

HYDRATION STRUCTURES AND DYNAMICS: AN ALTERNATIVE PERSPECTIVE ON REMEDIATION PROCESSES

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ABSTRACT: As environmental scientists, our understanding of solute behavior (e.g., fate, transport, remediation) is based on macro-scale properties such as solubility, diffusivity and phase partitioning. These gross physical properties of solutes are actually a result of molecular- and atomic-scale dynamics, which are described by thermodynamic and quantum mechanical principles. The perception that water is simply a passive solvent within which contaminants react and are transported overlooks the effects of contamination on water itself, except as it may influence gross physical properties of the water. The effect of solutes on the molecular structure of water and the manner in which water is able to accommodate solutes into its rather complex network is of particular importance in assessing its behavior and degradation in aqueous environments.

INTRODUCTION

Bulk Liquid Water. Water is not a random collection of H₂O molecules, but rather an extended network that is locally interconnected by hydrogen bonds (H-bonds) linking the oxygen and hydrogen atoms of neighboring water molecules. These electrostatic H-bonds are generally considered to be distinct from the covalent bonds that connect oxygen and hydrogen atoms within the same molecule; however, a recently published study indicates that the intermolecular H-bonds have significant covalent properties (Isaacs et al., 1999). This finding suggests that electrons are shared not only between atoms of the same water molecule (intramolecular), but also among atoms of neighboring water molecules (intermolecular).

The underlying geometry of bulk liquid water is tetrahedral, owing to the ability of each water molecule to hydrogen bond with four of its neighbors. This water network is dynamic, rather than static, and re-shuffles H-bonds among neighboring water molecules at a rate of millions to trillions of times per second. The ceaseless rearrangement of H₂O molecules with respect to each other creates 3-dimensional geometries that are unique to the chemicals solvated and to the surfaces interfaced. In addition to the tetrahedral geometry of bulk liquid, water also has the ability to form larger associations that are known as clusters. Water comprising these clusters (ranging from a few to several hundred water molecules) is more structured and less dynamic than that in bulk liquid. In other words, water molecules comprising clusters re-shuffle intermolecular connections at a slower rate and are structurally more rigid (e.g., possess less orientational flexibility) than do those in the bulk liquid. These two properties of water clusters translate into slightly different physical properties than those of the bulk liquid.

Water Clusters. Water clusters exist as both pure water and as “cages” or envelopes that surround chemicals that are dissolved in water. The latter may include millions of water molecules and are of particular interest to our discussion

because they constitute the structures that are responsible for the dissolution and aqueous behavior of contaminants. Essentially, water insulates solutes from its bulk tetrahedral network by forming hydration envelopes around them. Water molecules comprising the envelopes are connected to the bulk liquid via H-bonds and to the solute via H-bonds, dipole interactions or van der Waal forces, depending on the nature of the solute. Many recalcitrant organic chemicals are hydrophobic in nature and, thus, interact weakly with water comprising the envelope. Conversely, ionic and polar solutes interact more strongly with water molecules in the envelope. Within these hydration structures, solutes are contained in water with minimal (albeit unavoidable) breakage of H-bonds and the associated disruption to water's bulk network.

Water molecules comprising the hydration envelopes act as mediators for the interaction of contaminants with their "guest" compounds and with larger-scale structures such as mineral surfaces. For example, carcinogenic environmental chemicals are active, not through their direct effects on nucleic acids, but through the production of free radicals in DNA's hydration shell that, in turn, result in strand breakage. In a similar manner, sorption of contaminants on mineral surfaces is facilitated through hydration envelopes that actually mediate proton transfer and other critical processes responsible for electrostatic attraction. Physical chemists have described hydration envelopes for many common hydrophobic solutes, including volatile chlorinated/aromatic hydrocarbons and biogenic gases. Moreover, the orientation and rotational dynamics of solutes and of water molecules comprising such hydration envelopes have also been documented. These dynamics are the underlying basis of reactivity, solubility and a number of other well-known contaminant properties.

