

Studies on the Physicochemical Properties and Existence of Water Products (as Drinks) Advertised as Having Smaller Cluster Sizes of H₂O Molecules than Those of Regular Water

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(Received February 23, 2010; Accepted July 26, 2010;

Published online August 30, 2010)

The *in vitro* physicochemical properties of 6 bottled water products (as drinks), advertised as having cluster sizes of H₂O molecules smaller than those of regular water, were studied. No significant differences in the boiling temperature (BT, near 100°C) or freezing temperature (FT, near 0°C) were observed between all 8 aqueous solutions examined, including deionized water (DW) and tap water as controls, although DW had the lowest mean BT and highest mean FT values. The specific gravity of all the examined aqueous solutions, including the controls, changed in a temperature-dependently manner, showing the greatest value (near 1.000) at 4°C. Analyses of inorganic components revealed that various mineral components were dissolved in aqueous solutions examined other than DW, suggesting that the trends of the lowest BT and highest FT for the DW control were due to the absence of these solutes. These results did not demonstrate the presence of an abnormality in the hydrogen bonds between H₂O molecules in the sample solutions compared to the controls. In other words, the claims by the manufac-

turers in their advertisements concerning the cluster sizes of H₂O molecules for their water products were not confirmed by the findings of this study.

Key words—water, molecular cluster, hydrogen bond, boiling temperature, freezing temperature, specific gravity

INTRODUCTION

It is well known that water molecules in aqueous solution systems form clusters by the actions of hydrogen bonds and that the sizes of the H₂O molecular clusters are continually changing in their sizes. It is also generally accepted that many characteristic properties of water, such as a far higher boiling temperature (BT) and freezing temperature (FT) than expected from its chemical formula, as well as temperature-dependent changes in the specific gravity (SG), showing the greatest value at 4°C, are derived from this property of H₂O molecules.¹⁾ Indeed, hydrides of the 16th group elements other than oxygen (*e.g.* H₂S, H₂Se and H₂Te) are present as gases under standard ambient temperature and pressure, due to the absence of hydrogen bonds. It is therefore pointed out in many basic physicochemistry textbooks listing figures or tables for molecular weight-dependent changes in BT and FT of these compounds, that if H₂O molecules were not associated with each other by hydrogen bonds, the BT and FT of water would be *ca.* –80°C and –110°C, respectively.

Previously there was disagreement with respect to the relationships between the cluster sizes of H₂O molecules and the spectral data of H₂O in oxygen nuclear magnetic resonance (¹⁷O-NMR) spectrometry. First, based on the assumption that the length of the half-width (HW) of the H₂O peak on ¹⁷O-NMR spectra may reflect the speed of molecular movements, Matsushita described that good tasting water has smaller cluster sizes of H₂O molecules than bad tasting water,^{2–4)} and that reduction in the cluster sizes of H₂O molecules is achieved by treating the corresponding aqueous solutions with ultrasound radiation, passing through ceramic filters, and electrolysis.³⁾ Ishikawa *et al.*, who studied an aqueous solution treated with a magnetic field, also reported that the HW on ¹⁷O-NMR spectra may reflect the cluster sizes of H₂O molecules.⁵⁾ On the

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other hand, Okouchi *et al.* demonstrated that the HW length on ^{17}O -NMR spectra greatly varies depending on pH,^{6,7)} and this was confirmed by many reexaminations. Thus, it has generally been accepted in the academic field that the cluster sizes of H_2O molecules cannot be evaluated by ^{17}O -NMR spectrometry. Yamaguchi applied cold-spray ionization mass spectrometry (CSI-MS) to the detection of H_2O molecular clusters.⁸⁾ However, CSI-MS, which was established to observe the molecular ion peaks for the protonated H_2O molecular clusters ($[(\text{H}_2\text{O})_n + \text{H}]^+$), seemed to be unsuitable as an aid to evaluate the cluster sizes of neutral H_2O molecules. Since the binding energy of protons to the H_2O molecular clusters is significantly greater than that of the hydrogen bond between the H_2O molecules, the cluster sizes of protonated H_2O , generated in association with the strong potential field around the proton, can not precisely reflect those of neutral H_2O .

