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

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A forced cyclic-temperature-change operation (FCTCO) between 30 and -30 °C clearly demonstrated forced oscillation of self-organization (FOS) of hydration water in six foods (squid, sardines, scallops, 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

Although a concrete identification of the hydration water has not been demonstrated yet, one possible imagination would be visualized as shown in Figure 1 (Uedaira, 1982). A variety of water species have been considered and they were classified into three groups depending on the absolute value of the correlation time (τ_C, s) as $\tau_C = 10^{-12}$ s (Region-III), $\tau_C = 10^{-8\sim-11}$ s (Region-II), and $\tau_C = 10^{-6\sim-7}$ s (Region-I). The former two groups (Regions-II and-III) would belong to the hydration water based on the ability to self-organize.
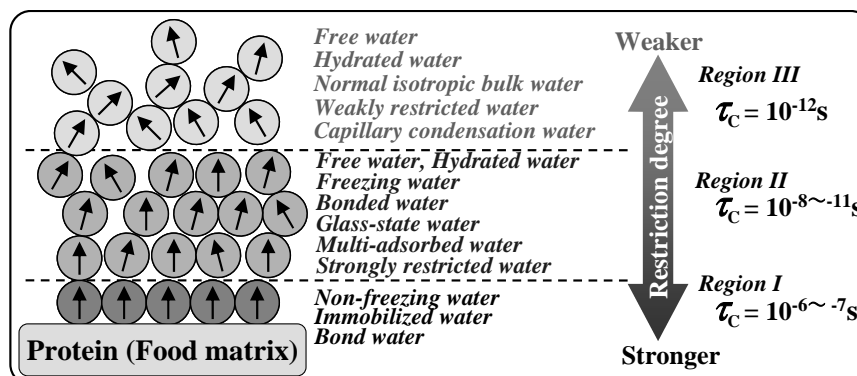

Figure 1 Schematic explanation of the water species adsorbed on macromolecules in food

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 2(a). To clearly demonstrate SO, the correlation time (τ_C, s) derived from an NMR parameter was effectively used (Hills et al., 1999; Belton et al., 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 2(b). All plots obtained for the water content of various food samples clearly had a typical hysteresis mode, as schematically shown in Figure 2(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 2(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 one with a higher τ_C represents a strongly restricted species. The value of τ_C is, thus, a useful parameter for characterizing the water species retained in a food tissue matrix. In our previous papers (Konishi et al., 2010; Konishi & Kobayashi, 2011), 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 foods. 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.). The two water species gave different effective water diffusivity values (De) and pre-exponential factors of De (Konishi et al., 2001(a), (b); Konishi et al., 2003).

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 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 the acceleration factor of self-organization (ΔASOW~τ_C : %-d.b./s) for all the foods; (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; and (4) to describe the amount of SO as a function of the ΔASOW~τ_C in comparing the order of the foods used in this study.
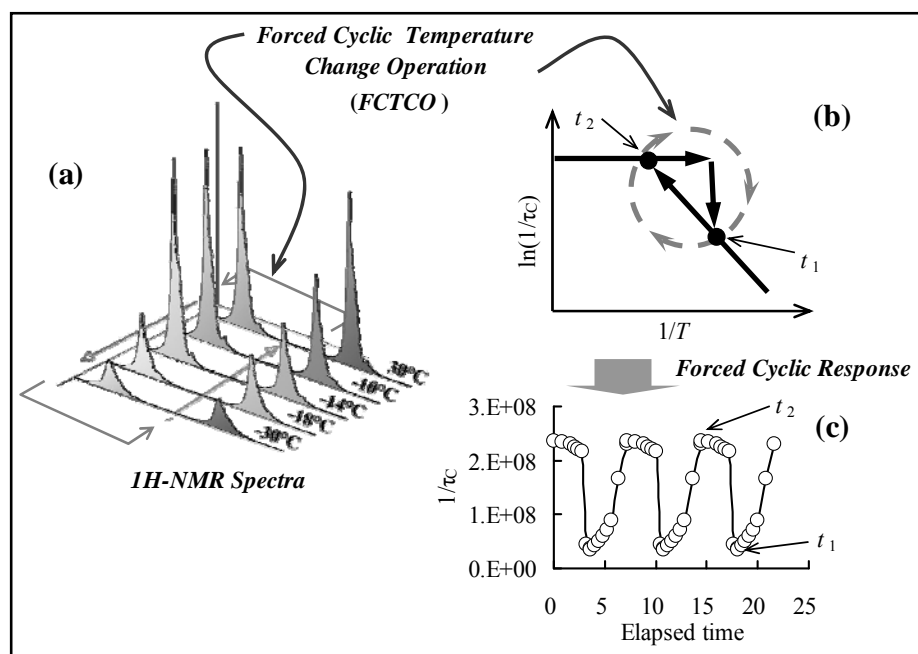

