AIDIC *Conference Series*, Vol. 10, 2011
Editor Sauro Pierucci
DOI: 10.3303/ACOS1110022

ISBN 978-88-95608-58-7 ISSN 2036-5969

DYNAMISM OF THE WATER SPECIES AS A PROBE MOLECULE IN FOODS

Yasuyuki Konishi[1]* and Masayoshi Kobayashi[2]

[1]Hokkaido Industrial Technology Center
379 Kikyo-cho, Hakodate, Hakodate, 041-0801, Japan
[1]Affiliation, left , times New[2]Advanced Technology Institute of Northern Resources
8-6, Tonden 2Jo 2Chome, Sapporo, Hokkaido

The water species retained in salmon, squid, sardine, beef (B_A), and pork (P_H) were quantitatively distinguished as a function of four parameters, moisture diffusivity (*De*, m^2/s), activation energy of *De* (E_D, kJ/mol), correlation time (τ_C, s) of the water species determined by a proton NMR technique, and hardness (N_P, Newton/m^2) of the foods. All four parameters evaluated for the five foods commonly demonstrated the existence of a critical value of τ_C ($C\tau_C = 1.0\times10^{-8}$s) at which the dynamism of water species should be divided into two regions discriminating two different water species as water species-A_1 (region I, $0.1\sim0.8\times10^{-8}$ s < $C\tau_C$, evaluating it as weakly restricted water species), and water species-A_2 (region II, $1.0\sim10\times10^{-8}$s > $C\tau_C$, evaluating it as strongly restricted water species).
A forced cyclic temperature change operation (FCTCO) between 30 and -30°C for the five foods brought a characteristic oscillation of $1/\tau_C$ (rotation rate of water molecule, s^{-1}). The oscillation obtained was understood as a commonly induced dynamic-change between a self-organization state and a liquid state of the water species appearing as a result of the FCTCO. The amplitude (α) of the oscillation obtained was evaluated differently depending on three components, the food structure matrix and the water species-A_1 and -A_2, indicating a clear discrimination among the three components. α of water species-A_1 was larger than that of water species-A_2 as a result of the former being the weakly restricted state and the latter, the strongly restricted state. The self-organization of water species-A_1 and -A_2 was strongly influenced by both the value of $1/\tau_C$ at the initial condition of the samples and the kind of food used and demonstrated a characteristic hysteresis as a function of the temperature. The value of $1/\tau_C$ given at the temperature inducing the self-organization clearly obeyed an Arrhenius equation, and the Arrhenius plots obtained gave different activation energy (E_{SO}) for the self-organization depending on water species-A_1 and -A_2 and the food.
Water activity (a_w) was clearly evaluated as a linear function of τ_C, indicating a different slope depending on the food used. This linear relation between a_w and τ_C gave two different slopes at $C\tau_C$ because of a dynamic change from water species-A_1 to -A_2 due to the progress of the dehydration of foods. The a_w-τ_C straight line obtained clearly gave a different line depending on the food used in the region of water species-A_2, whereas, in the region of water species-A_1, it gave the same straight line without depending on the food.
The pre-exponential factor (PF, which consisted of porosity, labyrinth factor, and activation entropy) of *De* showed a characteristic dynamism as a function of τ_C depending on the food used. For B_A and P_H, water species-A_1 gave an identical value of PF without depending on τ_C, whereas water species-A_2 gave a steep decay of PF with increasing τ_C. For sardine, squid, and salmon, in contrast, water species-A_2 gave a gradual increase of PF with increasing τ_C, suggesting a diffusion mechanism of water species -A_1 and -A_2 that differed depending on the food used.