Obviously, variables such as temperature and pressure affect contaminants via changes in their molecular structure and dynamics of water comprising both hydration envelopes and the bulk liquid. However, there are less obvious phenomena such as electromagnetic radiation, certain types of fields (magnetic, vorticity) and the presence of other solutes that profoundly effect hydration envelopes and their interaction with the bulk liquid. Many of these phenomena are inherent in conventional remediation and monitoring technologies.

DISCUSSION

Hydrophobic Gases. The behavior of biogenic gases (e.g., methane, carbon dioxide, hydrogen) in aqueous systems is a major area of research as a result of its applicability to everything from assessing redox conditions to quantifying the rate at which organic contaminants are degraded in the subsurface. Those dissolved gases possessing a molecular diameter <3 angstroms (e.g., hydrogen) have a substantially different effect on the structure of water than do other solutes. This is because small gases are able to "slip through the bars" of conventional water envelopes and clathrates, affecting the thermodynamic state of water's H-bond network in a different manner than do larger gases (e.g., methane, ethane). Figure 1 shows the change in entropy and in Gibbs free energy associated with the dissolution of various biogenic and noble gases at 25° Celsius (e.g., Tenaka and

Nakanishi, 1991). Notice that hydrogen and neon (both of which have a molecular diameter <3 angstroms) display the least entropy change and a free energy change that is comparable to that of n-octane. While these small gases have a relatively small enthalpic cost associated with rearranging water molecules to accommodate them (i.e., cavity formation), they offer water almost nothing in terms of network order (i.e., decreased entropy).

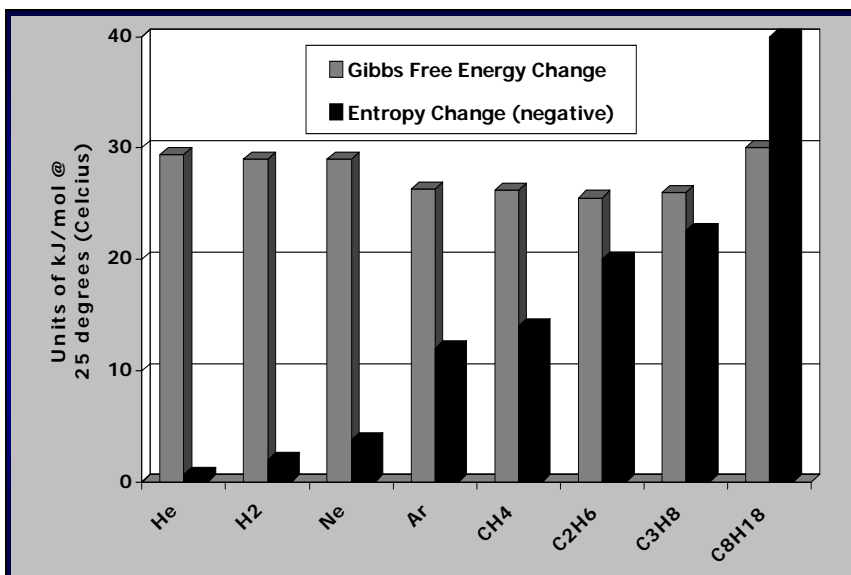


Figure 1. Gibbs free energy and entropy changes associated with solute dissolution in water.

Generally, the dissolution of a hydrophobic solute is believed to occur because the entropic gain to the water network exceeds the enthalpic cost of rearranging molecules to accommodate it. Large organic molecules are less soluble in water than are smaller ones (within a homologous series of organic compounds) because the enthalpic costs increase faster than the entropic gains. Hence, large hydrophobic compounds and very small gases are the most disruptive to water's network and, therefore, have the lowest aqueous solubilities. Figure 2 presents various physical properties of gases in water (Atkins, 1986). Notice that H₂ has both the highest diffusivity and lowest van der Waals constant of any of the gases, suggesting that it interacts with and is confined by hydration envelopes to a minimal extent. It also suggests that helium and neon are probably the best surrogates for hydrogen gas (as conservative tracers) and that these same noble gases are probably poor surrogates for light hydrocarbon and other biogenic gases, which interact with water via stronger van der Waals forces and possess lower diffusivities.