Figure 2 Schematic visualization the forced cyclic-temperature-change operation (FCTCO), the NMR-spectrum dynamism, and the $1/\tau_C$ oscillation obtained

2. Experimental

Materials and Methods

Pork (PH: produced in Hokkaido), beef (BA: produced in Australia and BH: produced in Hokkaido), squid, salmon, sardines, and scallops were chosen as food samples. The initial water contents (W_0) for PH, BA (and BH), squid, salmon, sardines, and scallops were W_0 = 230~320, 230~280, 300~360, 300~360, 210~270, and 180~230 %-d.b., respectively. The samples used were treated by a poultice-up process (PUP), which has conventionally been used to achieve a uniform distribution of water in drying foods. For the PUP, food was continuously ventilated when dried and transferred to a cool, dark storehouse, where it was kept for specific period of time.

The effective diffusivity (De) of water species was evaluated as a function of the water content because of the discrimination of the two water species: $-A_1$ and $-A_2$. Details regarding the experimental technique and the mathematical methods used to evaluate De can be found in our previous papers (Konishi et al., 2001(a), (b); Konishi et al., 2003).

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 the 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 2(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 Dynamism of the water activity (a_w) and the water correlation time (τ_C) during the dehydration of foods
Figure 3 demonstrates the water activity (a_w) and the water correlation time (τ_C) as a function of the water content
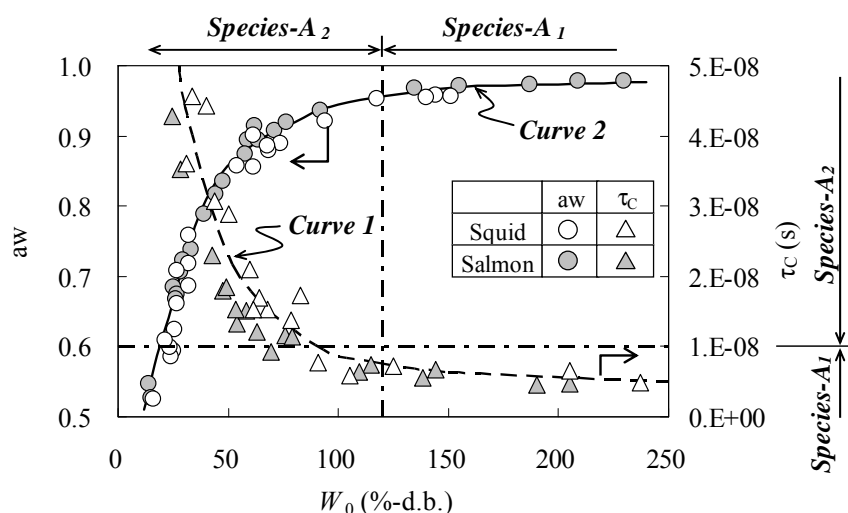