1. INTRODUCTION

In biochemical (Takaoka *et al.*, 2009), biomedical, and heterogeneous catalysis (Kobayashi *et al.*, 1997) systems, a probe molecule has conveniently been used to clarify the detailed mechanism of a dynamic process in their

Please cite this article as: Konishi Y. and Kobayashi M., (2011), Dynamism of the water species as a probe molecule in food, AIDIC Conference Series, 10, 197-206 DOI: 10.3303/ACOS1110022

complicated systems. The same technique should be applied to the field of food technology because the food system includes a biological dynamism influenced by changes in environmental conditions derived from food production processes, such as dehydration, hydration, heating, mechanical crashing, and evacuation. In these processes, although isotope molecules have been conveniently used as probe molecules, water species retained in foods can be used as probe molecules because 60 to 70% of food materials consist of water species. To quantitatively describe the dynamic change of water species in foods, five parameters can be selected as an effective moisture diffusion coefficient, *De* (m^2/s) (Konishi *et al.*, 2001, 2003(a), (b)), activation energy of *De*, E_D (kJ/mol), pre-exponential factor of *De*, PF (m^2/s), hardness of foods, N_P (Newton/m^2), and correlation time of water species, τ_C (s) (Konishi *et al.*, 2010) evaluated by the proton NMR technique. Using τ_C, two water species, $-A_1$ and $-A_2$, can be conveniently discriminated, as has been demonstrated previously (Konishi and Kobayashi, 2009). Considering the water activity map presented by Labuza *et al.* (1970) and Schmidt (2004), the proportion of the two water species on a water activity space may be proposed. Considering the water activity map presented by Labuza *et al.* (1970) and Schmidt (2004), the proportion of the two water species on a water activity space may be proposed. The schematic in Fig. 1 demonstrates the adsorbed water amount as a function of water activity, a_w (Curve 1), and τ_C as a function of water content, W_0 (Curve 2). In the water species-A_2 region, the τ_C-value (see Curve 2) decreases steeply with increasing W, whereas, in the water species-A_1 region, it demonstrates an identical value without dependence on W. Considering Curve 1 (adsorption isotherm of BET for water species), water species-A_1 is characterized as multilayer adsorption water and free water, which are weakly restricted by the surrounding macromolecules, whereas water species-A_2 forms monolayer adsorption as strongly restricted species. In the present study, the discrimination of the two water species will be demonstrated more clearly using separate experimental data.

The molecular mobility parameter, especially τ_C, can conveniently visualize an interesting oscillating dynamism of $1/\tau_C$ that occurs in foods by using water species as a probe molecule, similar to the catalytic oscillating production of propanal from propene on Pt/SiO_2 (Kobayashi *et al.*, 1997). This catalytic oscillation is a self-initiated oscillation due to a regulation between the amounts of adsorbed oxygen and propene resulting from the surface reaction. The oscillating behavior of $1/\tau_C$, however, basically results from the hysteresis behavior of the water species in the food tissue matrix because its self-organization takes place at a freezing temperature of

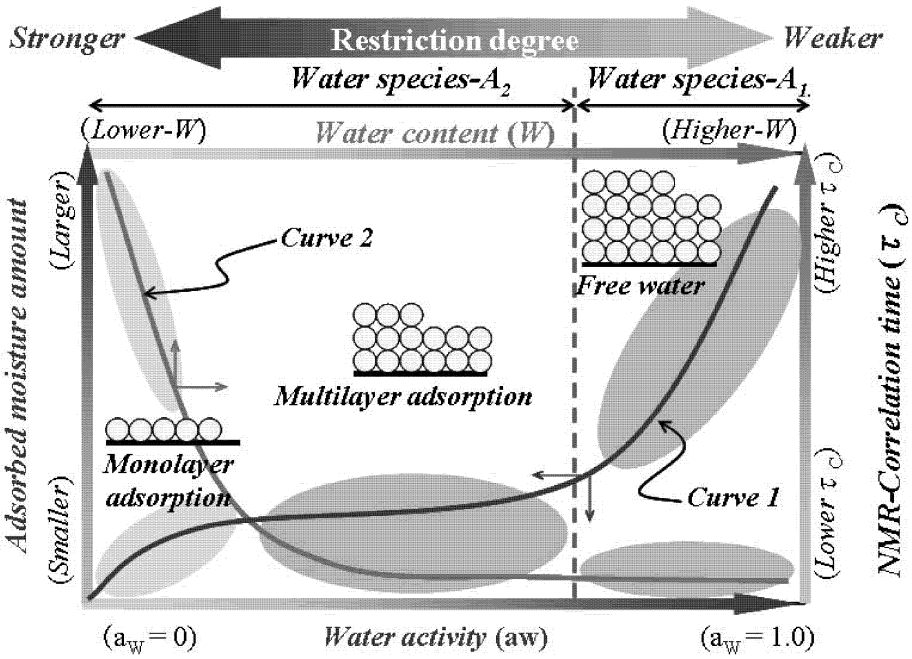

Figure 1: Discrimination of the water species retained in the food matrix.