It is interesting to note that certain recalcitrant compounds seem to degrade only under highly reducing conditions, where elevated H₂ concentrations may have an effect on water comprising both the bulk liquid and the hydration shells of contaminants. In addition to the fact that H₂ is the most thermodynamically favored electron donor (i.e., the most highly reduced molecule), its affect on the structure of water itself may be another reason for its

apparent rapid turnover in aqueous systems. Schuler and Conrad (1990) hypothesized that the rapid rate of H_2 oxidation (particularly at low aqueous concentrations) may be due to the presence of extracellular enzymes that are adsorbed to natural organic matter or mineral surfaces, primarily via interactions mediated by hydration envelopes.

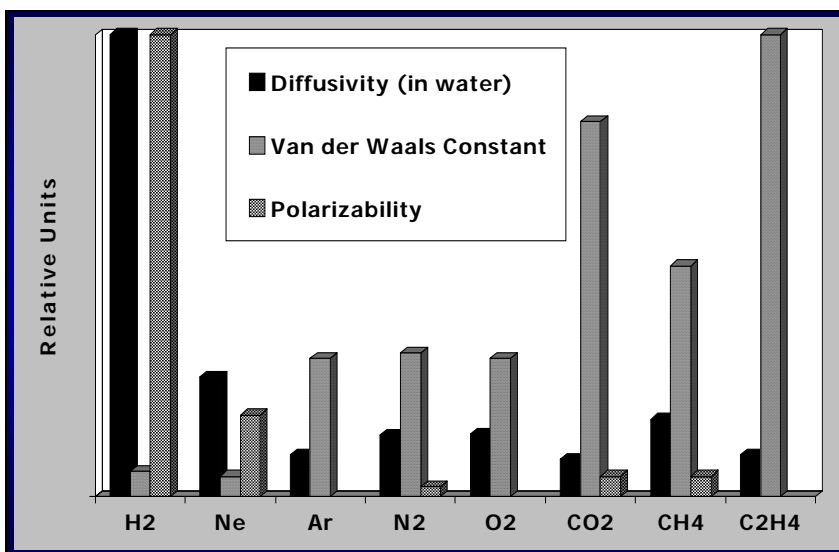


Figure 2. Relative diffusivities, van der Waal constants and polarizabilities among solutes.

Volatile Organic Compounds (VOCs). Similar to biogenic gases, the effect of hydrophobic solutes (such as VOCs) on the structure of water is related to the ordering of molecules in the hydration envelope. For this reason, hydrophobic solutes are often referred to as structure-makers, denoting that they increase the order (or decrease the entropy) of the water network immediately surrounding the VOC. Water molecules in the hydration envelope are not only more ordered (i.e., possess less orientational freedom) than those in the bulk liquid, they also rearrange or vibrate at a slower rate (Nakahara et al., 1996). This slower vibration rate is a result, or a consequence, of the fact that H-bonds in the hydration envelope are stronger than those in the bulk liquid. Although hydrophobic hydration results in an increased percentage of broken H-bonds compared to that in the bulk tetrahedral network, the H-bonds that persist are stronger (Mancera, 1996).

The effect of the hydration envelope on VOCs such as benzene is to increase the rotational movement of the solute, affecting its physical properties such as reactivity and diffusivity. Therefore, both the structure of the hydration envelope and the temperature of the water affect solute properties. As the temperature of the water rises, water molecules in the hydration envelope, as well as those in the bulk liquid, vibrate at an increasing rate until H-bonds begin to break, thus releasing solutes from their cages. This is the basis of in-situ thermal technologies, which are generally designed to either decrease sorption or increase volatilization by destroying the hydration structures that permit VOCs to remain

in solution and to interact (via H-bond mediated proton transfer) with natural organic acids or mineral surfaces.