Figure 3 a_w and τ_C as a function of W_0 for squid and salmon

(W_0) of squid and salmon. The horizontal axis means the dehydration time increased when moving to the left side. The dehydration degree, therefore, increases with decreasing W_0. The progress of the dehydration steeply decreases the a_w accompanying the steep increase of the (τ_C), indicating the W_0 to be evaluated as a function of (τ_C) for all of the sample foods. The τ_C can, therefore, effectively be used instead of the W_0. Curves 1 and 2 were divided into two regions at the specified values of τ_C and W_0 as water species-A_1 and -A_2 regions, recognizing that $\tau_C = 10^{-8}$ s for curve 1 and $W_0 = 120$ %-d.b. for curve 2. The water species-A_1 region gave almost constant values of τ_C and a_w without depending on W_0, whereas the water species-A_2 region demonstrated steep changes in the values of τ_C and a_w. Although the two water species were described in detail in previous papers (Konishi et al., 2010; Konishi & Kobayashi, 2011), they will also be discussed in later sections.

3.2 Characterization of the forced oscillation of the molecular mobility ($1/\tau_C$) of water species for the various foods

The forced oscillations of $1/\tau_C$ obtained were visualized for all of the foods used in this study. Figure 4 demonstrates the forced oscillating curves for sardines, scallops, 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 as seen in the figure).

Comparing the forced oscillation among the samples with widely dispersed water contents (or initial τ_C's), 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 scallops, can be easily recognized from the diagram in
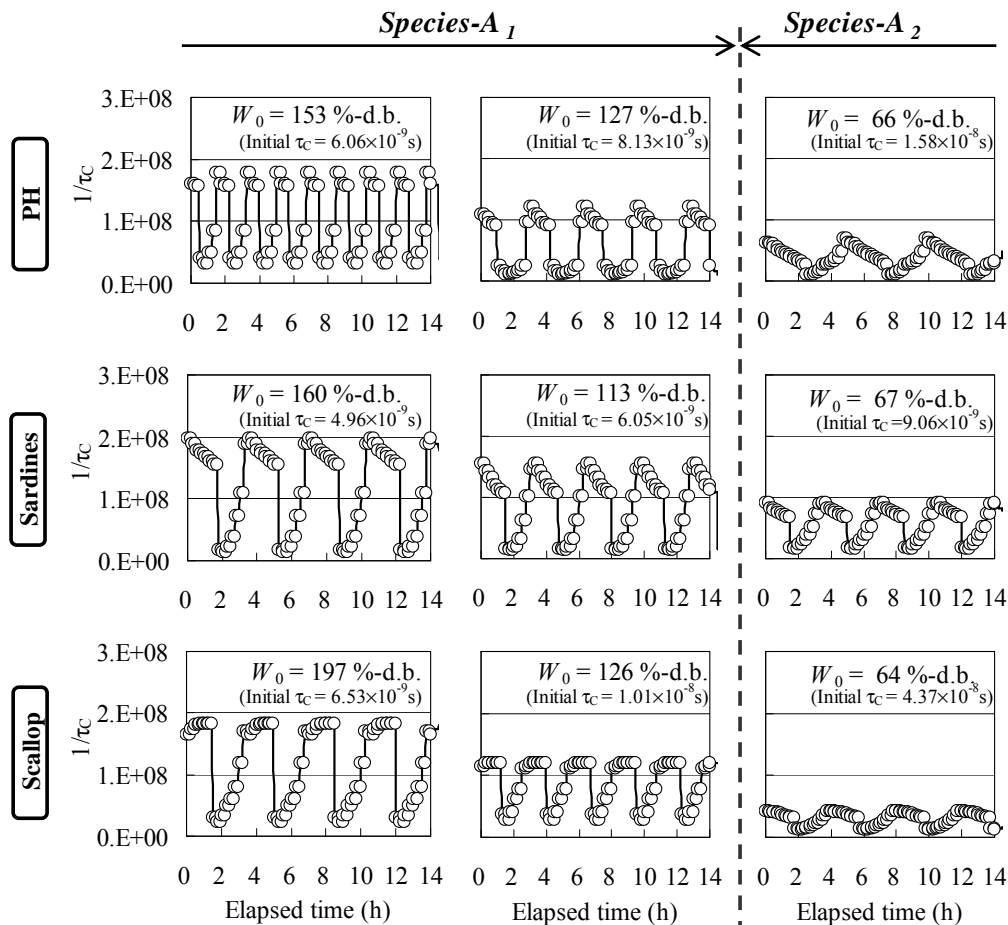

