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, \( \tau_C \) (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 \( \tau_C = 10^{-8} \text{ s} (= C\tau_C) \). The amplitude (\( \alpha \)) 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 \( \alpha \), whereas water species-A\(_2\) was recognized as a strongly restricted species with a lower \( \tau_C \) and smaller \( \alpha \). 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 (\( \tau_C \), s) derived from an NMR parameter (Hills et al., 1999) was effectively used (Belton et al. eds., 2003). Since the \( \tau_C \) 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 \( \tau_C \) represents a weakly restricted species, while that with a higher \( \tau_C \) represents a strongly restricted species. The value of \( \tau_C \) 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 \( C\tau_C = 10^{-8} \text{ s} \), 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 \( C\tau_C = 10^{-8} \text{ s} \) 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: \( \tau_C < 10^{-8} \text{ s} \) or \( W_0 > 120 \text{ %}-\text{d.b.} \)) and water species-A\(_2\) region (lower water content region: \( \tau_C > 10^{-8} \text{ s} \) or \( W_0 < 120 \text{ %}-\text{d.b.} \)) (Konishi et al., 2001(a)). The two water species gave different effective water diffusivity values (\( D_e \)) and pre-exponential factors of \( D_e \) (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 the FCTCO; (2) to visualize the forced oscillation of self-organization as a function of three parameters: molecular mobility (\(\ln{1/\tau_C} : \text{s}^{-1}\)), initial water content of the sample (initial \(\tau_C : \%\)-d.b.), and acceleration factor of self-organization (\(\Delta\text{ASOW}~\tau_C : \%\)-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 \(\tau_C\) of the water species, a nuclear magnetic resonance (NMR) technique was applied to measure the \(^1\text{H}\)-NMR spectra and spin-spin relaxation time \(T_2\) of water protons. \(^1\text{H}\)-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, \(\tau_C\), 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 $\tau_C$ of the sample). The amplitude ($\alpha$) of the oscillation was drastically reduced in the water species-A2 region, indicating a reduction in the molecular mobility ($1/\tau_C$). This reduction of $\alpha$, 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 $\alpha$ decreased with an increase in the initial $\tau_C$ or with a decrease in the water content of the food samples and finally gave zero at the specified initial $\tau_C$. In this $\tau_C$ region, the hysteresis behavior disappeared. Figure 4 illustrates the $\alpha$ as a function of the initial $\tau_C$, indicating the disappearance of the oscillation for squid, sardine, and scallop to become the initial $\tau_C$.
These results clearly demonstrate that the water content (initial $\tau_C$) 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 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 $-2.2 \times 10^{15}$, $-8.4 \times 10^{14}$, and $-5.1 \times 10^{14}$ 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 $1/\tau_C$ and the initial $\tau_C$. It is evident that the hysteresis of the MWC 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 $\tau_C$ of the sample. Figure 6 demonstrates, as an example, the ASOW as a function of the initial $\tau_C$ for scallop. All the other foods showed similar results. Based on the results obtained, the linear dependency of the ASOW~$\tau_C$ straight line indicates an inflection point at $\tau_C$. 

![Figure 4: $\alpha$ as a function of the initial $\tau_C$](image)

- $3.1 \times 10^{-8}$, $6.9 \times 10^{-8}$, and $4.4 \times 10^{-8}$ s, respectively. These results clearly demonstrate that the water content (initial $\tau_C$) 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 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 $-2.2 \times 10^{15}$, $-8.4 \times 10^{14}$, and $-5.1 \times 10^{14}$ s$^{-2}$, respectively. Squid, therefore, gives a higher probability of self-organization than does sardine because of the higher $\Delta \alpha \sim \tau_C$.

![Figure 5: The converted water content as a function of $1/T$ and the initial $\tau_C$ for scallop](image)
=10^{-8} \text{ 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 ∆ASOW~τ_C, which contributes to the positive probability of self-organization. The values of the ∆ASOW~τ_C for PH, BA, squid, salmon, sardine, and scallop are -1.15 \times 10^9, -8.19 \times 10^8, -1.41 \times 10^9, -5.49 \times 10^9, -4.61 \times 10^8, and -1.18 \times 10^9 \text{ %}-d.b./s, respectively. Salmon gave the highest probability of self-organization among all the foods used. The difference in the ∆ASOW~τ_C (%-d.b./s) among the six foods is similar to the difference in the acceleration parameter (Δα~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/τ_C) [z-axis] as a function of both the initial τ_C [y-axis] and the ∆ASOW~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 (τ_C < 10^{-8} \text{ s}, region I), one can clearly see that the α gave an appreciable value without depending on both the initial τ_C and the ∆ASOW~τ_C, indicating a similarity with no influence of the kind of food. The disappearance point of α (τ_C > 10^{-8} \text{ s}, region II) in the water species-A_2 region, contrastively, showed a drastic change among the foods.

Figure 6 ASOW as a function of the initial τ_C for scallop.

Figure 7 Three-dimensional visualization for the forced oscillation of the molecular mobility as a function of the ∆ASOW~τ_C and the initial τ_C.
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 -A1 and -A2 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 ($\alpha$) of the oscillation was decreased with increasing the initial $\tau_C$ (or decreasing the initial water content) and reached to zero at a specified $\tau_C$ 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


Konishi Y., Horiiuchi 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., Horiiuchi 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.

