

Protonated water in the nafion-water interfacial area

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Abstract

One more attempt to study nafion-water interface is described. Experiments showed that addition of 130 mg. of nafion into 10 ml of laboratory water changed its pH from 6 to 3.7 within 7 minutes, to 3.5 within 20 minutes and to 3.1 after 19 hours. So nafion emits remarkable amount of protons into water, enriches it with hydronium ions and achieves equilibrium at about pH=3. Water protonation can change its freezing and boiling points. It also influences the physical properties of water that can be registered with measuring devices with resolution not less than 10^{-5} .

Introduction

For many years scientists around the world have been attracted with puzzles that water poses, showing difficult to explain behavior in Nature. Water is a very active subject of scientific studies nowadays due to its unpredictable behavior and high sensitivity to external influences and participation in major biochemical processes. All scientists admit that water as a foundation of life on the Earth, and many amazing observations have been done that develop our understanding of major water properties. One of the most complete descriptions and analyses of modern achievements in “water science” is maintained by Martin Chaplin on the pages of his website¹.

But water is not so simple to understand and conceals many puzzles up to now. It is widely understood that unique properties of water and its solvating abilities are connected with dipole-like structure of its molecule and hydrogen bonding between water molecules. The first mention of the hydrogen bond, was probably made in 1912². The description of hydrogen bonding in its more well-known setting, in water, came some years later, in 1920, from Latimer and Rodebush³. Hydrogen bonding is about ten times weaker than covalent bonding. It's due to hydrogen bonding that water gets its unique physical properties and forms complex ever-changing clusters.

What makes water so difficult to understand is due to the limitations of present instrumentation. According to Heisenberg uncertainty principle we cannot tell for sure both momentum and position of a particle. But we also cannot separate one from another: water molecules are in eternal movement. So measuring instruments with high resolution can give us good understanding of a molecule position but will also influence water structure dramatically. Less invasive measurements using longer waves can give only statistical approach to energy distribution but do not reveal water structure. That is why we often see discrepancies in different publications. This is why theoretical approach to water clustering hypothesis is probably the only and the most successful one up to now.

The limits of the measuring instruments do not allow measuring the energy of hydrogen bonding directly and theoretical estimation by BLYP-D geometrically optimized structures of water clusters with estimated hydrogen bond energies $E_{\sigma/\sigma+m}$ in kJ/mol about 20.6 for dimer, between 25.6 and 27.6 for trimer, between 16.8 and 32.2 for pentamer, and about 42.0 for hexamer⁴ that makes it the subject to thermal influence with resonance wavelength about 7.2 μm . for 16.8 kJ/mol and 2.8 μm for 42.0 kJ/mol bonding energies, that can break the bonding. So water clustering is subject to thermal influences and frequent changes. The cleavage-formation of H-bonding of water molecules makes water liquid in the range between 0-100°C on the one hand, but also leads to formation of very complex evanescent structures inside⁵.

Furthermore, besides strong dipole interaction known as hydrogen-bond, water always forms hydration shells around non-dissociable particles or surfaces that are in contact with water, using weaker dipole-dipole interaction with energies of dissociation between 0.02 and 0.1 eV, and Van der Waals forces that are weaker than dipole-dipole interaction. Hydration shells around ions, formed in the process of salt solvation, depend on the ion charge and mobility.

The hydration shell that forms around proteins is of particular importance in biochemistry. This interaction of the protein surface with the surrounding water is often referred to as protein hydration and is fundamental to the activity of the protein⁶. The hydration layer around a protein has been found to have dynamics distinct

from the bulk water to a distance of 1 nm with effects on the surrounding water network extending beyond 2 nm.⁷

These hard to observe and understand water properties give basis for many speculations, sometimes not very well scientifically proven. One such speculation claims that there are “liquid crystals” in water formed in the water-surface interface near hydrophilic surfaces⁸. Is there a real basis for such speculation? Liquid crystals shall have anisotropic properties at room temperature that were not proven substantially during this hypothesis presentation. Additionally, there should be formed such bonding between water molecules that are not a subject to thermal influence at room temperature that was not shown.