It was therefore speculated that at present, the most reliable method to demonstrate abnormal changes in the H_2O molecular cluster sizes may be the detection of differences between the corresponding water samples and the controls of regular water in such fundamental physicochemical properties as the BT, FT and temperature-dependent changes in the SG. In recent years, many companies have developed and started selling water products as drinks, and some are advertised as having smaller cluster sizes of H_2O molecules than those of regular water. According to the manufacturers, such drinks are prepared by treating regular water with magnetic fields and/or by passing through ceramic filters (<http://www.modea.jp/vivo.html>, <http://www.o-xyz.com/xyzwater>, *etc.*), or are produced by natural filtration processes during the formation of underground water (<http://www.mizuhiroba.jp/sale/Item/ClusterClea>, <http://www.organicgermanium.co.jp/>, *etc.*). However, the real effects of such procedures on reducing the cluster sizes of H_2O molecules have not been confirmed, since no scientific paper has been cited, except for some established patents (*e.g.*, Japan Patent: No. 3558783, U.S. Patent: No. 5711950 and 6033678, *etc.*). However, the manufacturers generally advertise that reductions in the cluster sizes of H_2O molecules were demonstrated by the ^{17}O -NMR spectra data, referring to the work of Matsushita²⁾ and also that drinking the corresponding products may be preferable for human health due to their improved bioavailability of H_2O

(<http://www.modea.jp/vivo.html>, <http://www.o-xyz.com/xyzwater>, <http://www.mizuhiroba.jp/sale/Item/ClusterClea>, <http://www.Organicgermanium.co.jp/index.htm>, *etc.*). As part of the *in vitro* physicochemical studies on the existence of water products advertised as having preferable effects on human health^{9,10)} and on their actual *in vivo* effects,^{11–13)} we intended to elucidate whether the claims of such advertisements concerning the cluster sizes of H_2O molecules can be confirmed by differences in the BT, FT and temperature-dependent changes in the SG when compared to the controls. If the cluster sizes of H_2O molecules in the corresponding water products are really reduced, the physicochemical properties of such aqueous solutions must be significantly different from those of regular water.

MATERIALS AND METHODS

Materials — Cluster-clear (CC), XYZ-Water (XYZ) and Vivo-Water (VW) were purchased from Yuco. Inc. (Tokyo, Japan), Globe Science Inc. (Tokyo, Japan) and Beltec. Co. (Tokyo, Japan), respectively. Nanocluster Germanium Lourdes Water-400 (GeW-400), -800 (GeW-800) and -1200 (GeW-1200) were obtained from Organic Germanium Co., Ltd. (Hyogo, Japan). As described in the Introduction, these water products are advertised by the manufacturers as having smaller cluster sizes of H_2O molecules than those of regular water. As controls, DW and tap water (TW) were examined under identical conditions.

Examinations of the BT — A 300 ml beaker containing the aqueous solution to be examined was heated in a mantle heater with periodic stirring using a glass rod, and time-dependent changes in the temperature of the liquid phase were measured with a digital thermometer, until the heated solutions began to boil, showing no elevation of the fluid temperature. These procedures were performed four times for each sample solution examined.

Examination of the FT and temperature-dependent changes in the SG. After the measurement of BT, as described above, sample solutions were left at room temperature (RT) in a graduated cylinder. When the temperature of the solutions had fallen to RT, the graduated cylinder containing the solutions, on which a densimeter was floated, was embedded in sodium chloride (NaCl) with ice in a polyethylene bucket. Changes in the temperature and SG of the cooling sample solutions were period-

ically checked. Finally, an aliquot (5 ml) of the sample solutions cooled to near 0°C was injected into a test tube in a 100 ml beaker filled with ice-NaCl. The solutions cooled in a test tube were stirred with a glass rod, and the fluid temperature was repeatedly recorded. All of the examined solutions, treated in a same manner as described above, were supercooled to a temperature below FT and then frozen after slight elevation in the temperature. The temperature at which they were finally frozen was taken as the FT. The FT was measured three times for each sample solution.

Quantitation of Inorganic Component—Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) were used, as described previously,¹⁴⁾ to quantify Ca, Fe, K, Mg, Na, P, Sr, and Si (by ICP-AES) and 63 other elements (by ICP-MS) in the 6 water products and the controls. The inorganic anions in these 8 aqueous solutions were determined by ion chromatography.⁹⁾

RESULTS AND DISCUSSION

The results of measuring BT and FR of the 6 examined water products and the controls (DW and TW) are summarized in Table 1. As shown in Table 1, the BT of all 8 sample solutions, including the controls, were near 100°C, indicating that the values for the 6 water products were not significantly different from that of DW or TW. In the triplicate measurements of FT, the values for the controls were -0.4, -0.5 and -0.5°C (DW) and -0.5, -0.5 and -0.5°C (TW), respectively, while those for all water products were -0.5, -0.5 and -0.5°C except for GeW-1200 (-0.5, -0.5 and -0.6°C, Table 1). Thus, no significant difference in the BT and FT was observed between all 8 examined aqueous solutions, including the two controls, although it was noteworthy that the DW control tended to have the lowest mean BT and highest mean FT values.

