Why does hot water freeze faster than cold water from the same source?

(Brief analysis of the reasons)

Introduction

Under normal atmospheric pressure water (as a substance, composed of H_2O molecules), which does not contain remarkable amount of contaminants, is liquid in the range of temperatures between 0^oC and 100^oC ($32^oF – 212^oF$, $273^oK – 373^oK$). If we try to decrease water temperature below 0^oC it turns into a solid substance. What happens to water molecules when it freezes?
Two major factors contribute to change of water stage from liquid to solid: 1. decrease of inner kinetic energy that stabilizes connections between water molecules and 2. hydrogen bonding that is also a major contributor to water molecule connections in hexagonal ice. The first mention of the hydrogen bond was probably made in 1912(1). The description of hydrogen bonding in its more well-known setting, in water, came some years later, in 1920, from Latimer and Rodebush(2). This hydrogen bonding for ice and liquid water may differ.

But why might warm water freeze sooner than cold one?

Hypothesis

A good hypothesis for this effect is as follows: additional time is needed for reconstruction of water structure that accompanies change of water temperature to a level below 0^oC.

The structure of ice may differ from the structure of water clusters formed in water in the liquid state. Whenever molecules bond together they decrease the level of their potential energy(3). So an external energy is required to cleave a bonding. During water heating process water becomes less clustered with more molecules in a transitional (free) state. If water contains more free (unbounded) molecules, time required for freezing such water and formation of hexagonal ice depends mostly on the speed of heat exchange.

On the other hand, when cold liquid water is exposed to the same temperatures below 0^oC in the same freezing chamber it requires additional energy to cleave existing bonding and construct hexagonal bonding of ice. It may take additional time as far as cleaving energy is extracted from water molecules that form hexagonal bonding.

Description of the process

Does water have any structure at all when we speak about liquid water? What structure can water have? Long ago, being far away from the technics of modern science, people recognized water as a structured substance(4). Nowadays, water structuring is widely admitted and thoroughly studied(5). All major estimations of probable water structuring were made by computer simulations. Why?

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 a 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. This 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. Theoretical estimation of hydrogen bonding by BLYP-D of geometrically optimized structures of water clusters with estimated hydrogen bond energies represented as Eσ/σ+m in kJ/mol is 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 hexamer(6). Such levels of bonding energy make water the subject to thermal radiation influence with wavelengths of 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.

Furthermore, besides strong intermolecular H-O interaction known as hydrogen-bond, water molecules always form hydration shells around ions, 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 (1eV = 96.5 kJ/mol), and also 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. So water clustering is subject to thermal influences and frequent changes. The cleavage-formation of H-O bonding of water molecules makes water liquid in the range between 0-100^{o}C on the one hand, but also leads to formation of very complex evanescent structures that also depends on the factor of water purity along the temperature. Influence of salts, dissolved in water, changes its colligative properties(7), decreasing freezing point. But it’s not only salts that may influence water colligative properties but also excessive protons in water, forming hydronium ions and produced by water protonation from different sources of protons(8). In this publication, it is shown that water heating decreases water protonation level and thus eases water freezing.

So, measurements of time, needed to freeze cold and hot water, is subject to many parameters that make these measurements difficult and may mislead researchers. That’s why contradictions may be observed in different experiments. But water restructuring still remains the major contributor for the time difference. If water at the room temperature have mostly icosahedral symmetry of clusters, as was proposed in (9), and shall form hexagonal ice, a cleavage of at least one hydrogen bonding is needed to break pentagonal symmetry, and formation of two hydrogen bonds is needed for hexagonal symmetry. Energy released during formation of hexagonal symmetry may be used for cleavage of pentagonal symmetry. This process takes longer time than breaking bonding from external sources. That’s why freezing of cold water may take longer time than freezing of warm water with less clustering.