water and can be visualized by the forced cyclic temperature change operation (FCTCO) between 30 to -30°C.
The objectives of this study with the use of water species as a probe molecule in five foods are as follows: (1) to demonstrate the dynamic behavior of the five parameters (*De*, E_D, PF, N_P, and τ_C) specified by the kinds of foods and the environmental conditions; (2) to demonstrate a critical point of the four parameters (*De*, E_D, PF, and N_P) as a function of τ_C; (3) to characterize the oscillating behavior of $1/\tau_C$ derived from the self-organization of water species; and (4) to discriminate the water species-A_1 and -A_2 among the five foods using a linear relation of water activity (a_w) and τ_C.

2. EXPERIMENTAL

Five foods, salmon, squid, sardine, beef (produced in Australia, B_A, and in Hokkaido, B_H), and pork (produced in Hokkaido, P_H), were used as typical examples, and all of them had an initial moisture content of 230~280%-d.b. (dry base, W_D). Before using the drying sample prepared with any water content, a poultice-up process (designated as PUP) was used to keep the water distribution uniform in the food samples. For the PUP, the samples were stored in an incubator for 36 h, and the temperature was regulated at 2ºC. The sample weight was continuously recorded by the output of a strain-gage transducer using a data-logger. In the present experimental drying conditions, it was reconfirmed that the drying operations were within a falling-rate period.
For the discrimination of the water species retained in the five foods, a nuclear magnetic resonance (NMR) technique was effectively applied to measure molecular mobility (correlation time τ_C) using the ^{1}H-NMR spectra and spin-spin relaxation time of water protons. The ^{1}H-NMR spectra were obtained using a JEOL A-500 FT-NMR spectrometer operating at 500MHz for protons. The observed frequency width was 20 kHz. The 90º pulse width was 12.5 μs, and the number of pulse repetitions was 8. The proton chemical shifts were measured by using a slight amount of water containing deuterium oxide as an external reference. All the NMR measurements were performed at 23.5±0.5ºC. The spin-spin relaxation times, T_2, were obtained by the spin locking method, and, from the obtained T_2, the correlation time of a water proton, τ_C, was evaluated using Equation (1).

$$\frac{1}{T_2} = \frac{\gamma^4 \cdot \hbar^2 \cdot I(I+1)}{5r^6}\left(3\tau_c + \frac{5\tau_c}{1+\omega_0^2 \cdot \tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2 \cdot \tau_c^2}\right) \quad (1)$$

where T_2 is the spin-spin relaxation time of the water proton (s), γ is the gyromagnetic ratio of a proton (= 2.675×10^8 rad·T^{-1}·s^{-1}), $\hbar$ is the modified Plank's constant (6.63×10^{-34} J·s), I is a nuclear-spin quantum number of a water proton (= 0.5), r is the proton-proton distance of a water molecule (0.16 nm), ω_0 is the resonance frequency of NMR (= 3.14×10^9 s^{-1}), and τ_C is the correlation time of a water proton (s).
The FCTCO used in this study was conducted in a specified temperature region between Ts_1 (initiation temperature inducing the self-organization) and Ts_2 (the temperature returned from the self-organization), at which hysteresis behavior appeared to be due to the self-organization of water species. In the temperature region, to make the hysteresis (self-organization region), the samples were kept for 13(±2) min at the given temperature, and each of the temperature-up and -down operations was successively conducted. The holding time (13(±2) min) of the temperature to evaluate the relaxation time for the NMR technique was included in the cyclic temperature change operation time.
The water activity (a_w) of samples was measured using an electrolyte resistive measurement cell (LabMaster-aw, NOVASINA Co.). The hardness of the samples was measured using a creep tester equipped with a V-shaped plunger of 30 mm in width and 1 mm in thickness to press a meat sample to 60% of its size, 2~8×10×50 mm, to determine the value of N/m^2.