The SG values at RT for all aqueous solutions examined, including the controls, were approximately 0.997, and then gradually elevated in association with cooling, before reaching almost 1.000 at 4°C, followed by a slight reduction during further cooling in ice-NaCl. Temperature-dependent changes in the SG values for a water product (XYZ) and the TW control as examples are illustrated in Fig. 1. These results indicated that at a temperature

Table 1. Boiling and FT of Examined Aqueous Solutions

Samples	Boiling Temperature ^{a)}	Freezing Temperature ^{a)}
CC	101.2 ± 0.7°C (n = 4)	-0.50 ± 0.00°C (n = 3)
XYZ	101.6 ± 1.7°C (n = 4)	-0.50 ± 0.00°C (n = 3)
VW	100.9 ± 0.8°C (n = 4)	-0.50 ± 0.00°C (n = 3)
GeW-400	101.2 ± 0.7°C (n = 4)	-0.50 ± 0.00°C (n = 3)
GeW-800	100.9 ± 0.9°C (n = 4)	-0.50 ± 0.00°C (n = 3)
GeW-1200	101.3 ± 1.0°C (n = 4)	-0.53 ± 0.05°C (n = 3)
DW	100.3 ± 0.2°C (n = 4)	-0.47 ± 0.05°C (n = 3)
TW	101.9 ± 1.4°C (n = 4)	-0.50 ± 0.00°C (n = 3)

a) Mean ± standard deviation.

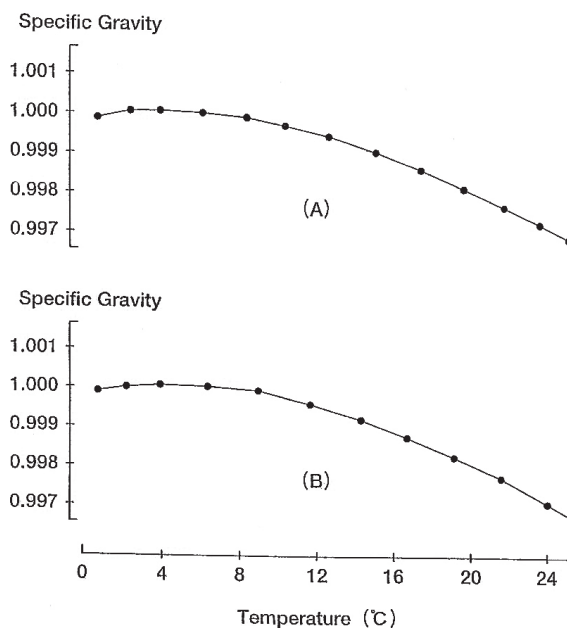


Fig. 1. Temperature-Dependent Changes in the SG Values of XYZ (A) and TW (B)

slightly higher than the FT, the hydrogen bonds between the liquid H₂O molecules in the water products, as well as those in the controls, were strong enough to yield SG values that were slightly larger than those of the solid H₂O molecules.

The results of ICP-AES and ICP-MS analyses revealed that various cationic mineral components, such as Ca, K, Mg, Na, B, Se, Ba and Li, were present in the aqueous solutions examined, except the DW control, at concentrations of up to 11.61 mg/l (Ca in GeW-400), 5.43 mg/l (K in GeW-1200), 12.26 mg/l (Na in GeW-400), 2.93 mg/l (Mg in XYZ), 13.2 µg/l (B in GeW-800), 6.1 µg/l (Se in GeW-1200), 6.5 µg/l (Ba in GeW-800), 7.9 µg/l (Li in GeW-800) and 40.4 µg/l (Fe in TW). The concentration of Ge, which is artificially dissolved in GeW-400, -800 and -1200 at 400, 800 and 1200 mg/l

(1.2, 2.4 and 3.5 mM) as 2-carboxyethyl germanium sesquioxide, respectively (this was confirmed by analyses in a previous work¹⁰), was determined to be 2.9 µg/l in XYZ and below the detection limit (0.1 µg/l) in CC, VW and the controls. The levels of anions obtained by ion chromatography were up to 8.60 mg/l (in XYZ) for Cl⁻, 18.53 mg/l (in GeW-400) for NO₃⁻, and 9.59 mg/l (in GeW-1200) for SO₄²⁻. In other words, all samples other than DW contained various anionic and cationic mineral components, and the total concentrations of such solutes were the highest for GeW-1200. These results suggest that the observation of the lowest BT and highest FT for the DW control may be due to the absence of such solutes. They also agreed with the finding that GeW-1200 exhibited the second highest BT and the lowest FT, although measurements of the BT and FT were performed without controlling for the atmospheric pressure.