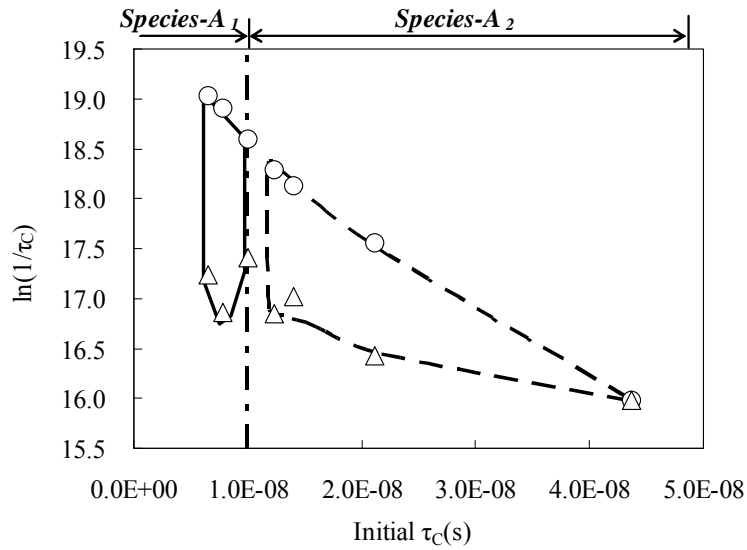Figure 4 Oscillating self-organization characterized by the kind of food

Figure 5 Width of ln(1/τ_C) for forced oscillation as a function of the initial τ_C for scallop

Figure 4 by the width of ln(1/τ_C), given as a distance between the peak top and peak bottom of the oscillating curves in Figure 4. Figure 5 visualizes the dynamism of α as a function of the initial τ_C, indicating a broken-line circle for scallops as an example. The α can be recognized as a width between the top and the bottom for the broken-line circle, and it decreases with an increase in the initial τ_C or with a decrease in the water content of the food samples and finally reaches zero at the specified initial τ_C. In this τ_C region ($\tau_C > 4.4 \times 10^{-8}$ s for scallop), the hysteresis behavior disappears. Focusing on water species-A_1 and -A_2 regions, the two regions were clearly divided at $\tau_C = 1 \times 10^{-8}$ s.

Figure 6 illustrates the α as a function of the initial τ_C, indicating the disappearance of the oscillation for squid, sardines, and scallops to become the initial $\tau_C = 3.1 \times 10^{-8}$, 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 disappearance was sensitively
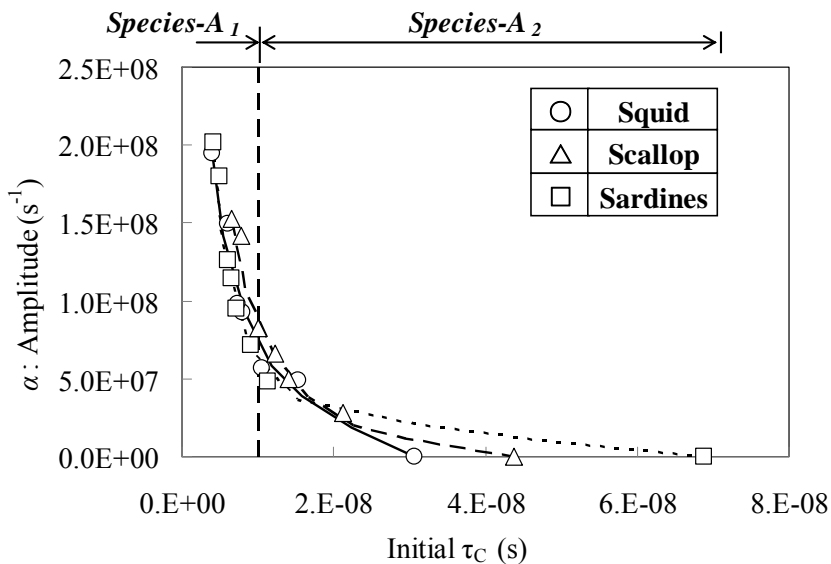