3. RESULTS AND DISCUSSION

3.1 A critical τ_C value appeared in the dynamism of physicochemical parameters

As has been demonstrated in the Proceedings of the International Conference on Application of Magnetic Resonance in Food Science (edited by Belton *et al.*, 2003), the NMR technique was recognized as a useful tool to analyze food materials (Ruiz-Cabrera *et al.*, 2004; Schmidt, 2004). Each of the parameters, *De*, E_D, *PF*, and N_P, for the five foods demonstrates a characteristic dynamism as a function of the mobility parameter, τ_C, derived from the NMR method. Figure 2 illustrates the three parameters, *De*, E_D, and N_P, as a function of τ_C. The specified τ_C-value (designated as $C\tau_C$) at which the three parameters commonly indicate an anomalous change is clearly evident. This anomalous change at $C\tau_C$ is possibly attributed to a drastic change of water species from species-A_1 to species-A_2 derived from the dehydration operation. The progress of the dehydration brings a drastic change in the strength of the restriction of water species retained in the food tissues accompanying a steep growth of τ_C. This steep growth of τ_C resulted from the mechanical change in the structure of the food tissue matrix inducing a drastic change in the form of adsorption of water species, as shown in Fig.1 by the shift from a multilayer form to a monolayer form. On the *De*-value in Fig.2 (A), although the data were widely scattered, P_H, B_A, B_H, squid, and salmon showed a steep decay at $C\tau_C$, whereas sardine demonstrated an increase. Focusing on the E_D-curves in Fig.2 (B), two food groups were recognized again as the group of squid, salmon, and sardine (group-I), which showed an increase in the region of water species-A_2, and the group of P_H, B_A, and B_H (group -II), which demonstrated a steep decrease. This opposite tendency between the two food groups-I and -II would result from a difference in the physical change in the structure of food tissues induced from the dehydration operation. The physico-chemical meaning of this phenomenon is discussed further in the next section.

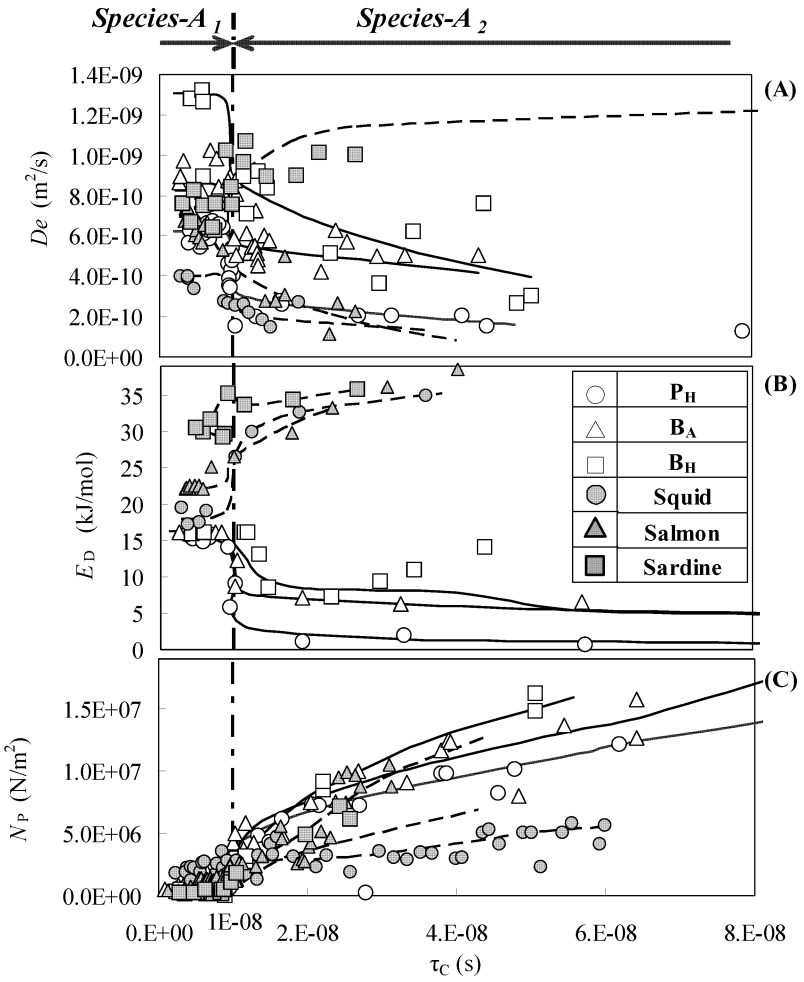

Figure 2: Physicochemical parameters, De, E_D, and N_P, as a function of τ_C.

