

Article

The Case for Tetrahedral Oxy-subhydride (TOSH) Structures in the Exclusion Zones of Anchored Polar Solvents Including Water

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Abstract: We hypothesize a mechanistic model of how negatively-charged exclusion zones (EZs) are created. While the growth of EZs is known to be associated with the absorption of ambient photonic energy, the molecular dynamics giving rise to this process need greater elucidation. We believe they arise due to the formation of oxy-subhydride structures $(\text{OH}^-)(\text{H}_2\text{O})_4$ with a tetrahedral (sp^3) $(\text{OH}^-)(\text{H}_2\text{O})_3$ core. Five experimental data sets derived by previous researchers were assessed in this regard: (1) water-derived EZ light absorbance at specific infrared wavelengths, (2) EZ negative potential in water and ethanol, (3) maximum EZ light absorbance at 270 nm ultraviolet wavelength, (4) ability of dimethyl sulphoxide but not ether to form an EZ, and (5) transitory nature of melting ice derived EZs. The proposed tetrahedral oxy-subhydride structures (TOSH) appear to adequately account for all of the experimental evidence derived from water or other polar solvents.

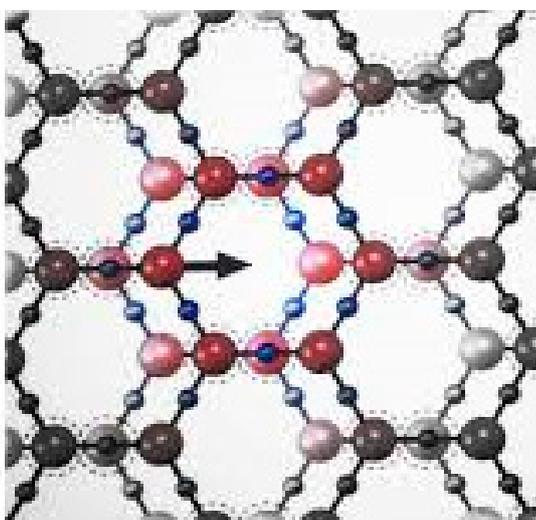
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1. Introduction

In 2003, Zheng and Pollack stated that “solute-solute interactions in aqueous solutions are generally thought to occur on a scale in nanometers” [1]. They further presented evidence that attractive and repulsive forces exhibited at this scale could extend to distances on the order of 100 μm . Subsequent research by Zheng *et al.* demonstrated the exclusion zones (EZs) these forces generated could extend to $360 \pm 50 \mu\text{m}$ [2]. Existing literature does not adequately explain how or why negatively-charged EZs form at all [2–8]. Although Pollack has offered what might be termed a trigonal “ sp^2 bond-type offset hexagonal sheet model” as a possible explanation for EZ structures, as illustrated in Figure 1, this model is problematic in several regards.

Figure 1. Representation of Pollack’s suggested sp^2 offset hexagonal water sheet model.



It does not offer an irrefutable account for: (1) enhanced absorbance of infrared light at $\sim 3436 \text{ nm}$ and 2907 nm (equivalent to wavenumbers ~ 2919 and $\sim 3430 \text{ cm}^{-1}$), (2) EZ negative potential of ~ -160 to -200 mV in Nafion[®]-water or Nafion[®]-ethanol, (3) maximum light absorbance at 270 nm ultraviolet wavelength in water, (4) presence of EZs in dimethyl sulphoxide but not ether, and (5) the transitory occurrence of EZs in melting ice. We are unaware of any other researchers who have proposed models that fully address these issues. Thus arose a need for an explanatory model that could attempt to account for all historical experimental data related to EZs.

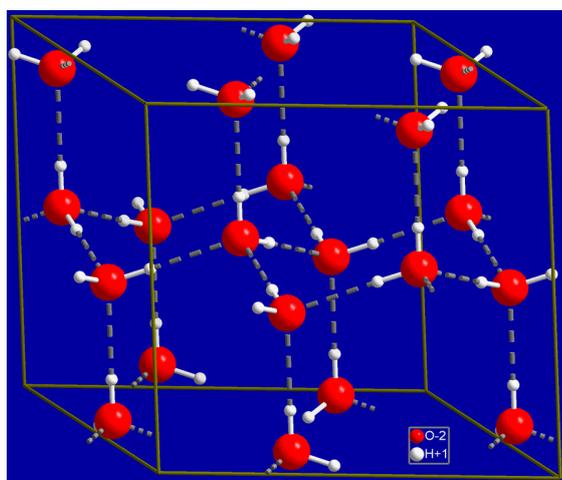
2. EZ Growth Model

We propose an EZ growth model for water, partially melted ice, or polar solvents adjacent to solid or gel anchors containing O^- or OH functional groups able to hydrogen bond to water or polar solvents. Molecules containing OH functional groups include the amino acids serine, threonine and tyrosine, components of rabbit muscle protein, plus polyvinyl alcohol shown to form EZs [1,2]. Molecules containing O^- functional groups include sulphonate in Nafion[®] [3]. Each of these three proposed EZ systems will now be discussed separately in detail.