In support of this hypothesis there were mostly visual observations of microsphere movements near hydrophilic surfaces. But what this visual observation can show in reality? To check this, the following experiments were performed.

Experiments.

There were three major participants in the vast majority of the laboratory experiments: pure water, microspheres and nafion. First, it was necessary to understand properties of water used in the experiments. Inquiries about the lab water processing technology revealed that the water used for the experiments in the laboratory passed through reverse osmosis process three times and was exposed to UV radiation from mercury lamps three times. So this water was ultrapure and highly ionized with pH ranging from 5.75 to 6. It means that the water was rich of hydronium ions unbalanced with hydroxide.

Second participant was microspheres. Laboratory used Invitrogen microspheres of different materials covered with latex⁹. This is what the manufacturer writes about, for example, amidine particles: “this positively-charged hydrophobic 0.5 μm Amidine latex is particularly suited for the preparation of latex intermediates. The only surface functional group present on the particle is amidine, which is not sensitive to the aggregating effects of polyvalent cations”.

Measurements of pH change, when microspheres were added to water, showed that all microspheres used in the laboratory lowered the water pH level (fig.1). It might mean that all microspheres were charged positively causing water deoxidation. ΔU represents the change of probe electrode potential after addition of microspheres.

Microsphere	concentration n/ml	pH*	ΔU
Carboxylate 0.1 μm	75 billion/ml	5.15	42 mV
Carboxylate 0.45 μm	800 million/ml	5.35	31 mV
Carboxylate 4.5 μm	800 thousand/ml	5.65	14 mV
Polystyrene 2 μm	9 million/ml	5.5	23 mV
Amedin 0.52 μm	530 million/ml	5.7	11 mV
		* Initial pH = 5.9	

Fig.1

All

measurements were produced with Thermo scientific Orion 350 (10) with H⁺ sensitive electrode. Electrode: 8220BNWP PerpHecT ROSS combination pH electrode with glass body, micro tip and waterproof BNC connector

Third participant was nafion. Nafion is a very well-studied material, described in many publications¹⁰⁻¹⁴. That is what the inventor of nafion Walther Grot of DuPont writes about it¹⁰: “a meltfabricable precursor polymer is prepared by the copolymerization of TFE (C₂F₄, mw=100) and perfluoro 3,6-dioxa-4-methyl-7-octene sulfonyl fluoride (CF₂=CFO-C₃F₆-O-C₂F₄-SO₂F, mw446)”. It is the first of a class of synthetic polymers with ionic properties which are called ionomers. Molecular formula C₇HF₁₃O₅S.C₂F₄ (fig.2)

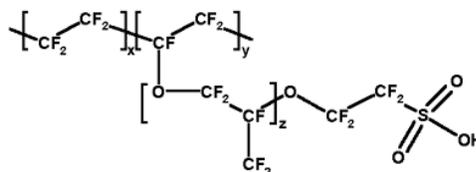


Fig.2

Whenever nafion contacts water, “the water content of the membrane is increased, the hydrophilic domains swell in size and form an interconnected network of transmembrane channels. Above the percolation threshold, protons are able to pass completely through the PEM via the hydrophilic regions. The acidic proton of the sulfonic acid can be substituted for another general cation, M^+ , which is denoted as M-Nafion”¹⁵ and protons are released into water transmitting excessive energy of the M-Nafion formation reaction.

Simple experiments showed that addition of 100 mg. of nafion tubing into 10 ml of laboratory water changed its pH from 6 to 3.7 within 7 minutes, to 3.5 within 20 minutes and to 3.1 after 19 hours (fig.3).