3.2 Physico-chemical meaning of the appearance of Cτ_C

Our interest is focused on the physico-chemical meaning of Cτ_C and the reason that it appears at the specific value of τ_C=10^{-8} s. To respond to this question, the water diffusivity in a food tissue matrix may be analyzed. The apparent diffusivity, *De*, is generally expressed by Equation (1) (Butt, 1980).

$$De = \left(\frac{\varepsilon}{\chi}\right) \cdot D = \delta \cdot D_0 \cdot exp\left[\frac{-E_D}{R \cdot (T_D + 273)}\right] \quad (2)$$

where ε is the porosity of the meat tissue, χ is the labyrinth factor of the meat tissue, D is the water diffusion coefficient, δ is the diffusibility, and D_0 is the frequency factor of D.

Since the pre-exponential factor (PF) of *De*, δD_0, can easily be evaluated by the E_D- and *De*-values estimated from Figs.2 (A) and (B), it can be visualized as a function of τ_C. Figure 3 illustrates PF as a function of τ_C for the five foods. The five curves obtained in Fig.3 demonstrate again the existence of Cτ_C in all the foods dividing the two water species-A_1 and -A_2 regions. In addition, two food groups are evident in Fig.2 (B), as the group of B_A and P_H (group II) demonstrates a steep decay, whereas the group of squid, salmon, and sardine (group I) indicates a steep increase in the water species-A_2 region. This extraordinary difference strongly indicates an opposite variation of PF with increasing τ_C between groups-I and -II. The anomalous behavior of groups-I and -II is clear, as the PF value for group-II is 15~40 times larger than that of group-I in the water species-A_1 region, and, for group-II, it is 10~35 times larger than for group-I in the water species-A_2 region. This inverse variation should induce a different mechanism of water diffusion between the two food groups in the water species-A_1 and -A_2 regions. On the detail of the water diffusion mechanism, although further research is needed, the mechanical structure of food tissue matrix as a labyrinth factor (χ) and the porosity (ε) would differ as a result of the progress of dehydration (with increasing τ_C) depending on the kind of food.

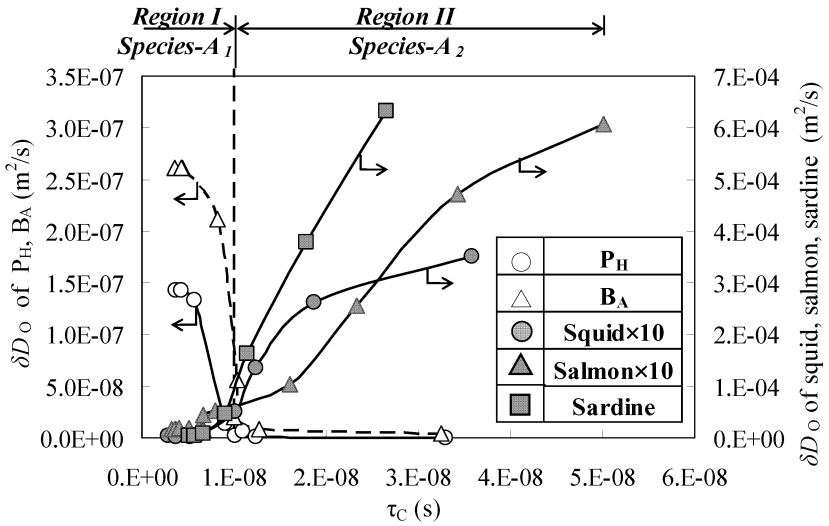

Figure 3: PF dynamism as a function of τ_C to recognize Cτ_C.

