Oscillating Self-organization of Hydration Water in Foods Derived by a Forced Temperature Cycling

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A forced cyclic temperature change operation (FCTCO) between 30 and -30 °C clearly demonstrated a forced oscillation of self-organization (FOS) of hydration water in six foods (squid, sardine, scallop, salmon, beef, and pork) through the use of a specified parameter, τ_C (the correlation time of a water molecule proton, s). The FOS, described as a function of $1/\tau_C$ (molecular mobility, s^{-1}), was distinguished based on the variety of water species and the kind of food. The oscillating modes obtained demonstrated the existence of two different water species regions, $-A_1$ and $-A_2$, which were divided at $\tau_C = 10^{-8}$ s (= $C\tau_C$). The amplitude (α) of the FOS for water species-A_1 was larger than that for water species-A_2. Water species-A_1 was characterized as a weakly restricted species with a higher $1/\tau_C$ and larger α, whereas water species-A_2 was recognized as a strongly restricted species with a lower τ_C and smaller α. The probability of self-organization showed a linear dependency as a function of the amount of self-organized water (ASOW).

1. Introduction

In our previous paper (Konishi & Kobayashi, 2011), the self-organization (SO) behavior of water species in foods was demonstrated at a specified temperature region lower than 0°C, as schematically shown in Figure 1(a). To clearly demonstrate the SO, the correlation time (τ_C, s) derived from an NMR parameter (Hills et al., 1999) was effectively used (Belton et al. eds., 2003). Since the τ_C is the rotation time of a water molecule proton, $1/\tau_C$ (molecular mobility; Hills, 1999) is the rotation rate of the water proton at a given water content and temperature of a food sample. Arrhenius plots of $1/\tau_C$ for the food samples can thus be visualized as a function of $1/T$, as shown in Figure 1(b). All the plots obtained for the water contents of various food samples clearly had a typical hysteresis mode, as schematically shown in Figure 1(b), indicating a steep reduction of $\ln(1/\tau_C)$ at a specified temperature. This steep reduction resulted from the SO. At the hysteresis-temperature region between t_1 and t_2, the forced cyclic temperature change operation (FCTCO) was repeated, and a forced oscillating curve could be seen, as shown in Figure 1(c). The obtained oscillating curves provide information on the characteristics of the various kinds of food and the multifunctional water species.