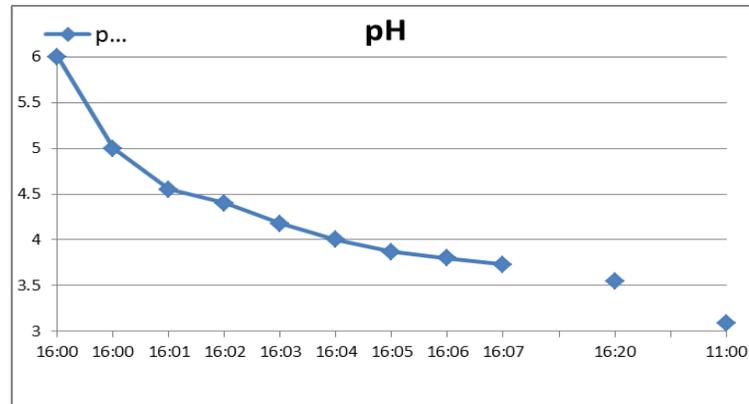


Fig.3.

So, addition of nafion makes water highly protonated and rich with hydronium ions that are not balanced with hydroxide ions.

The following experiments were set up to observe “exclusion zone” formation (fig.4). A small section of nafion tube of 3 mm diameter was placed between the walls of narrow glass chamber made of microscope slides.

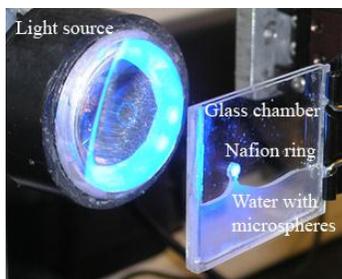


Fig.4

Light source consists of a set of blue LEDs, positioned in the form of a ring with a diffuser and a lens, forming dark field illuminator, concentrating light on the object.

Glass chamber with the distance between walls of 1 mm made of microscope slides of 1 mm thick

Nafion ring of outer diameter of about 3 mm.

Water with Amedin 0.52mk microspheres.

The glass chamber was made of glass slides for microscope of 1 mm thick (Fisherbrand Microscope Slides Catalog #12-550C) and covered with NaN_3 on SAM of 11-bromo-undecyl-trichloro-silane (BUTS). The contact angle between water and NaN_3 surface is very close to 90° (due to presence of azote on the glass surface), greatly reducing meniscus, and thus allowing more precise observation of air-water boundary without remarkable distortion of reflected light. The sides of the chamber were formed using 1 mm thick polydimethyl-silane (PDMS) layer.

The chamber is illuminated with monochromatic light coming from blue LEDs placed on a plane in the form of a ring. The light from LEDs passes through a diffuser and is collected by a lens on the surfaces of the glass chamber. There was a microscope with attached video camera on the other side of chamber. This is a typical example of dark field microscopy.

The following series of jpg images (fig.5) represents a typical observation of formation of a zone that is free of microspheres around nafion ring after the chamber is filled with water with microspheres. The presented series of images represents typical picture of dark field microscopy when all not quite transparent particles become a secondary source of light and thus are eliminated brighter than transparent pure water. Like in the lecture, it is possible to observe that dark zone around nafion ring widens with the time. (The figures near the lines on the pictures show distance (in μ) between the lines and presented just for the dark zone width estimation only).

