

Changes of Water Colligative Properties in Distillation and Filtration Processes.

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Abstract

The results of the demineralized water distillation, filtration and evaporation processes experimental studies are presented. Influence of CO₂ on water pH level during these processes was checked. It was shown that replacement of air with nitrogen gives the same readings of pH, and both distilled/filtered and residual waters change pH level and boiling/freezing points during the process. Hypothesis is discussed that the real reason for these changes is proton's high mobility and small size that allow its easy evaporation from the bulk water and penetration through filters in the process of filtration. Redistribution of excess protons concentration during evaporation process causes change of water specific latent energy and might be a real cause of colligative properties change of both residual water and condensed vapor/filtered water. Enriched with excess protons water vapor from the Earth's surface can transfer positive charges to clouds, causing formation of a huge potential difference from the atmosphere to the ground.

Introduction

Water purification using water distillation and reverse osmosis (RO) filtration is widely used in chemistry and biology for scientific observations. Both of these processes become important nowadays due to remarkable pollution of natural drinking water sources. It was noticed that both of these processes change water pH level and this feature was attributed to CO₂ influence.

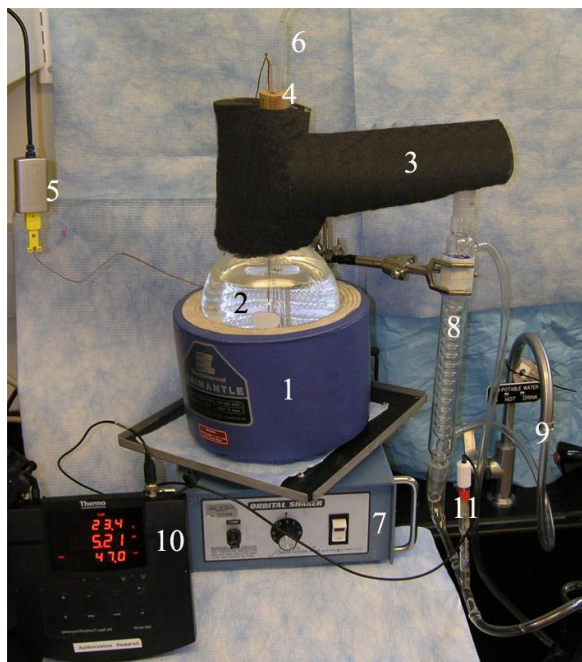
It is also necessary to remark that formation of the excess proton in water and its behavior attracted attention for more than two centuries, beginning with the publication by Grotthuss in 1806 of the mechanism by which an excess proton or "protonic defect" diffuses in liquid water through the continuous formation and cleavage of covalent bonds.^(1,2,3,4) A wide review of the Grotthuss mechanism development and use in different studies was made by Samuel Cukierman⁽⁵⁾. But still it does not cover the whole scope of interest to role of protons in solutions.

It is believed that protons in water exhibit mobilities exceeding those of other simple monovalent cations, and that an excess proton is able to diffuse throughout the entire hydrogen bond network of water at a rate much exceeding conventional diffusion. And it may be easily understood just taking into account that formation of proton covalent bonding to a water molecule shall cause emission of an excess energy in the form of a photon in a wavelength range of about 270 nm. This photon in turn can cause cleavage of covalent bonding and emission of a free proton from the same or a neighboring molecule. Thus, once created in water, an excess proton can prolong its life for some time until meeting an anion and this may play remarkable role in many chemical and biological systems.

Many sophisticated methods are used to study the phenomena nowadays such as fluorescence spectrometry, ultrafast infrared spectroscopy and others. They give very good evidences of the mechanism at work, which can be used further for deriving remarkable conclusions from simple observations based on measurements of hydronium concentration in water with pH meters.

Experimental studies.

To check CO₂ influence on water distillation process studies of the process were produced using experimental setup, which consists of the following elements (Fig.1):



1. Heater designed to handle two liters flask,
2. Flask with a branch (3) at the top,
4. Flask plug with two glass tubes inserted. One for nitrogen supply (6), and another for water sampling. And also a thermocouple enclosed in sealed glass tube connected to a computer (5).
7. Stirring device.
8. Condenser with glass tube helix placed into a glass tube of bigger diameter serving as a cooler with tap water (9) flowing through it.
10. pH-meter with electrode (11).

The flask was filled with 2 liters of water that was demineralized using three passes through reverse osmosis system and further exposed to UV light from mercury lamp (further referred to as Demineralized Dissociated (DMD) water).