A water species with a lower τ_C represents a weakly restricted species, while that with a higher τ_C represents a strongly restricted species. The value of τ_C is thus a useful parameter to characterize the water species retained in a food tissue matrix. In our previous papers (Konishi et al., 2010), it was demonstrated that, at a critical value of $C\tau_C = 10^{-8}$ s, the water species was clearly divided into two water species, $-A_1$ and $-A_2$, for all kinds of food (Konishi & Kobayashi, 2011). The value of $C\tau_C = 10^{-8}$ s was experimentally recognized as being replaced by the specified water content (W_0), 120 %-d.b., indicating two different regions: water species-A_1 region (higher water content region: $\tau_C < 10^{-8}$ s or $W_0 > 120$ %-d.b.) and water species-A_2 region (lower water content region: $\tau_C > 10^{-8}$ s or $W_0 < 120$ %-d.b.) (Konishi et al., 2001(a)). The two water species gave different effective water diffusivity values (De, m^2/s) (Konishi et al., 2001(b)) and pre-exponential factors of De (Konishi et al., 2003).
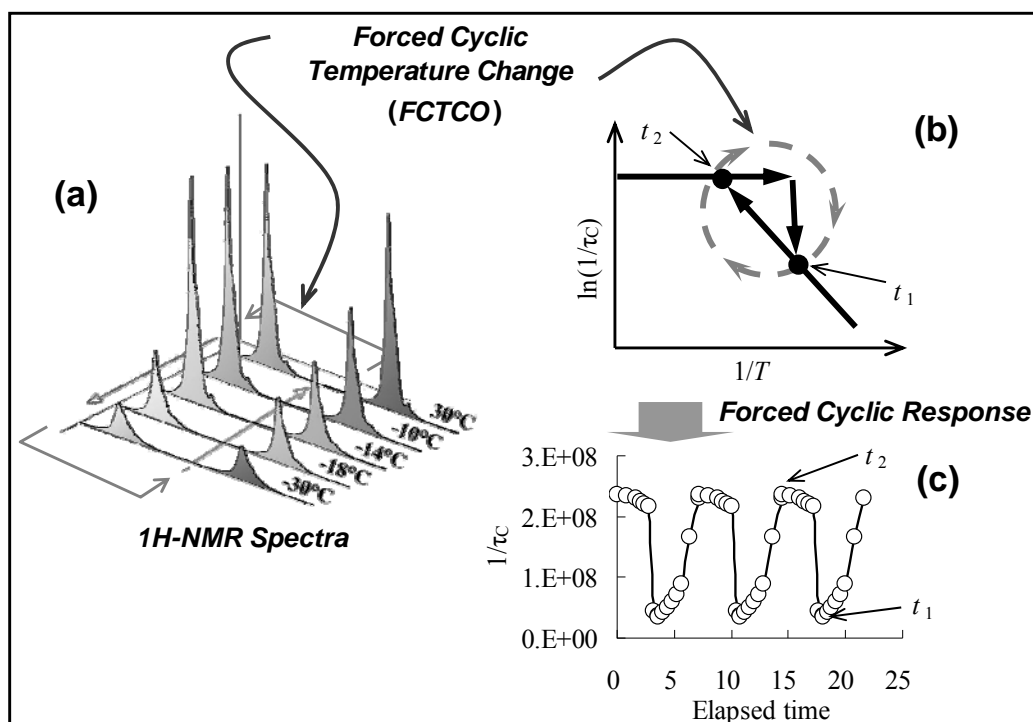
Figure 1 Schematic visualization of the forced cyclic temperature change operation (FCTCO), the NMR-spectrum dynamism, and the $1/\tau_C$ oscillation obtained.

The aims of this study are (1) to discriminate the self-organization of the two water species for various foods by using a dynamic NMR technique obtained by the FCTCO; (2) to visualize the forced oscillation of self-organization as a function of three parameters: molecular mobility (ln $1/\tau_C$: s^{-1}), initial water content of the sample (initial τ_C : s), and acceleration factor of self-organization ($\Delta ASOW \sim \tau_C$: %-d.b./s) for all the foods; and (3) to evaluate the amounts of the self-organized water species as a function of the three parameters to demonstrate the variety of food characteristics.

2. Experimental

Materials and Methods
Pork meat (PH: produced in Hokkaido), beef meat (BA: produced in Australia and BH: produced in Hokkaido), squid, salmon, sardine, and scallop were chosen as food samples. The initial water contents for PH, BA (and BH), squid, salmon, sardine, and scallop were 230~320, 230~280, 300~360, 300~360, 210~270, and 180~230 %-d.b., respectively.

To evaluate the correlation time (τ_C) of the water species, a nuclear magnetic resonance (NMR) technique was applied to measure the ^{1}H-NMR spectra and spin-spin relaxation time (T_2) of water protons. ^{1}H-NMR spectra were obtained using a JEOL A-500 FT-NMR spectrometer operating at 500 MHz for protons. The spin-spin relaxation times, T_2, were obtained by the spin-locking method. From T_2, the correlation time of a water proton, τ_C, was evaluated using the equation described by Abragam (1963).

The time sequence for the FCTCO was as follows: when the temperature was gradually decreased, a steep reduction of $1/\tau_C$ at a specified temperature (t_1) appeared (as seen in Figure 1(b)), and, at the peak bottom of the $1/\tau_C$ (molecular mobility) when the temperature was gradually increased, the locus of $1/\tau_C$ showed a typical hysteresis reaching the temperature (t_2) previously used. The FCTCO was carefully repeated between t_1 and t_2, and a forced oscillation of $1/\tau_C$ was then clearly visualized. In the course of the FCTCO, 2 min to increase or decrease the temperature and 13 min to evaluate the T_2 as the time for the operation of the NMR equipment were required; a total of 15 min was thus needed for measurements at each temperature in the course of the hysteresis period. The oscillating curves obtained were demonstrated as a function of the elapsed time, including the 15 min.