Figure 6 α as a function of the initial τ_C

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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 $\Delta\alpha \sim \tau_C$ value obtained for each food can be used as a parameter for evaluating 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, scallops, and sardines were determined to be -2.2×10^{15}, -8.4×10^{14}, and -5.1×10^{14} s^{-2}, respectively. Squid, therefore, gives a higher probability of self-organization than do sardines because of the higher $\Delta\alpha \sim \tau_C$.

3.3 Hysteresis behavior 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 2(a) and expressed as the modified water content (MWC, %-d.b.). The MWC was evaluated by using equation (1).

$$MWC = initial\ water\ content \times \frac{Peak\ area\ of\ the\ NMR\ spectra\ at\ the\ given\ t}{Peak\ area\ of\ the\ proton\ NMR\ spectra\ at\ the\ initial\ water\ content} \qquad (1)$$

Figure 7 demonstrates the MWC as a function of $1/T$ and the initial τ_C. It is evident that the hysteresis of the MWC is similar to the $1/\tau_C$ hysteresis presented in Figure 2(b), indicating a steep reduction of MWC at the same temperature, as in the case of $1/\tau_C$.

Since the steep reduction of MWC at the specified temperature is clearly evaluated as an ASOW at the given water content (or the initial τ_C), the ASOW evaluated is linearly reduced with increasing the initial τ_C of the sample. Figure 8 demonstrates, as an example, the ASOW as a function of the initial τ_C for scallops. All other foods showed similar results. Based on the results obtained, the linear dependency of the ASOW$\sim\tau_C$ straight line indicates an inflection point at $\tau_C = 10^{-8}$ 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 4.

In the water species-A_2 region in Figure 8, the slope of the ASOW$\sim\tau_C$ straight line is clearly changed depending on the kind of food used. The slope may be designated as a parameter of ΔASOW$\sim\tau_C$, which contributes to the positive probability of self-organization. The absolute values of the ΔASOW$\sim\tau_C$ for PH, BA, squid, salmon,

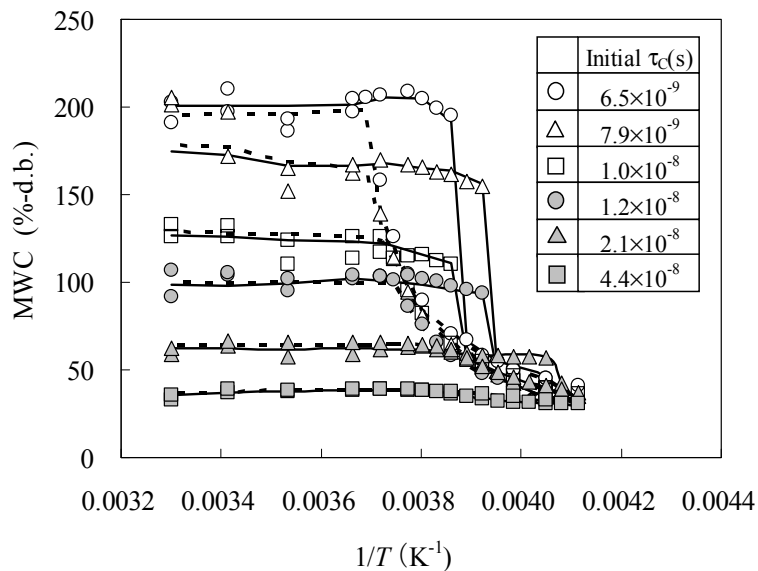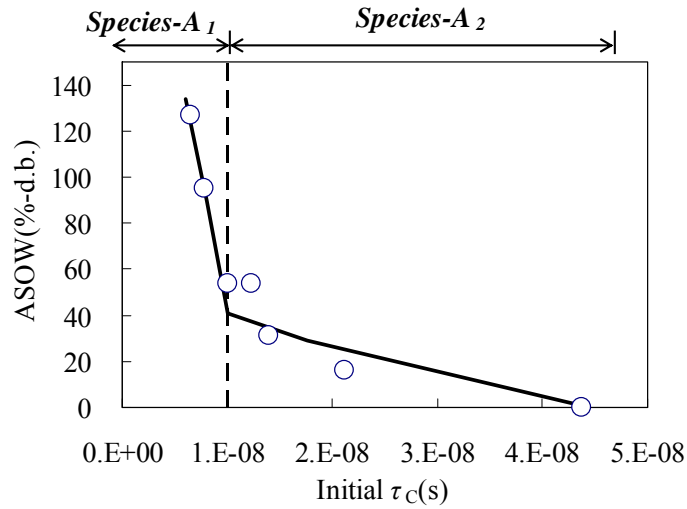*Figure 7 MWC as a function of 1/T and the initial τ_C for scallops*