Fig.1

During the process of distillation water samples of both condensed distilled and residual water were taken six times after formation of 250-300 ml of distilled water each time. First measurement was made before the process of distillation. Measurements of distilled water pH require thorough stirring since water tends to construct complex clusters around the electrode causing inaccurate readings and instability. These clusters can be destroyed mechanically (by stirring) and thus average distribution of H⁺ ions can be measured.

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 (11).

The results of the measurements are shown on the graph fig.2



Fig. 2

The graph shows change of pH level of both distilled and residual water during distillation process. This result was a little bit puzzling and was attributed to the influence of CO₂ in the air and dissolved in the water according to the reaction $2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{CO}_3$ (carbonic acid) $\rightarrow (\text{H}_3\text{O}^+)$ (hydronium ion) + (HCO_3^-) (bicarbonate ion). But there was still something strange in the function

shapes. Why CO₂ influences only distilled water? To check the level of CO₂ influence the following experiment was performed.

First, the air in the flask was purged for fifteen minutes with nitrogen gas coming from the glass tube in the plug (fig.1 (6)). Then water in the flask was exposed for one hour to vacuum of 370 mm of mercury pressure. During this time the flask was stirred thoroughly (fig.1 (7)) for one minute every fifteen minutes to remove gases adsorbed to the walls. Then vacuum was replaced with nitrogen again and the process of distillation began by switching on the heater. This procedure removed most of the CO₂ from the system.

The results of this last procedure are shown on the graph fig. 3.

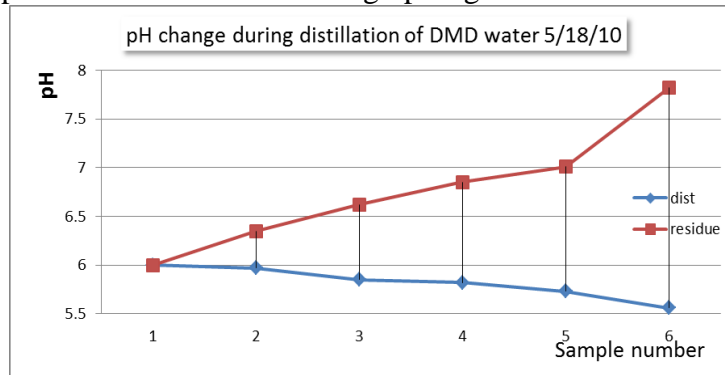


Fig. 3

So it became evident that the CO₂ did not play a crucial role in the boiling process. Thus the supposition came that major role belonged to excess protons high mobility and the process just shown that concentration of free protons in residual water became hundred times lower than in distilled water at the end of process and the boiling remarkably reduced concentration of free protons in residual water.

Additionally, measurements of boiling and freezing points of distilled water and residual water show some differences. After boiling out of about three quarters of initial 2 liters volume (when 400-300 ml remains) the boiling point of residual water rises by three degrees Centigrade (to about 103°C). Measurements of freezing point were made using water crystallization observation in a glass chamber with the distance between walls of 1 mm, placed into polarized microscope. These observations show that distilled water freezes at a lower temperature (of about three degrees Centigrade).

It also gave basis for the assumption that the reason for difference of residual and distilled water physical properties is caused by the fact that process of distillation removes excess protons from water, causing decrease of the overall kinetic energy of residual water at a given temperature.

To check this hypothesis there were several other experiments produced for different types of water.

The same distillation process but using water from Seattle city supply system in BIOE building shows the following results: (fig. 4.)