3. Results and Discussion

3.1 Characterization of the forced oscillation of the molecular mobility of water species for the various foods

The forced oscillations of $1/\tau_C$ obtained were visualized for all the foods used in this study. Figure 2 demonstrates the forced oscillating curves for sardine, scallop, and PH as typical examples. As is evident in the oscillating response curves obtained, the amplitude, period, and waveform changed depending on the kind of food and the water content (which can be replaced with the initial τ_C of the sample). The amplitude (α) of the oscillation was drastically reduced in the water species-A_2 region, indicating a reduction in the molecular mobility ($1/\tau_C$). This reduction of α, in the case of scallop, can be easily recognized from the diagram in Figure 3 by the width of $\ln(1/\tau_C)$, given as a distance between the peak top and peak bottom of the oscillating curves in Figure 2. The α decreased with an increase in the initial τ_C or with a decrease in the water content of the food samples and finally gave zero at the specified initial τ_C. In this τ_C region, the hysteresis behavior disappeared. Figure 4 illustrates the α as a function of the initial τ_C, indicating the disappearance of the oscillation for squid, sardine, and scallop to become the initial τ_C
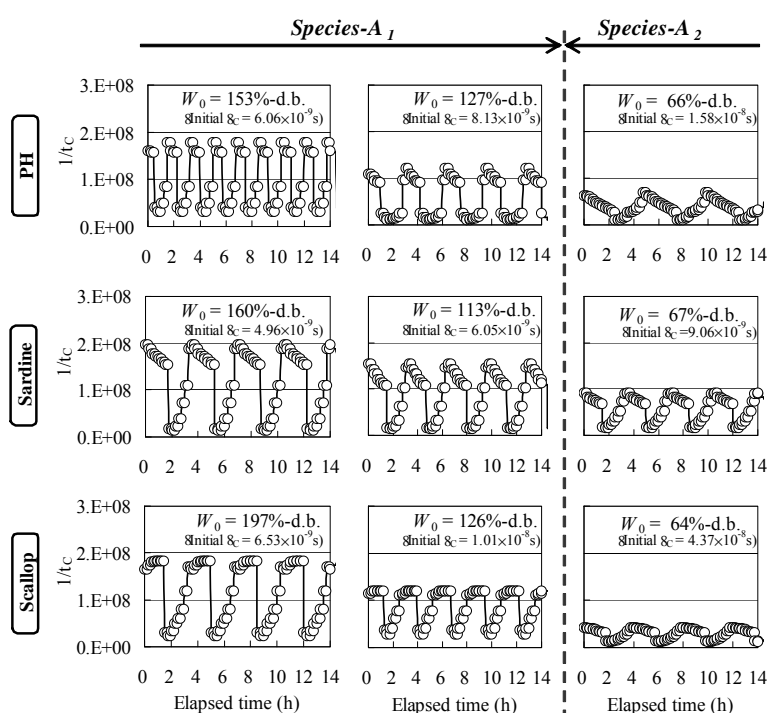

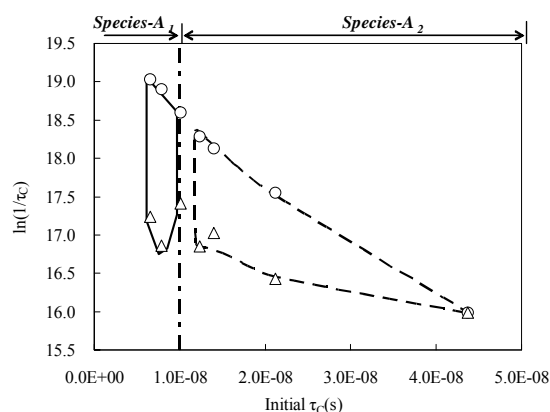Figure 2: Oscillating self-organization characterized by the kind of food