2.1 Water EZs

Figure 2 illustrates a proposed structure for ice [9]. Exclusion zones derived from water have been shown to have negative potentials (charge). Thus it follows that melting ice would also likely exhibit transitory exclusion zones with a net negative charge and would also expel protons (H^+) to create such a negative charge.

Figure 2. Three dimensional molecular structure for ice showing hydrogen atoms as white spheres, oxygen atoms as red spheres, hydrogen to oxygen bonds within a single water molecule as solid white lines and hydrogen bonds between adjacent water molecules as dashed grey lines.



To illustrate this process, we refer again to Figure 2. The following may occur:

- An ambient, incident photon (e.g., in the ultraviolet wavelength region), strikes and ruptures a non-hydrogen bonded hydrogen atom in a water molecule on the top surface of a block of ice. Note that H^+ and OH^- exist in water free of incident radiation. The addition of specific wavelengths of infrared, visible light or ultraviolet light at varying amplitudes to water is expected to shift the HOH auto-dissociation in favour of additional proton formation [10,11].
- In our example, we use the topmost central water molecule in Figure 2 as it has 2 hydrogen bonds plus 2 hydrogen atoms which are non-hydrogen bonded to other water molecules. We believe this configuration is the most susceptible to rupture and formation of H^+ . Rupture at this site should occur prior to the water molecule directly below it, to which it is hydrogen bonded and which has 3 hydrogen bonds, since it should take more energy to rupture a combination O-H-HOH bond than a single O-H bond.
- The OH^- functional group remaining after H^+ ejection then forms a hydrogen bond with a new water molecule to make it more stable via a fourth tetrahedral bond.

This hypothesized two-step process is illustrated in Figures 3 to 5 below:

Figure 3. Non-EZ ice sub-structure (oxygen atoms as red circles, hydrogen atoms as white circles, solid black lines as oxygen-hydrogen bonds within a single water molecule, dashed black lines as hydrogen bonds between oxygen and hydrogen atoms in adjacent water molecules). Water molecule “A” corresponds to Figure 2’s topmost central water molecule.

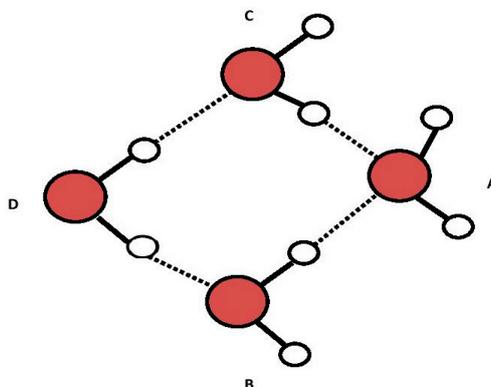


Figure 4. Ruptured ice-substructure containing an OH^- function group at “A” and an ejected proton H^+ after a photon absorption event of sufficient energy.