3.3 Hysteresis dynamism derived from the self-organization of water species retained in foods

The physico-chemical parameter, τ_C, can conveniently be used to evaluate the mobility of water species retained in foods. Since 1/ τ_C (s^{-1}) is understood as a rotation rate of the water species, the rate can be expressed as a function of 1/T and obeys an Arrhenius equation. Figures 4 (a) and (b) illustrate an Arrhenius plot for the water species-A_1 and -A_2, respectively, using sardine as an example. All the Arrhenius plots obtained clearly demonstrate a typical hysteresis mode, and a steep drop of 1/τ_C resulted from a self-organization of water species-A_1 and -A_2 at a specific temperature lower than 0°C. The self-organization that appeared at the different

values of $1/\tau_C$ can obey again the Arrhenius equation, as shown by the broken lines in Figs.4 (a) and (b). The Arrhenius plots obtained propose an apparent activation energy (E_{SO}) for the self-organization of water species-A_1 and -A_2 indicating 182 and 116kJ/mol, respectively. The same analysis of the Arrhenius plots was applied for squid, salmon, beef, and pork, and the evaluated E_{SO}-values are summarized in Table 1. Comparing the values among the foods, beef and pork demonstrate larger E_{SO} for water species-A_2 than for water species-A_1, whereas, for salmon, squid, and sardine, the E_{SO}'s obtained for water species-A_1 were larger than those for water species-A_2. These results clearly demonstrate that the self-organization dynamism is sensitively influenced by the type of water species and the food matrix structures as proteins and carbohydrates. Based on the hysteresis behaviors presented in Fig.4, it can be presumed that the FCTCO between the two temperatures, Ts_1 (temperature at which the self-organization of the water species was initiated) and Ts_2 (temperature given at the forced cyclic operation) will demonstrate the characteristic oscillating behavior of $1/\tau_C$. Figure 5 is a schematic illustration of an imaginary response curve that is obtained by the FCTCO. The hysteresis behavior obtained will clearly present a characteristic dynamism of water species that is sensitively influenced by the kind of food and the kind of water species used as a probe molecule. This idea is discussed as the actual evidence in the next section.

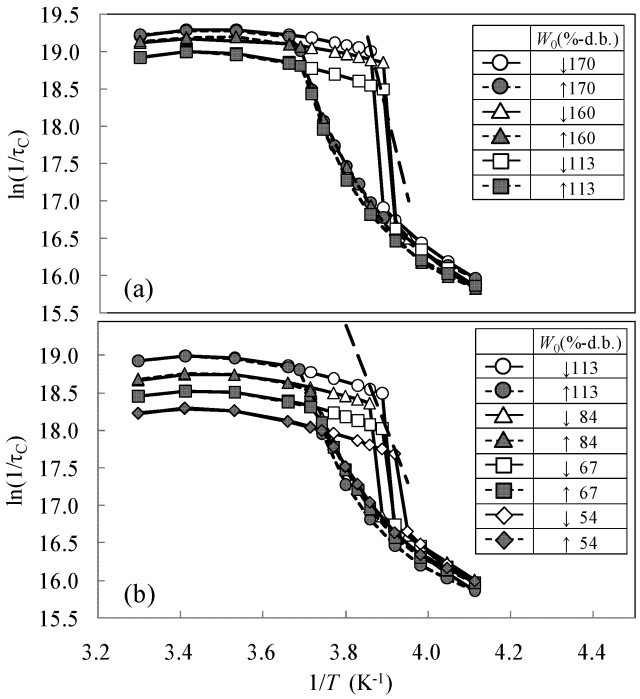

Figure 4: Arrhenius plot of $1/\tau_C$ for sardine to recognize the self-organization of water species-A_1 (a) and -A_2 (b).

Table 1: Activation energy of self-organization for water species-A_1 and - A_2 retained in B_A, P_H, squid, salmon, and sardines.