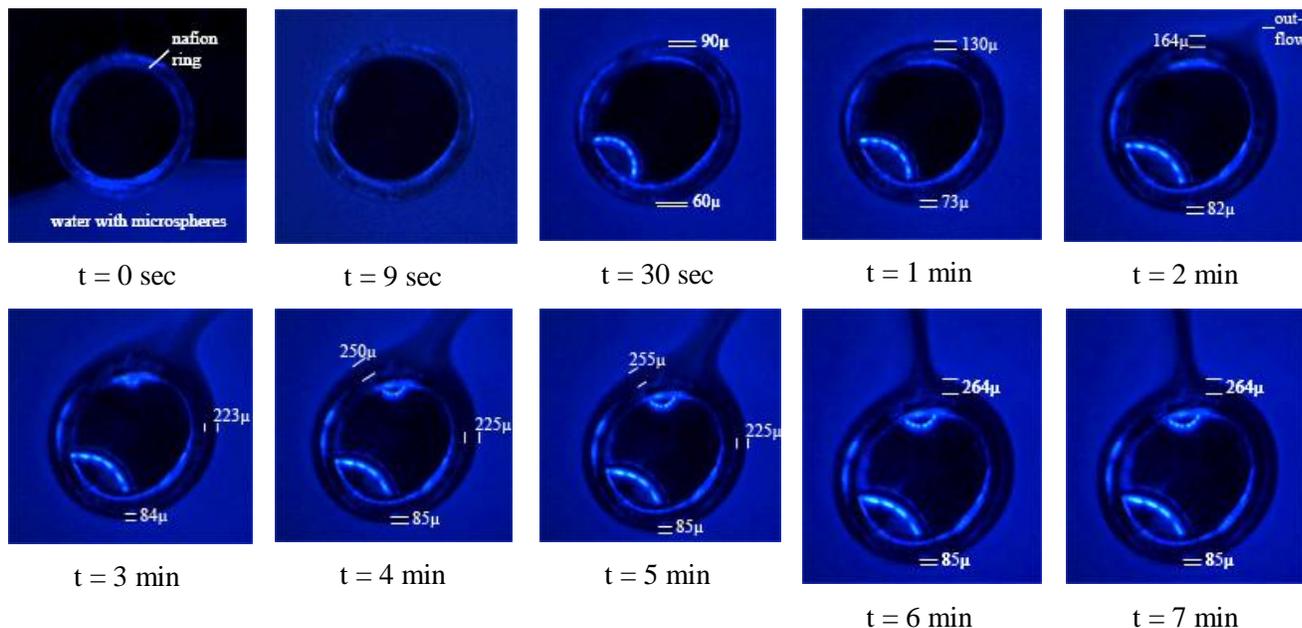


Fig 5.

The total sequence of events may be described as follows: after water comes into contact with nafion ($t=9\text{sec}$), microspheres (illuminated as blue field) begin movement and form a zone around nafion that is free of microspheres (dark field). The dark field inside the nafion ring is the air. Some bright blue fields of water with microspheres inside the ring were formed after the first 30 seconds, due to tiny gaps between nafion ring and chamber walls. They look slightly brighter because they do not fill the whole space between the walls but touch only one of them forming small drops on that wall. After the first 30 seconds a zone around nafion ring, free of microspheres, has a thickness of about $60\mu\text{m}$ at the bottom and $90\mu\text{m}$ at the top of the ring.

Formation of an outflow can be noticed in the upper part of the zone after two minutes and is formed into a well-developed outflow in a couple of minutes. This process stabilizes within seven minutes and the system comes to a more or less stable equilibrium. A zone free of microspheres has width of about $90\mu\text{m}$ at the bottom and about $260\mu\text{m}$ at the top of the nafion ring.

Discussions.

The series of pictures on fig.5 represents development of a zone around nafion clear of microspheres that coincide with the videos presented in the lecture⁸. This movement was attributed in the lecture to hypothesis that water forms a “liquid crystal” that shall have a higher density and structure that exclude microspheres. But what might be the mechanism of the liquid crystal formation? Is there a basis for such speculation? There should be formed some bonding between water molecules that can withstand kinetic energy of thermal motion at a room temperature. But as it was shown in the introduction there should not be such bonding in water. But why and how the liquid crystal might be formed?

First, it would be interesting to remark that there were remarkable discrepancies in the lecture. It was noticed that all attempts to measure the level of water pH in the zone showed increased concentration of protons in the region (fig.6) compared to bulk water. On the other hand measurements of potential difference between the region and the bulk water showed that the region has negative potential compared to bulk water (fig.7).