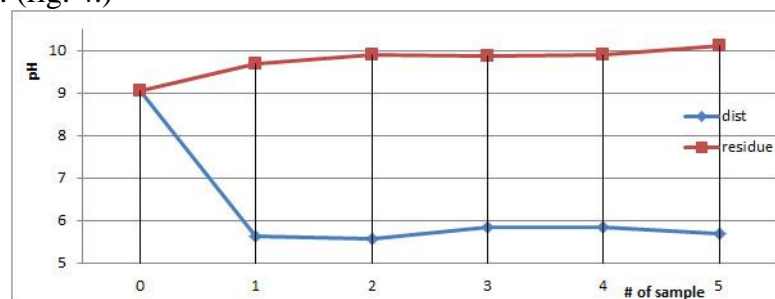
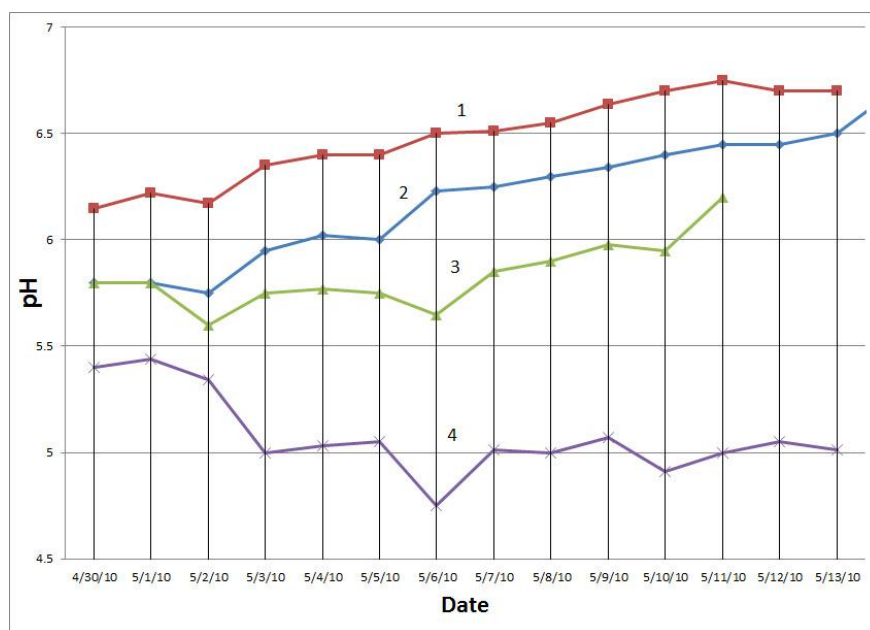


Fig. 4

Thus the difference between condensed distilled water and residual water becomes evident even at the first stage of distillation process.

Further evidence of the fact that a vapor removes free proton from water was obtained using daily measurements of DMD water pH level. Measurements were made every day during two weeks beginning 30 April 2010 (fig. 5) using the following samples:



1. – boiled DMD water kept in 200 ml open beaker in a light tight metal which allows for free evaporation from the beaker.

2. – fresh DMD water in 200 ml open beaker in the same metal box.

3. – DMD water in 200 ml open beaker kept exposed to light on a laboratory shelf.

4. – DMD water kept in a closed plastic tank exposed to light in the laboratory.

Fig. 5

All samples were taken from the same source of DMD water.

First curve shows changes of pH level of sample 1 water that was boiled for three minutes. This graph shows difference of pH level between sample 1 and sample 2, which was caused by short rise of temperature to boiling point. Then this boiled water was left for free evaporation at a room temperature for two weeks and shows slow increase of pH level from 6.2 to 6.7 (curve 1.).

The same happens with sample 2 (curve 2.). Both functions have similar shape. This shows that free evaporation in the dark also removes free protons from water through slow evaporation.

Evaporation of water exposed to bright fluorescent light in the laboratory coming from commercial “hard white” fluorescent tubes also removes free protons, but light slows down the process and occasionally may restore the level of water dissociation (curve 3.).

On the contrary, water kept in a tightly closed plastic tank for several months before beginning of measurements increases the level of dissociation and then keeps it at a constant level (curve 4.).

Further evidence of the free protons in evaporated water can be extracted from measurements of pH level of water collected into two glass dishes during rains in Seattle in the University district. These measurements also always show water with pH between 5.8 – 6.3. This may support the hypothesis that clouds and water falling from clouds has higher concentration of free protons than residual bulk water on the Earth after evaporation.

This feature was always attributed to influence of CO_2 through reaction $2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{CO}_3$ (carbonic acid) $\rightarrow (\text{H}_3\text{O}^+)$ (hydronium ion) + (HCO_3^-) (bicarbonate ion). But this reaction also raises an uneasy question of HCO_3^- ion presence while not dismissing excess proton presence. But a very simple consideration of the fact that CO_2 and vapor always coexist in the lower atmosphere and this reaction does not remove CO_2 from the atmosphere, so it has limited influence. Probably both reactions can take place and it is not clear which process predominates. The latter requires further studies. Besides, CO_2 presence shall influence rain water even in a much lesser degree.