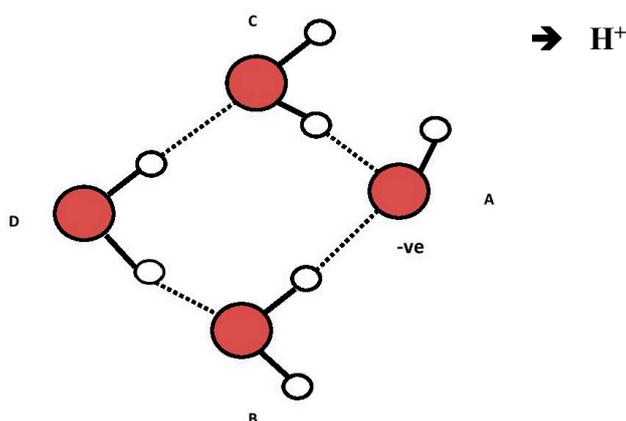
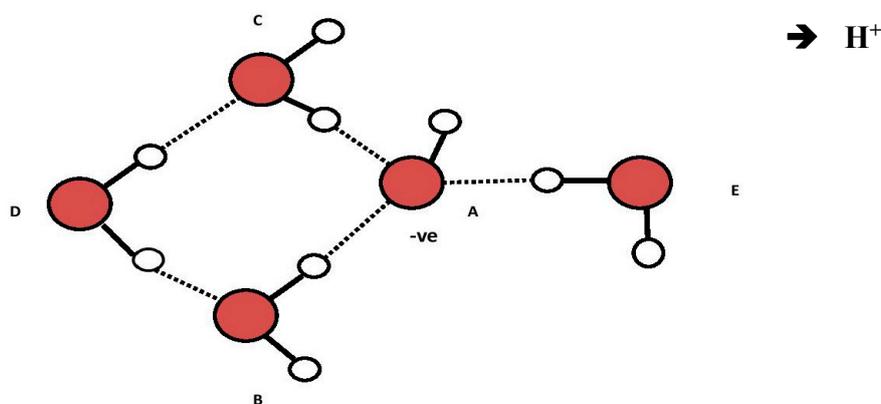


Figure 5. Anticipated hydrogen bonding of the hydroxyl species containing oxygen atom “A” with a new non-ice water molecule “E”.

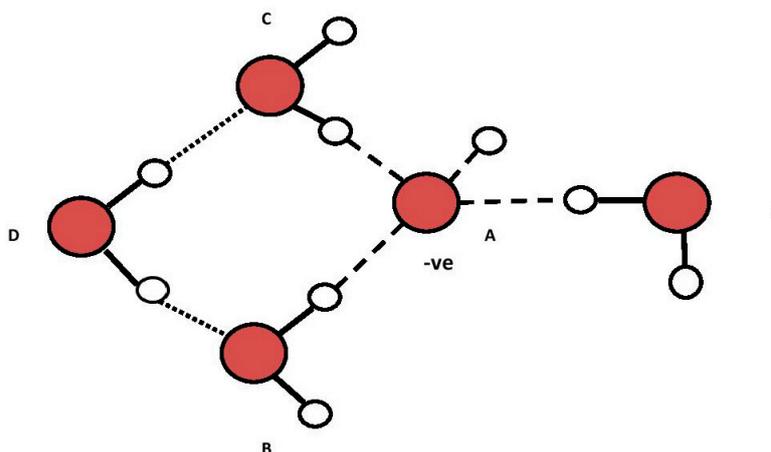


The proposed ABCE structure of Figure 5 precisely matches the hydroxyl-tetrawater cluster designated “OHW4I” (a), containing a tetrahedral (sp^3) (OH^-) (H_2O)₃ core, shown by Chaudhuri *et al.* [12] (p. 1164). This particular structure highly absorbs infrared light at both ~ 3436 nm and 2907 nm (*i.e.*, 2910 and

3440 cm^{-1}), which closely matches the ~ 3426 nm and 2914 nm (*i.e.*, 2919 and 3432 cm^{-1}) for water-derived EZs [3]. Chaudhuri shows that different isomers of $(\text{OH}^-)(\text{H}_2\text{O})_4$ have different infrared spectra. What is of additional significance is that Novoa *et al.* describe and show under “2” that the infrared absorbance peaks in the structures Chaudhuri identified as OHW4I happen to be the most stable of all the possible variants for $(\text{OH}^-)(\text{H}_2\text{O})_4$ [13] (p. 7845). It is therefore likely that water-derived EZs contain a negatively-charged specific hydroxy-tetrawater isomer containing a tetrahedral (sp^3) $(\text{OH}^-)(\text{H}_2\text{O})_3$ core with an H_4O^- sub-core.

Another possible structure for Figure 5 is shown in Figure 6 in which the three hydrogen bonds “B”, “C” and “E” to the oxygen in “A” and the hydrogen to oxygen bond in “A” undergo resonance to make them equivalent (dashed lines from “A” oxygen). Such resonance, if it occurs, could establish TOSH structures as EZ anchors inside the EZ field due to enhanced bond strength of three of the four TOSH O to H bonds (see Figure 5 vs. Figure 6).