Figure 8 ASOW as a function of the initial τ_C for scallops

sardines, and scallops are evaluated as -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. From the comparison among the absolute values obtained, salmon gave the highest probability of self-organization among all of the foods used. The difference in the $\Delta ASOW \sim \tau_C$ (%-d.b./s) among the six foods is similar to the difference in the acceleration parameter ($\Delta\alpha \sim \tau_C$, s^{-2}) of the self-organization of water species in the foods, which is strongly associated with the $\alpha's$ presented in Figure 6.

3.4 Discrimination of the two water species, -A$_1$ and -A$_2$, based on the pre-exponential factor of effective diffusivity (_De_)

Focusing on the discrimination of the two water species, -A$_1$ and -A$_2$, all the data presented in Figures 3, 4, 5, 6, and 8 still were not entirely clear. The pre-exponential factor of effective diffusivity (_De_) can be used effectively for the clear discrimination between the two water species. The value of _De_ is expressed by equation (2) (Butt, 1980),
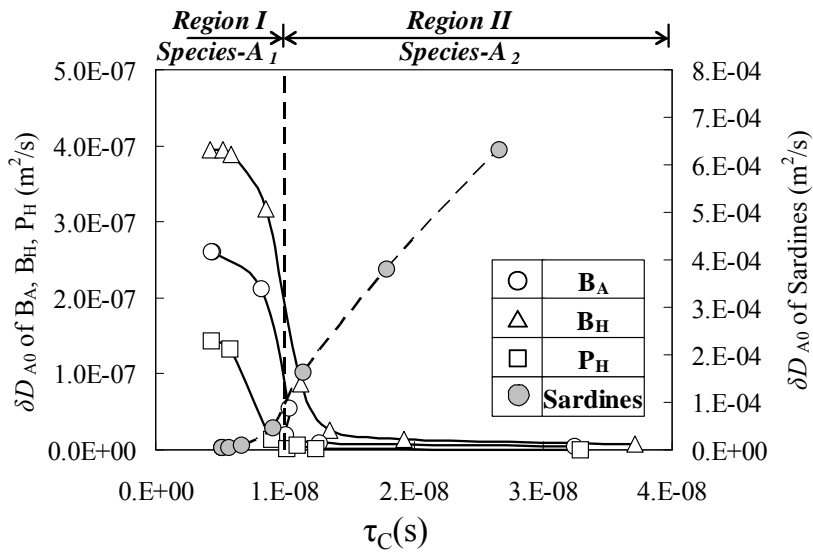
$$De = \delta D_{AO} \; exp \left(E_D / (R \cdot T_D) \right), \tag{2}$$