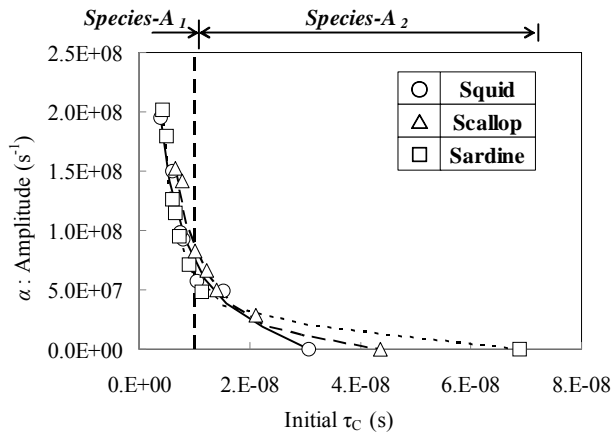Figure 3: Width of $\ln(1/\tau_C)$ for forced oscillation as a function of the initial τ_C for scallop

Figure 4: α as a function of the initial τ_C

=3.1×10⁻⁸, 6.9×10⁻⁸, and 4.4×10⁻⁸ s, respectively. These results clearly demonstrate that the water content (initial τ_C) for the self-organization appearance was sensitively changed depending on the kind of food. In addition, since the slope of each $\alpha \sim \tau_C$ straight line in the species-A_2 region gave a specified value depending on the food, one may designate it as an acceleration factor for self-organization, $\Delta\alpha \sim \tau_C$ (s⁻²). The $\Delta\alpha \sim \tau_C$ obtained for each of the foods can be used as a parameter to evaluate the acceleration degree for the self-organization appearance of the water species for the given food, assuming an acceleration parameter. A higher $\Delta\alpha \sim \tau_C$, therefore, means an easier self-organization appearance. The $\Delta\alpha \sim \tau_C$ values of the water species for squid, scallop, and sardine were evaluated to be -2.2×10¹⁵, -8.4×10¹⁴, and -5.1×10¹⁴ s⁻², respectively. Squid, therefore, gives a higher probability of self-organization than does sardine because of the higher $\Delta\alpha \sim \tau_C$.

3.2 Hysteresis behaviour of the amount of self-organized water species

The amount of self-organized water species (ASOW) can be evaluated by an examination of the graphical integration of the proton NMR spectrum presented in Figure 1(a) and expressed as the modified water content (MWC, %-d.b.). The MWC was evaluated by using the initial water content of the sample food corresponding to the ratio of the peak area of the proton NMR spectra. Figure 5 demonstrates the MWC as a function of $1/T$ and the initial τ_C. It is evident that the hysteresis of the MCW is similar to the $1/\tau_C$ - hysteresis presented in Figure 1(b), indicating a steep reduction of MWC at the same temperature, as in the case of $1/\tau_C$.

Since the reduced amount of MWC clearly indicates the ASOW at the given water content, the amount is linearly reduced by increasing the initial τ_C of the sample. Figure 6 demonstrates, as an example, the ASOW as a function of the initial τ_C for scallop. All the other foods showed similar results. Based on the results obtained, the linear dependency of the ASOW~τ_C straight line indicates an inflection point at τ_C
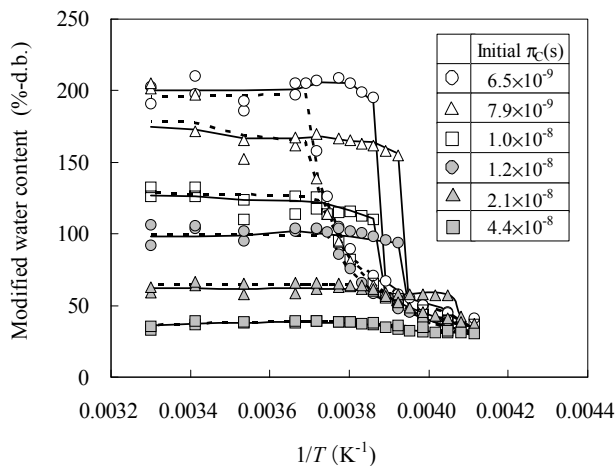