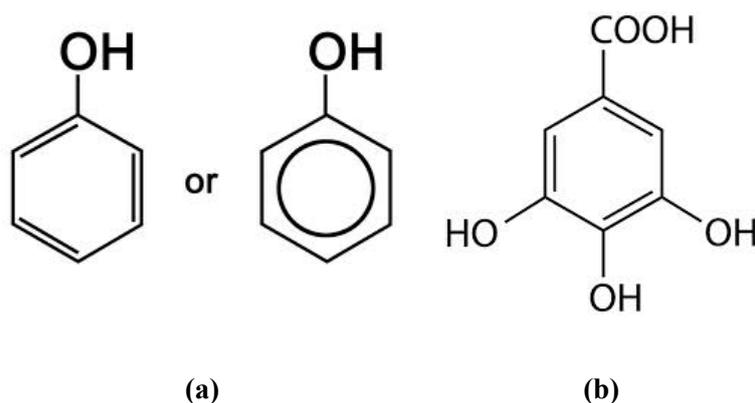
Figure 6. Potential anticipated resonance of hydrogen bonds (dark dashed lines) adjacent to hydroxyl oxygen to make their bond strengths equal.



The electrical potential for a single hydride ion ($1s^2$)/single hydrogen atom ($1s^1$) couple is estimated at -0.83 ± 0.11 V (*i.e.*, 0.83 ± 0.11 V for the H-/H one electron reaction couple) [14]. If the four hydrogen atoms attached to oxygen “A” as H_4O^- (oxytetrasubhydride) equally share the one electron of OH^- in a pseudo $1s^2$ orbital (*i.e.*, less swollen than a normal $1s^2$ orbital), they should have a potential of -0.208 ± 0.028 V, $\frac{1}{4}$ of 0.83 ± 0.11 V, which overlaps the potentials ~ -0.16 to ~ -0.20 V measured in EZs in water next to Nafion[®] by Zheng *et al.* [2,8]. The redox couple for this potential could be given by the following reaction:



Figure 7 illustrates phenol and gallic acid, respectively. Both of these molecules and water-derived EZs show maximum UV absorbance at 270 nm [15,16].

Figure 7. Phenol (a) and gallic acid (b).

The resonant frequency of un-hybridized and un-bonded electrons (designated “n” $\rightarrow\pi^*$) has been estimated as 270 nm [17]. There is one un-hybridized and un-bonded “n” type $2p_z$ electron in each carbon of a C-O phenol and gallic acid sub-cluster. There is also one un-hybridized and un-bonded “n” type $1s^2$ electron in the four hydrogen atoms of an HO_4^- oxytetrasubhydride structure (TOSH). Identical numbers of additional “n” electrons are contained in the oxygen atoms of C-O and H_4O^- . The resonant ultraviolet frequencies of C-O in phenol and gallic acid and TOSH structures are therefore expected to match.

2.2. Non-Water EZs

Experimental data on heavy water and non-aqueous polar solvent (e.g., ethanol) EZs suggests oxytetrasubhydride structures are analogous to those in EZs suggested for water. Figures 8 to 10 are the ROH polar solvent analogues of Figures 3–5 (e.g., R shown in green is C_2H_5 and, R^+ is C_2H_5^+ for ethanol). Further credence to the oxytetrasubhydride structure hypothesis is suggested by their super-imposable electrode potentials of ~ -160 to ~ -200 mV.

Figure 8. ROH solvent sub-structure [oxygen in red, R group (e.g. C_2H_5) in green and hydrogens in white, dotted lines indicate hydrogen bonding between ROH molecules].

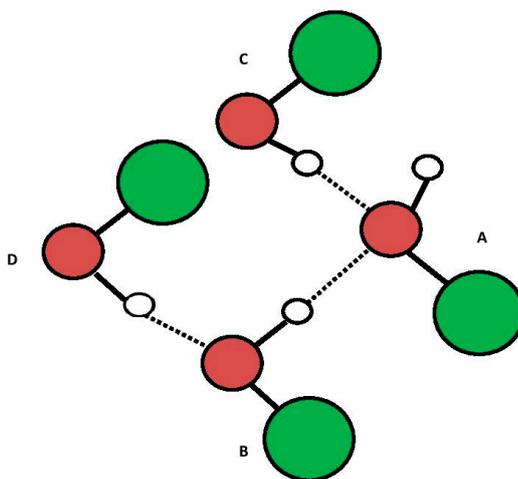


Figure 9. ROH solvent sub-structure [oxygen in red, R group (e.g., C₂H₅) in green and hydrogens in white, dotted lines indicate hydrogen bonding between ROH molecules].