The question remained also why DMD water had such low level of pH, since it was never distilled. Measurements of initial, filtered using reverse osmosis, and residual waters were done with different

RO systems. All of them showed that residual water has higher pH level and filtered water has lower pH level than initial water. These results also support the idea that protons penetrate through filters, anions remain in the residual water and thus filtered water pH level is decreased and residual water pH level increased.

Discussion

First thing to pay attention to is certainly limitation of pH measurement accuracy and precision. pH values might be affected by the low ionic strength (pH electrodes are calibrated at a particular ionic strength and low ionic strength solutions may give erroneous results)⁽⁶⁾. However in all the measurements described here the ionic strength was similar so different pH measurements could be directly compared. Additionally, intensive stirring allows good averaging of the reading, and thus the level of pH measurements error is reduced and does not affect the trend itself.

The second question is: does replacement of atmosphere with nitrogen and also application of reduced pressure (vacuum) eliminate influence of CO₂ on pH level? It is necessary to take into account that possible presence of CO₂ in water does not compromise the idea itself due to its low influence. Residual water increases pH level during boiling process, which means that level of hydronium ion is decreased. Presence of CO₂ on the contrary shall increase concentration of hydronium ions, and the rise of the temperature shall accelerate the reaction $2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{CO}_3 \rightarrow (\text{H}_3\text{O}^+) + (\text{HCO}_3^-)$.

The physics of the processes is straightforward. The high mobility of protons and their low mass allow them to leave water easier and quicker than any other ion can do during boiling process. The same happens during reverse osmosis filtration process – residual water has higher pH level and lower hydronium concentration than filtered. The same factor should play crucial role in changing colligative properties of distilled water, that is lowering its freezing temperature and increasing boiling temperature of residual water.

These two last properties look strange at the first glance. They seem to be specific feature of mixing solutes with the water⁽⁷⁾. But these results can be also explained more or less correctly by exchange of the specific latent energy during filtration/evaporation processes. Enriching water with protons increases intrinsic translational energy and thus enthalpy of water due to high mobility of protons. At the same time the residual water has reduced entropy and thus has increased boiling and decreased freezing points. More specifically, entropy is a logarithmic measure of the density of states:

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

where $k_B = 1.38065 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant, the summation is over all the microstates the system can be in, and the P_i are the probabilities for the system to be in the i_{th} microstate. The decrease of probability range level decreases entropy of the system.

The factor that vapor is enriched with excess protons, may play very important role for the life on the Earth. Thus evaporation from the Earth surface leaves an unbalanced negative charge in the form of hydroxide ions in the ground water. This might be the real reason for the negatively charged Earth and positively charged clouds that take place in nature, as described in the famous Lectures on physics by Richard Feynman⁽⁸⁾. This charge distribution and formation of a huge potential difference Feynman attributed to nuclear radiation from the Earth and radiation from the Sun. This assumption has some problems, however the hypothesis of excess protons in water vapor can easily explain the phenomenon of Earth-clouds electrical charges distribution.

Furthermore, humidity level is a basic atmospheric property, which is always observed and reported. According to the statistics people living in the mountains and in the countries with high humidity level (like Cuba) live longer. It may be explained also, among other reasons, with the difference of free protons quantity they inhale during their lives. Additionally, people in the mountains drink naturally

distilled water from the mountain rivers that is also enriched with free protons, which may play a role as natural antioxidants.

Plants also filter water coming from the ground. This process of filtration can enrich water in the stems with excess protons that in turn, change its properties, lowering the freezing point and enabling plants to survive during severe frosts down to -25°C . Besides, many plants produce antioxidants in their fruits and leaves, and excess protons can take part in this process. This filtration factor might also play remarkable role in animal physiology as far as animals use filtration process in kidneys.

These hypotheses, based on the observations described, require detailed studies, attracting with its simplicity and promise far reaching consequences. Getting scientific evidences and being aware of this important feature of water may have remarkable influence on future refinement of drinking water. For example, a simple reversal of the sequence of the two processes, namely water filtration with reverse osmosis and followed with UV light treatment during purification process can remarkably change water properties and influence on human health while still ensuring water purity and safety. That is why these studies are so important and require further attention.

The most crucial question here is there a possibility to make these far reaching conclusions using simple pH measurements? The first advantage of pH measurements is that they are, probably, the least destructive, if compared to other sophisticated methods that require water molecule excitation, and give more or less realistic picture of the processes under observation. The second is they give broadly averaged information about substances under consideration. The most important pitfall: they require assumptions that can be derived from wide range of knowledge about water and its structure obtained from previous more complicated studies.

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