	E_{SO} (kJ/mol)	
	Species-A_1	Species-A_2
B_A	31	42
P_H	79	98
Squid	72	71
Salmon	160	63
Sardine	182	116

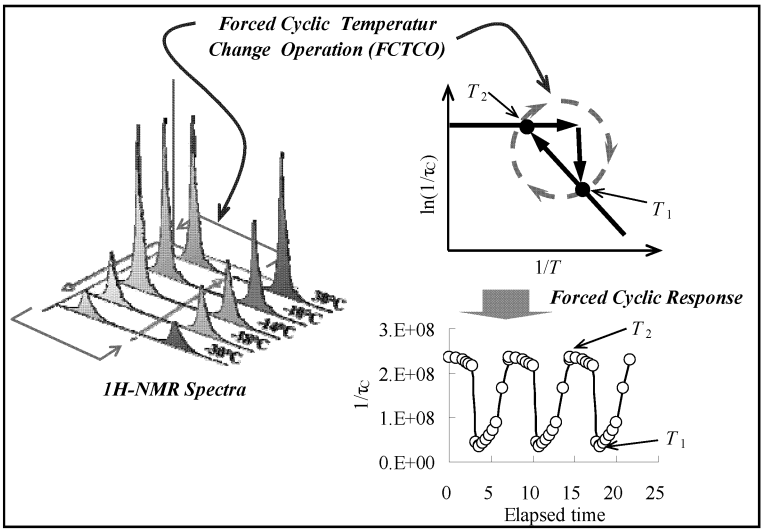

Figure 5: Schematic visualization of the cyclic- temperature-change-operation, the NMR-spectra dynamism, and the $1/\tau_C$ –oscillation obtained.

3.4 Oscillating behavior of $1/\tau_C$ derived from the self-organization state of water species that appeared in the course of the FCTCO

Figure 6 illustrates the typical examples of the oscillating behavior induced by the FCTCO. As is evident from the figure, the oscillating behavior obtained clearly demonstrates a characteristic dynamism depending on the kind of food and the water species (A_1 and A_2). In all foods, the amplitude (α) of the oscillation for water

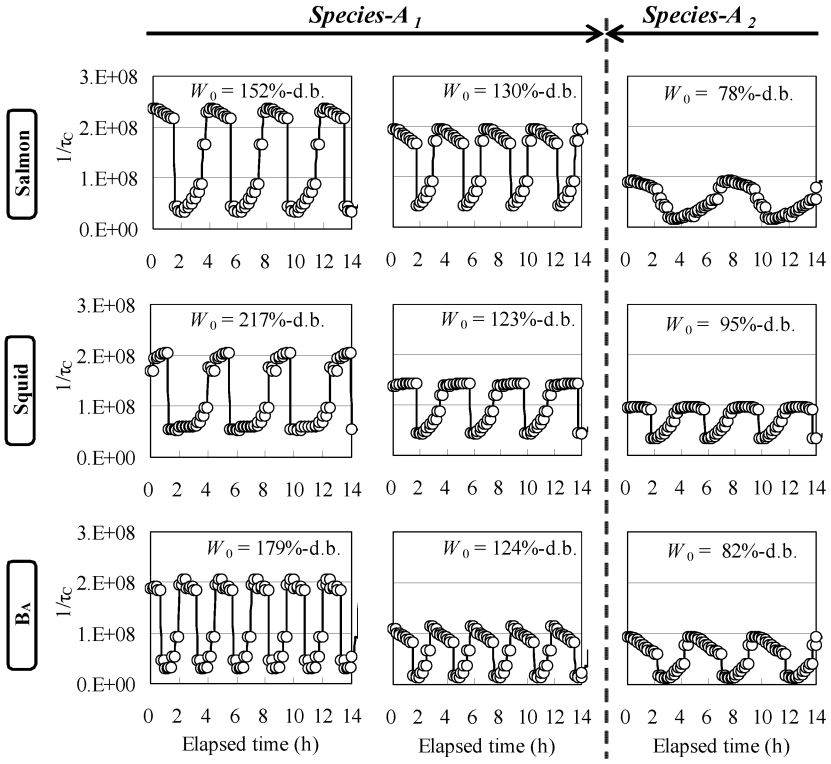

Figure 6: Oscillation characterized by the kind of food.

species-A_1 is larger than that for water species-A_2 because the restriction strength of the former is smaller than that of the latter, indicating the effect of self-organization on water species-A_1, which is larger than that on water species-A_2. The amount of the water species can be evaluated roughly from the peak area of the proton NMR spectra, and the results obtained clearly demonstrated a similar hysteresis as shown by the curves in Fig.4 indicating that the amount of self-organized water species-A_1 was larger than that in species-A_2. This result would be reasonable because the proton NMR technique can detect only mobile water. Although the wavelength and frequency of the oscillation are also characterized as dependent on the kind of the water species and the kind of food, the detailed results will be reported in future papers.