Figure 5 The converted water content as a function of 1/T and the initial τ_C for scallop.
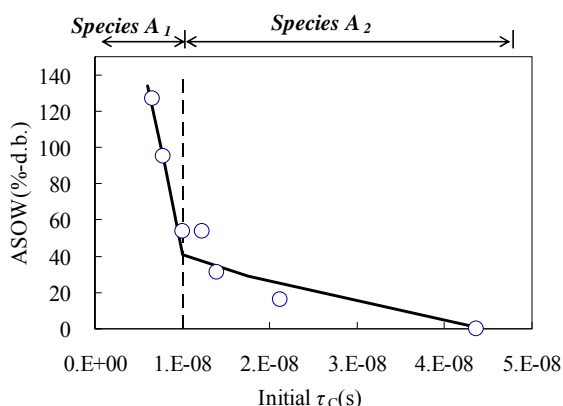
Figure 6 ASOW as a function of the initial τ_C for scallop.

$=10^{-8}$ s, pointing again to the existence of two water species, -A$_1$ and -A$_2$, and is similar to the oscillation mode difference between the two water species, as shown in Figure 2.

In the water species-A$_2$ region in Figure 6, the slope of the ASOW~τ_C straight line is clearly changed depending on the kind of food used. The slope may be designated as a parameter of ΔASOW~τ_C, which contributes to the positive probability of self-organization. The values of the ΔASOW~τ_C for PH, BA, squid, salmon, sardine, and scallop are -1.15×10^9, -8.19×10^8, -1.41×10^9, -5.49×10^9, -4.61×10^8, and -1.18×10^9 %-d.b./s, respectively. Salmon gave the highest probability of self-organization among all the foods used. The difference in the ΔASOW~τ_C (%-d.b./s) among the six foods is similar to the difference in the acceleration parameter ($\Delta\alpha$~τ_C, s^{-2}) of the self-organization of water species in the foods, which is strongly associated with the α's in Figure 4.

3.3 Three dimensional map for the self-organized water species

Figure 7 represents a three-dimensional plot of $\ln(1/\tau_C)$ [z-axis] as a function of both the initial τ_C [y-axis] and the ΔASOW~τ_C [x-axis], for PH, squid, and salmon as typical foods. Since the α is sensitively changed depending on the kind of food, one can recognize a characteristic map mode, as shown in Figure 7. In the water species-A$_1$ region ($\tau_C <10^{-8}$ s, region I), one can clearly see that the α gave an appreciable value without depending on both the initial τ_C and the ΔASOW~τ_C, indicating a similarity with no influence of the kind of food. The disappearance point of α ($\tau_C >10^{-8}$ s, region II) in the water species-A$_2$ region, contrastively, showed a drastic change among the foods.
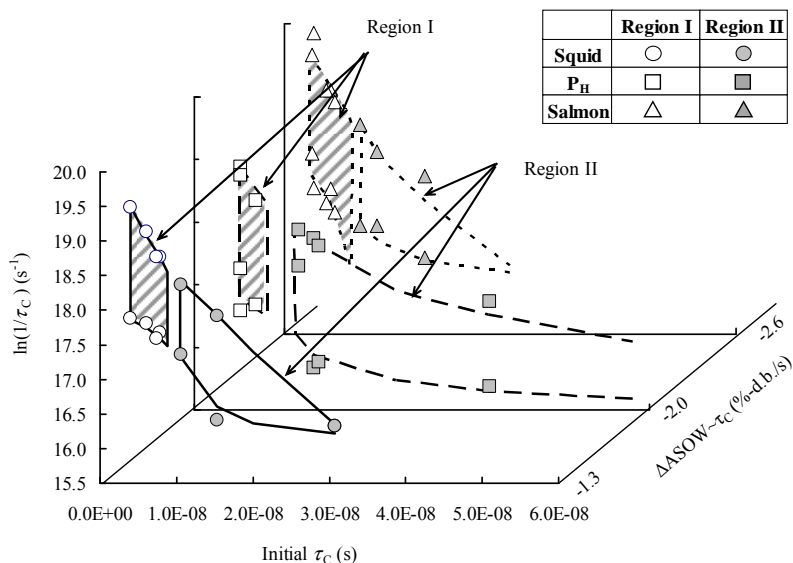