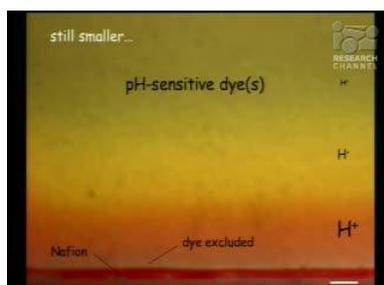


Fig.6

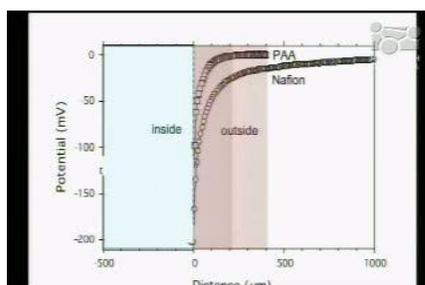


Fig.7

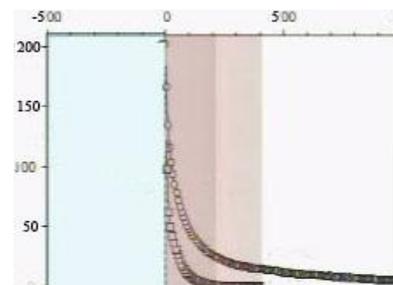


Fig.8

This is a remarkable contradiction. Higher concentration of protons shall show positive potential difference relative to the distant water. But this contradiction can be easily explained with the fact that extra pure demineralized water used for the experiments in the laboratory has very high resistivity and mechanism of conductivity that can be described as protonic defect movement (Grotthuss mechanism¹⁶). Devices, measuring potential difference, must have very high input impedance produced by isolated electrode, so they can measure potential difference induced by higher concentration of hydronium ions. But the real distribution of potential in highly protonated water should look the same as Fig.7 except vertical axes should be reversed (Fig.8).

A second discrepancy was application of the idea of a “liquid crystal” (fig.9) without proper analysis of the possible bonding mechanism and rejection of all other reasons (fig.10) that might cause movement of microspheres in the nafion-water interface, Moreover, a long range repulsive force was labeled as “mysterious”.

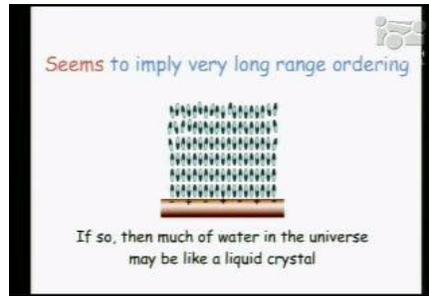


Fig.9

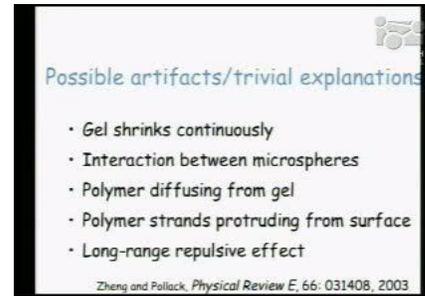


Fig.10

The major feature of this microsphere free interface region formation (fig.5) is that it coincides with the time scale in the graph (fig.3), representing change of water pH after nafion is set into contact with water. The simplest explanation of the microsphere-free-zone development is as follows: after coming into contact with water nafion releases protons into water and enriches water with hydronium ions. Hydronium ions create a potential gradient that repels positively charged microspheres and forms the microsphere-free-zone around nafion ring.

Moreover, such feature as difference in thickness of the zone between the top and the bottom of the nafion ring can show that properties of water in the zone differ from the properties of the water with microspheres in density and, probably, in viscosity. Besides the water surrounding nafion formed the outflow that allows it to escape to the top of the chamber. All this seems to be intuitively clear: protons have very high mobility in water and their high translational energy increases the entropy of the zone when concentration of protons increases according to Gibb's equation.

$$S = -k_B \sum_i P_i \ln P_i$$

where $k_B = 1.38065 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant,
 P_i - the probabilities for the system to be in the i^{th} microstate.

So, entropy is function of the states of the energy and protons, with their high translational energy, increase overall range of energetic probabilities of the system, as far as their concentration in nafion-water interface is hundred times higher than in surrounding water with microspheres. The increase of probabilities range increases the entropy of the system. So this water shall have higher overall mobility and is less likely to form a liquid crystal.