Bioremediation technologies are also dependent on hydration structures and dynamics. Both intracellular and extracellular enzymes responsible for the biological catalysis of recalcitrant compounds are fully hydrated and interact with the substrate (e.g., VOC) via their respective hydration envelopes. Hence, changes in both the contaminant hydration structure and dynamics, affecting the molecular-scale properties of the contaminant itself, influence the susceptibility to and kinetics of biodegradation. Due to the difference in the size and polarity among chlorinated ethanes, their respective hydration envelopes may be characterized by different free energies (thermodynamics). Even among this homologous group of compounds, changes in the Gibbs free energies for hydration are an order-of-magnitude less for the moderately recalcitrant 1,1,1-trichloroethane than for the readily degradable 1,1,2,2-tetrachloroethane (Paulsen and Straatsma, 1996).

In addition to organic substrates (e.g., benzene, chlorinated ethanes), the hydration of electron acceptors is also critical. Figure 3 indicates that water solvates both O_2 and CO_2 , which serve as electron acceptors for aerobes and H_2 -utilizing methanogens, with what are known as *Structure I* cages or clathrates (Franks, 1973). Clathrates are a specific class of water cluster that surrounds solutes with molecular diameters less than 7 angstroms; *Structure I* consists of 46 water molecules in the form of a dodecahedron (Franks, 1973). By contrast, ionic electron acceptors (e.g., nitrate, ferric iron, sulfate) interact with hydration structures predominantly via dipole or electrostatic (rather than van der Waals) forces, which reorient the surrounding polar water molecules of the bulk liquid. For example, the first hydration shell or layer surrounding the Fe^{3+} ion consists of 6 water molecules in the form of an octahedron (Degreve and Quintale, 1996). This first shell is surrounded by a second shell, consisting of 15 water molecules that H-bond with those in both the first shell and the bulk liquid.

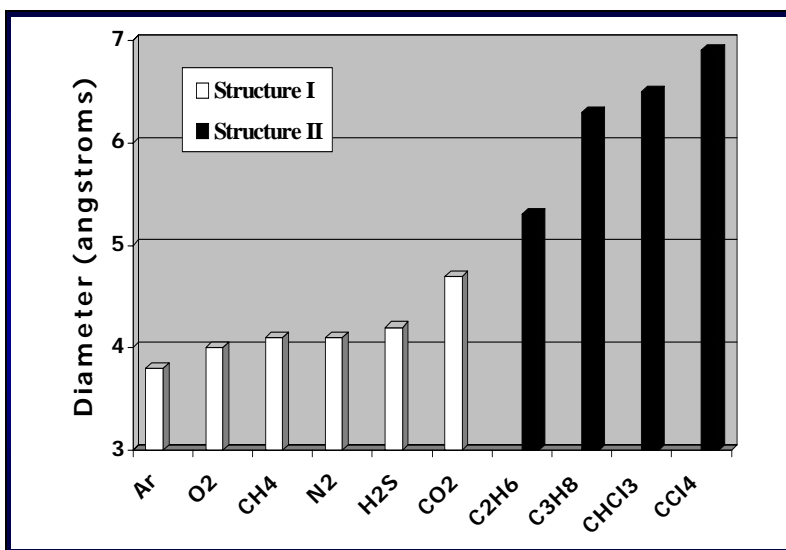


Figure 3. Clathrate structures of various aqueous solutes as a function of molecular diameter.