References:

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Footnote:

This interest to “Mpemba effect” in the long row of many other effects caused by water clustering seems to be encouraging. Water gives a ground for many sometimes controversial speculations. It would be perfect if Royal Society of Chemistry could attract attention of the scientific world to changes of other water colligative properties depending on the content of ions in water, and especially of hydronium ion (H_3O^+), that contributes to many interesting and important effects in life on the Earth including (but not limited):
1. Hydronium ions, accumulated in the clouds due to evaporation from the surface of the Earth and absorption of protons coming from the Sun and from the space, contribute to scary atmospheric lightnings, which bring many problems.
2. Hydronium ions can participate in the reaction of neutralization of reactive oxygen species in the living cells. This phenomenon deserves much more attention than it has up to now.
3. Change of water colligative properties can contribute to survival of plants and microorganisms in the frost.

Water enrichment with protons due to different reasons, such as external sources of protons, influence of water processing, chemical interaction with minerals and organic materials, and other reasons, deserves more attention. Many interesting experiments can be made to reveal physical properties of water rich of hydronium ions. Regrettably I don’t have an ability to continue and scrutinize observations described in (8).

Protonated water shows amazing behavior, like the one observed in a thin glass wall chamber with distance between walls of 1 mm.: www.naturelaws.org/Video/PWform.flv The chamber is positioned vertically with walls perpendicular to axis of observation. A section of Nafion ring of 3 mm in diameter and 1 mm. long is placed in the middle of the chamber (fig.1). Positioned behind the chamber, a ring of diffused blue LEDs with a lens forms a dark field in the center of the ring and illuminates the chamber, making observation more informative.

What happens in the movie: distilled water with pH of 6.0 fills the chamber at the beginning from bottom to the top. The main heroes of the movie are positively charged Amedin microspheres of 0.52 mkm size mixed with water in the concentration of 800 million/ml. When microspheres are added to the water they change water pH to 5.5.

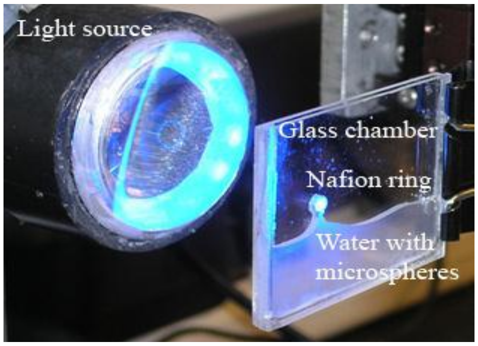

Fig.1

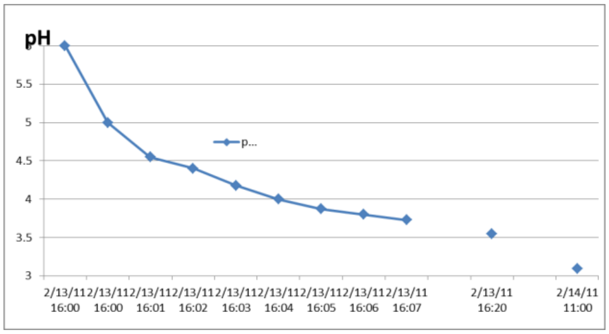

Fig.2 Change of water pH due to influence of nafion.

After the chamber is filled with water with charged microspheres, microspheres begin moving out of the Nafion ring forming a zone free of microspheres. This process coincides in time with change of water pH when Nafion is added to water (fig.2 Nafion tube of 3mm. in diameter and 3cm.long diped into 10 ml of distilled water with pH 6.0). 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”(10) and protons are released into water bearing off excessive energy of the M-Nafion formation reaction.

Zone of protonated water formed around nafion ring does not mix with the bulk water with microspheres and on the third minute forms an outflow to the top, behaving like a material with properties distinguished from the bulk water. Scientists are trying to estimate properties of protonated water interfacing nafion using such methods as Raman spectroscopy and others, but there is a possibility to use nondestructive indirect methods in a variety of experiments that also might be very informative.

But the most interesting thing is estimation of the role of protonated water in the animals’ body (especially in the man). The level of protonation of water that we drink everyday may also play certain role in apoptosis suppression. Chemists from Berkley showed how protons neutralize reactive oxygen species in the living cells. There are also evidences that water with low pH and free of calcium invests into duration of human life extending it remarkably.

Thank you for your attention.

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