On the other hand, water with microspheres forms hydration shells around charged big microspheres that have very low mobility and therefore will decrease entropy of this water due to water molecules binding to the microspheres. So, the water in this region might have higher density and viscosity. That is probably why protonated water around nafion forms the outflow where protons escape up to the surface of water. This escape also establishes an equilibrium that makes this zone stable for many hours without further propagation.

Water enriched with hydronium ions also shows such features as was shown in the lecture:

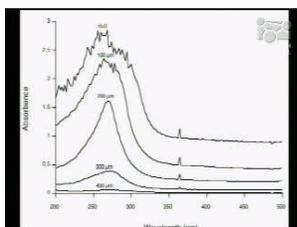


Fig.11

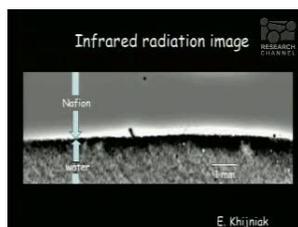


Fig.12



Fig.13

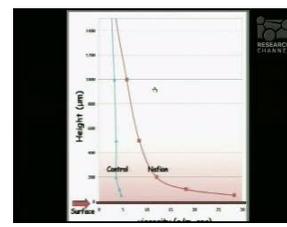


Fig.14

Fig.11 shows increase of UV light absorption in the region. The wavelength of maximal absorption is about 270 nm and coincides with energy of covalent bonding between oxygen and hydrogen. This also supports the idea that the region has higher concentration of hydronium ions with excessive proton covalently bonded to oxygen. The concentration of excessive protons is thousand times higher than in bulk water.

Fig. 12 represents IR picture (courtesy of Dr. E. Khijniak) of the interface region and shows that IR radiation from the region is lower than that of the bulk water. It might mean that this region evaporates more intensively and has lower surface temperature. And it might also mean that water molecules are more constrained in the region with microspheres and has less energy for evaporation.

Fig. 13 and 14 represent change of the microspheres velocity in the experiments of “falling ball viscometry”. Nafion was placed at the bottom of a glass chamber that was filled with water and synthetic microspheres, with density higher than water, were spread on the surface (fig.12). It was not said in the lecture what kind of microspheres were used but it is evident from the picture that it was the same type of microspheres used in the laboratory that are charged. So, fig 14 represents change of microspheres velocity due to repulsive force and potential gradient. As far as nafion emits protons into water, the nafion-water interface forms potential gradient that slows down positively charged microspheres.

Two other experiments presented in the lecture to support “liquid crystal” hypothesis with NMR tomography (fig.15) and light polarization (fig.16 and 17) were hard to interpret and do not really support the hypothesis.

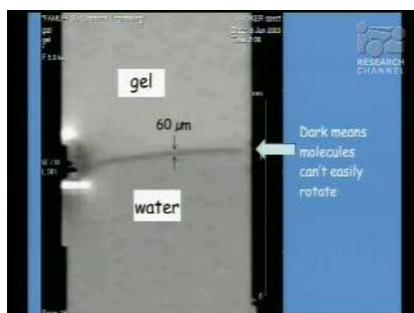


Fig.15

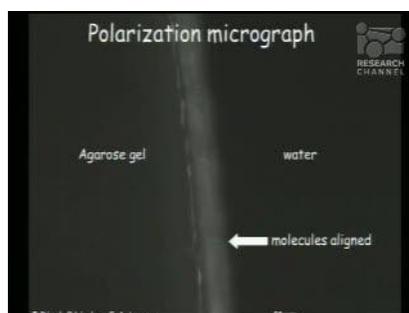


Fig.16

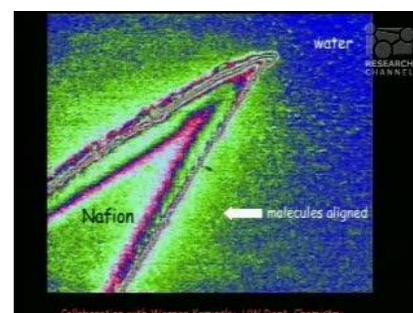


Fig.17

First NMR tomography (fig.15) uses very strong magnetic field of 7-9 Tesla that aligns all protons' magnetic momentums. This certainly changes internal energy of the system and also influences water clustering and thus cannot be used as a proof of “liquid crystal” existence. The only evidence that this picture may represent is that the concentration of protons in the dark region is lower. Where this region with lower concentration of protons is situated is not clear.