For both the nonpolar and ionic electron acceptors, water molecules in the hydration envelopes act as mediators and as buffers between the solute and the bulk water or other solutes. Because there is extensive H-bonding between water molecules in the hydration envelopes and the bulk liquid, changes in the bulk properties of water are translated into differences in the availability and reactivity of biodegradation reactants. Simply stated, the hydration envelopes of all solutes are affected by any re-structuring of the bulk phase.

CONCLUSIONS

There are number of ways in which the hydration structures and dynamics of water could be useful in understanding or designing remediation systems. Perhaps the simplest is the selection of surrogates that are used as conservative tracers for both organic contaminants and for biogenic gases. The increasing use of such tracers over the past five years is related to the monitoring requirements of the MNA remediation option and to the understanding of biodegradation dynamics within a contaminated plume. As previously mentioned, helium has a similar effect on the structure of water as does hydrogen gas. Similarly, argon and other moderately-sized nonpolar gases are good tracers for the common biogenic gases (e.g., O₂, CO₂, CH₄, H₂S) because they are contained within *Structure I* hydrate clathrates. The largest of molecules contained within clathrates possess a molecular diameter in excess of 5 angstroms and include C₂ and C₃ hydrocarbon gases and the chlorinated methanes. These larger compounds form *Structure II* clathrates, which consist of 136 water molecules and represent the concatenation of 4-, 5- and 6-sided polygons (Franks, 1973). Compounds possessing a molecular diameter greater than 7 angstroms are hydrated by customized envelopes rather than by specific clathrate structures.

Clathrates are currently being utilized in the mitigation of the greenhouse gas, carbon dioxide, and seem to be very stable under low temperatures and high pressures. The formation of CO₂ hydrates either in deep ocean basins or in engineered processes is being tested as a method to sequester this greenhouse gas from the atmosphere. In essence, CO₂ clathrates are being entombed at the bottom of the oceans. While the environmental impacts of such a technology are poorly understood, the process does pose the prospect that other clathrate formers (e.g., methylene chloride, carbon tetrachloride) could be sequestered under the appropriate conditions, which may or may not be applicable to the environment.

Another remedial application related to hydration dynamics is related to the effects of electromagnetic (EM) radiation on bulk water, hydrate structures and solutes. Table 1 lists the molecular and atomic effects of EM frequencies within various ranges. The reason that radio and microwave frequencies are used in heating water is that they cause water molecules to vibrate and reorient in both the bulk liquid and the hydration envelopes. While IR radiation is sufficient to distort the H-bonds of water, UV radiation is capable of actually breaking its covalent bonds. Similarly, the exposure of water to magnetic fields has been shown to re-structure water such that number of clusters (water only) increases

relative to the tetrahedral bulk phase. H-bond network effects (e.g., electron rearrangements) induced by magnetic or electric fields are due to the slight polarization of water molecules and depend on the exact location of a molecule in the chain or cluster (Hermansson and Alfredsson, 1999). Magnetic fields actually induce current flow that affects the solute's molecular rotation and orientation, both of which are related to its chemical properties. As presented on Figure 2, the biogenic and light hydrocarbon gases (particularly H₂) possess a polarizability much greater than that of water itself.

Table 1. Effects of EM radiation within various frequency ranges.

<u>FREQUENCY (Hz)</u>	<u>EFFECT</u>
10 ⁷ to 10 ¹¹ Radio/Microwaves	Rotations & vibrations (molecular orientation)
10 ¹² to 10 ¹⁵ IR/UV/Visible Light	Electronic shell excitation (molecular distortion)
10 ¹⁶ to 10 ¹⁹ X-Rays	Electron excitation (quantum effects)
>10 ²⁰ Cosmic Rays	Nuclear excitation

The purpose of this paper is not to suggest specific technologies, but to consider contaminants (and associated remediation processes) from the perspective of their effects on the molecular structure and dynamics of water. Perhaps a greater understanding of the structure/dynamics of water will provide insights into methods of investigating, tracing and remediating recalcitrant contaminants that otherwise would not be obvious.

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