Figure 9 Pre-exponential factors as a functio of τ_C for BA, BH, PH, and sardines

where $\delta = \varepsilon / \chi$, ε *is porosity,* χ is the *labyrinth factor,* D_{A0} is the pre-exponential factor of D, D is the diffusion coefficient, E_D is the activation energy of D, R is the gas constant, and T_D is the temperature. The pre-exponential factor, δD_{A0}, was easily evaluated because E_D was experimentally determined. Figure 9 demonstrates δD_{A0} as a function of the initial τ_C. The values of δD_{A0} for BA, BH, and PH demonstrate a steep reduction, whereas sardines demonstrate a steep increase at the $C\tau_C = 1 \times 10^{-8}$ s. These results exactly visualize the clear discrimination between the two water species, -A_1 and -A_2, even though both belong to the hydration water. This extraordinary change at the $C\tau_C$ is caused by the diffusion mechanism change, which was derived from the pore structure change of the food tissue matrix. The pore structure change was accelerated at the $C\tau_C$ according to the progress of the dehydration operation. Details of this evidence will be reported in future papers.

3.5 Three-dimensional map for self-organized water species

Figure 10 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 10. In the water species-A_1 region ($\tau_C < 10^{-8}$ s, region I), it is clear 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. In the water species-A_2 region ($\tau_C > 10^{-8}$ s, region II), on the other hand, the mode of the α showed a drastic difference among the foods. The disappearance of the self-organization indicating $\alpha = 0$, especially, was given at a different initial τ_C value depending on the kind of food, as also seen in Figure 6.

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 11 illustrates the ΔASOW~τ_C as a function of the ASOW. One can clearly recognize the larger ASOW as the larger ΔASOW~τ_C, except in sardines, indicating the following probable order of self-organization: squid > PH > scallops > BA.
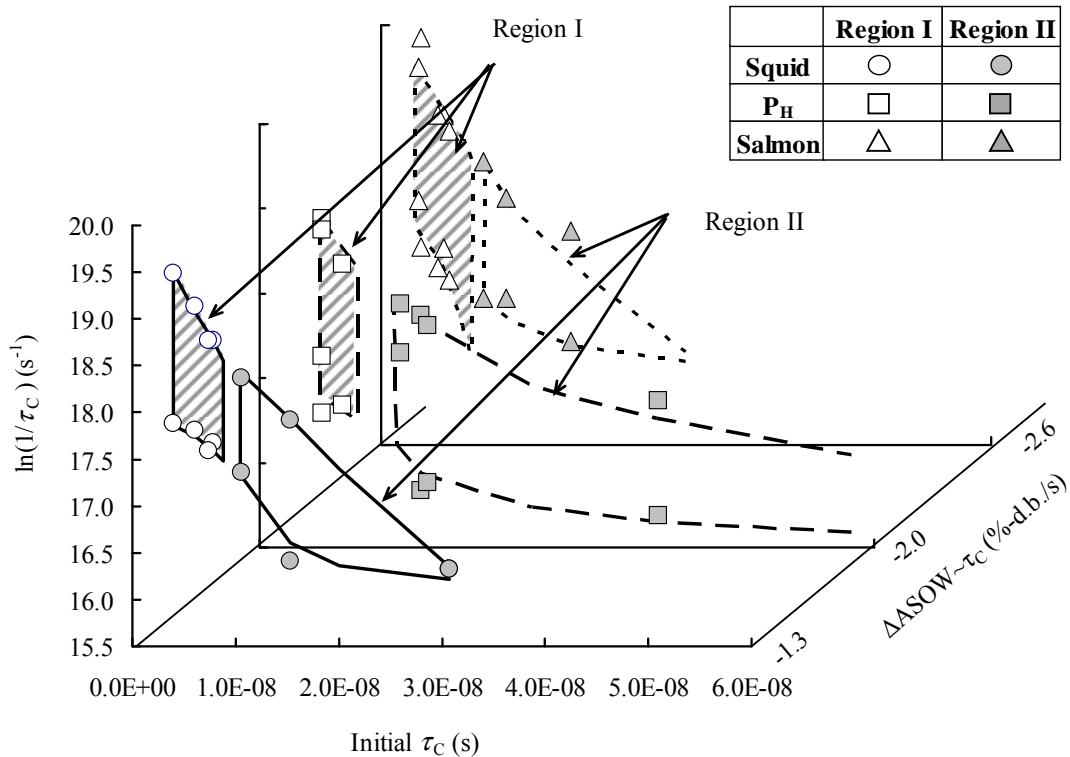