Second, measurements of polarization (fig.15 and 16) can prove only that polarization of light changes when light is reflected from any surface. Additionally, there might be some reflections at the boundary of water with high density (microspheres region).

On the other hand highly protonated water that is produced near the nafion-water interface (and may be near other materials with hydrophilic properties) has colligative properties that differ from water with equilibrium of hydronium and hydroxide ions¹⁷. As it was described in the publication, this may produce remarkable influence on many biochemical processes in nature and is worthy of further studies.

Conclusion.

Experiments showed that addition of 130 mg. of nafion into 10 ml of laboratory water changed its pH from 6 to 3.7 within 7 minutes, to 3.5 within 20 minutes and to 3.1 after 19 hours. So nafion emits remarkable amount of protons into water, enriching it with hydronium ions and achieving equilibrium at about pH=3. Water protonation can change its freezing and boiling points. It also influences water physical properties that can be registered with measuring devices with precision not less than 10^{-5} .

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References:

1. Martin Chaplin, Water science. <http://www.lsbu.ac.uk/water/>
2. J. Chem. Soc. 101, 1635
3. JACS, 42, 1419
4. Wendler K., Thar J., Zahn S., Kirchner B., "Estimating the Hydrogen Bond Energy" J. Phys. Chem. A 2010, 114, 9529–9536
5. Martin Chaplin, Water Clusters: Introduction, <http://www.lsbu.ac.uk/water/abstrct.html>
6. Zhang, L.; Wang, L.; Kao, Y. -T.; Qiu, W.; Yang, Y.; Okobiah, O.; Zhong, D. (2007). "[Mapping hydration dynamics around a protein surface](#)". Proceedings of the National Academy of Sciences 104 (47): 18461.
7. Ebbinghaus, S.; Kim, S.; Heyden, M.; Yu, X.; Heugen, U.; Gruebele, M.; Leitner, D.; Havenith, M. (2007). "[An extended dynamical hydration shell around proteins.](#)". Proceedings of the National Academy of Sciences of the United States of America 104 (52): 20749–20752.
8. Pollack G.H., Water, Energy, and Life: Fresh Views from the Water's Edge <http://www.uwv.org/video/player.aspx?dwrid=22222>
9. <http://products.invitrogen.com/ivgn/en/US/adirect/invitrogen?cmd=IVGNcatDisplayCategory&catKey=89001>
10. <http://www.nafion.mysite.com/>
11. Gierke, T. D.; Munn, G. E.; Wilson, F. C. J. (1981). "The morphology in nafion perfluorinated membrane products, as determined by wide- and small-angle x-ray studies". [Journal of Polymer Science: Polymer Physics Edition](#) 19 (11): 1687–1704.
12. Heitner-Wirguin, C. (1996). "Recent advances in perfluorinated ionomer membranes: structure, properties and applications". [Journal of Membrane Science](#) 120: 1–33.
13. Mauritz, K. A., Moore, R. B. (2004). "State of Understanding of Nafion". [Chemical Reviews](#) 104: 4535–4585.
14. K. Schmidt-Rohr & Q. Chen (2008). "Parallel cylindrical water nanochannels in Nafion fuel-cell membranes". [Nature Materials](#) 7 (1): 75–83.
15. D. B. Spry and M. D. Fayer, "Proton Transfer and Proton Concentrations in Protonated Nafion Fuel Cell Membranes", J. Phys. Chem. B 2009, 113, 10210–10221
16. de Grotthuss, C.J.T. (1806). "Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique". *Ann. Chim.* 58: 54–73.
17. Danilov G. "Changes of Water Colligative Properties in Distillation and Filtration Processes", <http://www.naturelaws.org/observ.pdf>. 8/12/2010.