with little difference.

We performed a number of experiments to address whether EZ water is derived from long-range order or diffusiophoresis. The experiments were divided into two categories; 1/chemical changes (pH value) induced in the water, and 2/detecting polarization of water using PLM. The purpose of the PLM experiments was to determine whether all hydrophilic surfaces exhibited a visually detectable exclusion zone and if the EZ is birefringent as previously claimed.

2. Materials and methods

2.1. Chemical experiments

The samples consisted of: agar (2%; weight: 0.8–1.28 g; size: 1.5–2 cm diameter masses; Difco, Maryland, USA); agarose (5%; weight: 0.7–1.2 g; size: 1.5–2.5 cm diameter masses; California, USA), Nafion 117 sheet (0.2 mm thick; weight: 0.058–0.108 g; Texas, USA), aluminum foil (purity: >99.9%, thickness: 0.0254 mm; weight: 0.0025–0.0053 g; ESPI Metals, Oregon, USA), and zinc wire (diameter: 0.508 mm, purity: >99.9%; weight: 0.06–0.08 g; length: ~2.5 cm; ESPI Metals, Oregon, USA) (see Table 1). All control samples were filtered, deionized water (10 ml). All water used in this experiment was obtained from an Elix[®] 100 Water Purification System supplier.

The hydrogels (agar and agarose) were prepared using the following method: 0.8 g agar powder was added to 40 ml water. 1 g of agarose powder was added to 20 ml of water. Both samples were prepared in 100 ml Schott bottles by heating in a microwave oven with periodic swirling until just boiled. The samples were allowed to cool and solidify and portions were cut out from the hydrogel solid before being weighed and placed in individual sample jars. The aluminum foil and zinc wire samples were cut with scissors before weighing and placing in sample jars. Water (10 ml) was added to each sample jar and the jars closed with plastic lids.

The pH measurements were performed using a pH probe (Sentix 940-3; WTW, Xylem Analytics Australia) and reader (Multi 3430; WTW, Xylem Analytics Australia). Prior to use, the pH probe was calibrated to pH 4 and pH 7 using buffer solutions supplied by YSI (Ohio, USA) and has an accuracy of ± 0.004 .

The samples of hydrophilic materials were immersed in water over a period of days and the pH levels were recorded intermittently at the indicated time points. No active mixing was applied. All experiments were performed at ~23 °C with ambient room lighting. Samples were sealed with a plastic lid between pH recordings to reduce the amount of atmospheric CO₂ absorbed.

2.2. Polarized light microscopy study

A polarized light microscope (Nikon Eclipse 50iPOL; Nikon Corporation, Japan) with mounted camera (Nikon DS-Fi1; Nikon Corporation, Japan) was used to collect images via imaging software (NIS Elements – F package version 3.22.00; Nikon Corporation, Japan) (see Fig. 1). The microscope magnification was calibrated using a Nikon MBM11100 Stage Micrometer (Coherent Scientific, Australia).

A standard $\frac{1}{4}$ wave plate was used to show birefringence. Although this plate is usually oriented at 45° to the fixed polarizer, Newton, Haffegge et al. [32] developed a technique to greatly enhance the colors produced by weakly birefringent samples by simply rotating the wave plate to <10° from the fixed polarizer. This enhancement technique was applied in all views of birefringence in this study with the wave plate set at 7.5° ($\pm 1^\circ$) to the fixed polarizer.

Table 1
Chemical composition.

Material	Description	Concentration ^a
Nafion 117 sheet	C ₇ HF ₁₃ O ₅ S·C ₂ F ₄	
Agar	A phycocolloid extracted from a group of red-purple marine algae (Class Rhodophyceae)	2%
Agarose	C ₁₂ H ₁₈ O ₉ - a linear polysaccharide composed of repeating units of agarobiose extracted from marine algae (Class Rhodophyceae)	5%
Aluminium	Foil - thickness: 0.0254 mm	99.9%
Zinc	Wire - diameter: 0.508 mm	99.9%
Copper	Foil - thickness: 0.4 mm	99.9%

^a Filtered deionized water used for preparing all solutions.

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