Figure 10 Three-dimensional visualization of the forced oscillation of the molecular mobility as a function of the ΔASOW~τ_C and the initial τ_C
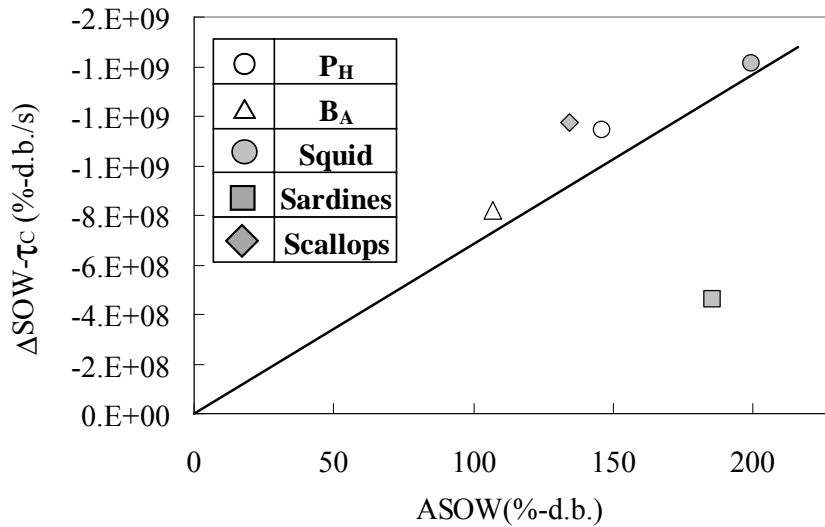
Figure 11 ΔASOW~τ_C as a function of ASOW for squid, sardines, scallops, PH, and BA

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 hydration water species, and distinguished two water species, -A_1 and -A_2, retained in the foods (Pork (PH), beefs (BA and BH)), squid, salmon, sardines, and scallops).

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

(3) The three-dimensional map for the hydration water was visualized by distinguishing the characteristics of the variety of foods used.

(4) The order of probability of the self-organization appearance of the water species is squid > PH > scallops > BA.

Acknowledgement

Nomenclature

ASOW	*amount on self-organization water species (-)*
ΔASOW~τ_C	*probability of self-organization (%-d.b./s)*
a_W	*water activity(-)*
BA	*beef meat produced in Australia (-)*
BH	*beef meat produced in Hokkaido, Japan (-)*
D	*moisture diffusion coefficient (m^2/s)*
D_{A0}	*pre-exponential factor of D*
De	*effective moisture diffusion coefficient (m^2/s)*
E_D	*activation energy of water diffusivity (kJ/mol)*

FCTCO	forced cyclic temperature change operation (-)
FOS	forced oscillation of self-organization(-)
MWC	modified water content (%-d.b.)
PH	pork meat produced in Hokkaido, Japan (-)
PUP	poultice-up process, which is used to achieve a uniform distribution of water in drying foods (-)
R	gas constant (=8.314J/K·mol)
SO	self-organization (-)
T	temperature given at the forced cyclic operation (K)
T_D	drying temperature (°C)
T_2	spin-spin relaxation time of water proton (s)
t_1	start temperature of hysteresis behaviour at FCTCO (K)
t_2	end temperature of hysteresis behaviour at FCTCO (K)
W_0	initial water content at the time of PUP operated (%-d.b.)

Greek letters

α	amplitude of the forced oscillation for water species-A_1 and -A_2 (s^{-1})
$\Delta\alpha{\sim}\tau_C$	acceleration parameter of the self-organization of water species (s^{-2})
ε	porosity of the food tissue (-)
τ_C	correlation time of water proton (s)
$C\tau_C$	critical correlation time of water proton (s)
χ	labyrinth factor of the food tissue (-)
δ	diffusibility (=ε/χ)
δD_{A0}	pre-exponential factor of De (m^2/s)

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