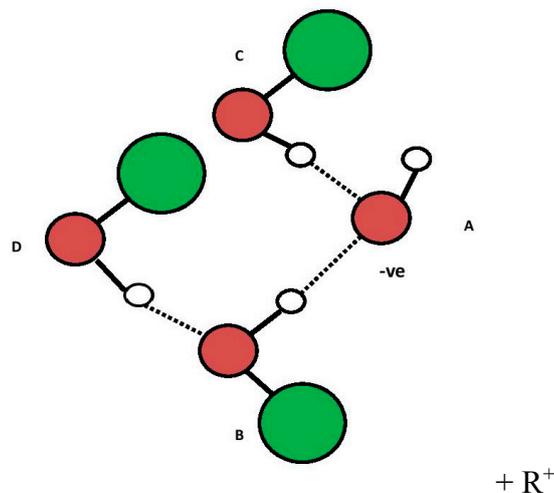


Figure 10. ROH solvent sub-structure [oxygen in red, R group (e.g., C₂H₅) in green and hydrogens in white, dotted lines indicate hydrogen bonding between ROH molecules, plus H₄O⁻ oxytetrasubhydride cluster].

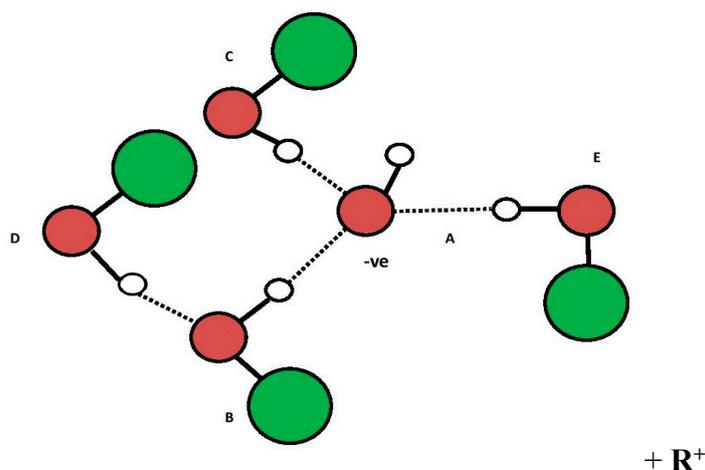
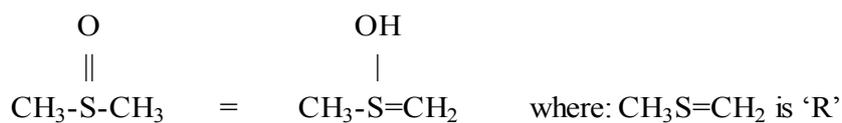


Figure 11 shows that dimethyl sulphoxide, unlike diethyl ether, can form a ROH isomer and a subsequent EZ via:

Figure 11. Dimethyl sulphoxide isomers.



2.2. EZ Anchors

It is believed that EZ water containing tetrahedral oxy-subhydride sub-clusters is stabilized by the presence of solid or gel-like non-billowable anchors containing OH (e.g., polyvinyl alcohol, polyacrylic acid, protein, amino acids, O⁻ [Nafion[®]] functional groups). Once the solid ice OH

functional group anchors melt with or without additional photonic energy inputs, they cease to be anchors. We believe this is responsible for the subsequent destruction of the EZ fields as evidenced by their lack of UV absorbance at 270 nm. This would suggest that intermediate TOSH anchors are of insufficient strength to sustain an EZ field in the absence of a stronger anchor such as Nafion®, polyacrylic acid, polyvinyl alcohol or amino acids in protein (e.g., rabbit muscle).

4. Conclusions

The following experimentally-derived empirical data sets from previous investigators have been assessed to validate the proposition that tetrahedral H_4O^- oxy-subhydride (TOSH) structures account for the properties observed in water, heavy water or polar solvent derived EZs:

- (1) Water-derived EZ light absorbance at specific infrared wavelengths.
- (2) EZ negative potential in water and ethanol.
- (3) Maximum EZ light absorbance at 270 nm ultraviolet wavelength.
- (4) Ability of dimethyl sulphoxide but not ether to form an EZ.
- (5) Transitory nature of melting ice derived EZs.

The mechanism of formation of the suggested TOSH structures has been described in detail. The likelihood of the proposition being valid is high since correlations with a wide variety of experimental data are good.

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Author Contributions

Paul H. LeMay introduced Klaus Oehr to Gerald Pollack's concepts of EZs, helped formulate the concepts of this paper as well as edit its contents. Klaus Oehr carried out all of the calculations and supporting literature searches necessary to prepare the paper. Both authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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