Figure 7 Three-dimensional visualization for the forced oscillation of the molecular mobility as a function of the ΔASOW~τ_C and the initial τ_C .
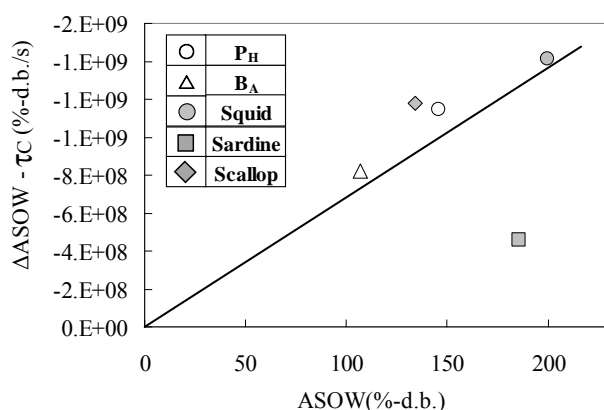
Figure 8 $\Delta ASOW \sim \tau_C$ as a function of ASOW for squid, sardine, Scallop, PH, and BH

Focusing on how the ASOW contributes to the probability of the self-organization of water species, one can presume that the water content (initial τ_C) of food would be an important parameter. Figure 8 illustrates the $\Delta ASOW \sim \tau_C$ as a function of the ASOW. One can clearly recognize the larger ASOW as the larger $\Delta ASOW \sim \tau_C$, except in sardine, indicating the following probable order of self-organization: squid >PH > scallop > BH.

4. Conclusions

(1) A forced cyclic temperature change operation (FCTCO) clearly demonstrated a forced oscillating behavior of the molecular mobility ($1/\tau_C$) of the water proton, because of the self-organization of hydrated water species, and distinguished two water species as $-A_1$ and $-A_2$ retained in the foods.

(2)The forced oscillating behavior obtained gave the characteristic modes depending on the kind of water species and the kind of foods. The amplitude (α) of the oscillation was decreased with increasing the initial τ_C (or decreasing the initial water content) and reached to zero at a specified τ_C depending on the kind of foods.

(3) The self-organization appearance probability of the water species was ordered as squid >PH > scallop > BH.

5. References

Abragam A..1963, The Principles of Nuclear Magnetism. Oxford at the Clarend Press, 347-349.

Belton P.S., Gil A.M., Webb G.A., Rutledge D., Eds., 2003, Magnetic Resonance in Food Science-Latest Developments, The Royal Society of Chemistry, Cambridge, UK.

Hills B.P., 1999, NMR studies of water mobility in foods. In"Water Management in the Design and Distribution of Quality Foods" ISOPOW 7(Y.H. Roos, R.B. Leslie, and P.J.Lillford, eds) Technomic Publishing, Lancaster, PA.

Hills B.P., Manning C.E., Godward J.A., 1999, A multistate theory of water relations in biopolymer systems. In: *Advances in Magnetic Resonance in Food Science* (edited by P. S. Belton, B. P. Hill and G. A. Webb). 45-62, Royal Society of Chemistry, Cambridge, UK.

Konishi Y., Horiuchi J., Kobayashi M., 2001(a), Dynamic evaluation of the dehydration response curves of food characterized by a poultice-up process using a fish-paste sausage-I. Determination of the mechanisms for moisture transfer, Drying Technology, 19(7), 1253-1269.

Konishi Y., Horiuchi J., Kobayashi M.,, 2001(b), Dynamic evaluation of the dehydration response curves of foods characterized by a poultice-up process using a fish-paste sausage-II, A new tank model for a computer simulation, *Drying Technology*, 19(7), 71-1285.

Konishi Y., Miura K., Kobayashi M., 2003, Drying efficiency design using multifunctional dynamics of water molecules in foods-H-NMR analysis of a fish paste sausage and squid, AIDIC Conference series, Vol.6, 183-190.

Konishi Y., Kobayashi M., Miura K., 2010, Characterization of water species revealed in the drying operation of Todarodes pacificus Steenstrup using water proton NMR analysis, International J. Food Sci.Tech.,45, 1889-1894.

Konishi Y., Kobayashi M., 2011, Dynamism of the water species as a probe molecule in foods, Chemical Engineering Transactions, 24, 475-480.