In this study, no aqueous solution sample was available as a positive control with larger or smaller cluster sizes of H₂O molecules than those of regular water, although it can be assumed, as described in the Introduction, that if hydrogen bonds were absent, the BT and FT of water would be *ca.* -80°C and -110°C, respectively. However, none of the samples examined, other than DW and TW as negative controls, demonstrated the presence of an abnormality in the hydrogen bonds between their H₂O molecules. In other words, the claims in the advertisements of the manufacturers concerning the cluster sizes of H₂O molecules have not been confirmed by the results of our experiments. If they intend to prove that the H₂O molecular cluster sizes in their water products are really smaller than those of regular water, they should present data showing significant differences in such fundamental physicochemical properties as the BT, FT and temperature-dependent changes in the SG between the sample solutions and the control(s), on the basis of more precise experiments than those we performed in this study.

REFERENCES

- 1) Tominaga, Y. (1998) Raman scattering of liquid water and hydrogen bond cluster. *J. Crystallograph. Soc. Jpn.*, **40**, 95–100 (in Japanese).
- 2) Matsushita, K. (1989) Seeking foods by NMR. *Gendaikagaku*, **Jan. 1989**, 62–67 (in Japanese).
- 3) Matsushita, K. (1990) Evaluation of construction of water and investigate flavor, and maturity. *Shokuhin to Kaihatsu*, **7**, 82–85 (in Japanese).
- 4) Matsushita, K. (1992) Tasty water and healthy water. *J. Water Environ. Technol.*, **15**, 98–102 (in Japanese).
- 5) Ishikawa, K., Tanabe, K., Okada, Y., Nagata, M., Masuda, S. and Gejima, Y. (1991) Basic studies on Magnetic treatment for water. *J. Kyushu Branch Jpn. Soc. Agric. Machinery*, **40**, 40–43 (in Japanese).
- 6) Okouchi, S., Ishihara, Y., Arai, T. and Uedaira, H. (1993) ¹⁷O-NMR and ¹H-NMR of drinking water. *J. Water Environ. Technol.*, **16**, 409–415 (in Japanese).
- 7) Okouchi, S., Ishihara, Y. and Uedaira, H. (1994) ¹⁷O-NMR of electrolyte aqueous solution and tap water processed by commercial purifier and reformers. *J. Water Environ. Technol.*, **17**, 517–526 (in Japanese).
- 8) Yamaguchi, K. (2004) Development of cold-spray ionization mass spectrometry. *Bunseki*, **2004**, 106–110 (in Japanese).
- 9) Hiraoka, A., Takemoto, M., Suzuki, T., Shinohara, A., Chiba, M., Shirao, M. and Yoshimura, Y. (2004) Studies on the properties and real existence of aqueous solution systems that are assumed to have antioxidant activities by the actions of active hydrogen. *J. Health Sci.*, **50**, 456–465.
- 10) Hiraoka, A., Inaba, H., Suzuki, E., Shinohara, A., Chiba, M., Shirao, M., Kubo, K. and Yoshimura, Y. (2010) *In vitro* physicochemical properties of neutral aqueous solution systems (water products as drinks) containing hydrogen gas, 2-carboxyethyl germanium sesquioxide, and platinum nanocolloid as additives. *J. Health Sci.*, **56**, 167–174.
- 11) Hiraoka, A., Sasaki, S., Yamada, T., Shinohara, A. and Chiba, M. (2006) Effects of drinking a water product with antioxidant activities *in vitro* on the blood levels of biomarker substances for the oxidative stress. *J. Health Sci.*, **52**, 817–820.
- 12) Hiraoka, A. and Shinohara, A. (2009) Effects of drinking a water product supplemented with the platinum nanocolloid on the oxidative stress and functions of liver and kidney. *Biomed. Res. Trace Elem.*, **20**, 186 (in Japanese).
- 13) Hiraoka, A., Miyakawa, S. and Shinohara, A. (2010) Effects of drinking hydrogen-rich water on the blood oxidative stress marker levels in human subjects. *J. Anal. Bio-Science*, **33**, 66 (in Japanese).
- 14) Shinohara, A., Chiba, A. and Kumasaka, T. (2009) Behavior of samarium inhaled by mice-exposure length and time dependent change. *J. Radioanalytic. Nucl. Chem.*, **281**, 119–122.