3.5 Discrimination of the water activity of foods revealed by the τ_C-dependency

Hills *et al.* (1999) demonstrated a linear relationship between the relaxation rate ($1/T_2$) and ($1-a_w$). Since T_2 is replaced by τ_C using Equation (1), τ_C can be related to a_w as a linear function (Konishi and Kobayashi, 2010). Based on this consideration, it is presumed that the linear function between a_w and τ_C should be an useful tool both to discriminate the two water species-A_1 and -A_2 and to differently characterize a kind of food. Figure 7 demonstrates a_w of four foods (B_A, salmon, squid, and sardine) as a function of τ_C. In the water species-A_1 region, the data for all foods roughly fall on the same linear line; whereas, in the water species-A_2 region, each food gave a different linear line indicating a characteristic molecular mobility (τ_C) depending on the kind of food. At a_w = 0.7, for example, salmon gave $\tau_C = 3.3\times10^{-8}$ s even though B_A gave $\tau_C = 8.7\times10^{-8}$ s. This result is very significant, as τ_C of B_A was much higher than that of salmon even though both foods gave the same value of a_w. Based on this result, the water activity does not yield sufficient information to design food products. For the exact design of requested food products, the information on the linear function between a_w and τ_C is required. In the present study, it remains unclear how to quantitatively evaluate the relationship between the taste of foods and the value of τ_C. To respond to this question, further work is needed.

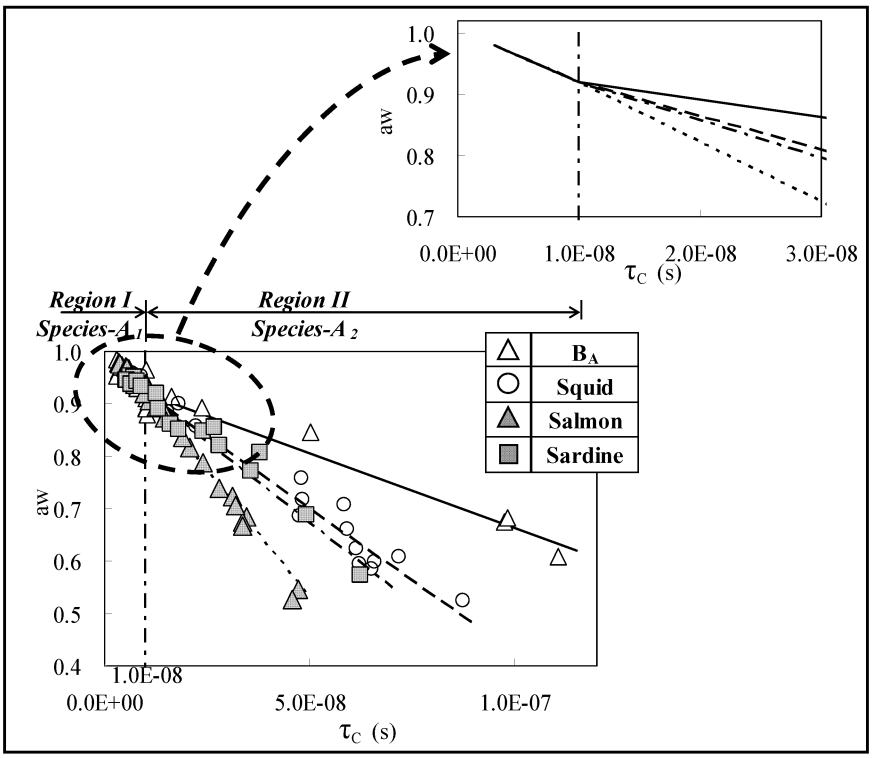

Figure 7: a_w as a function of τ_C to discriminate the kind of food.

4. CONCLUSIONS

(1) The dynamism of the three parameters, De, E_D, and N_P, for the water species-A_1 and -A_2 of five foods as a function of τ_C clearly exhibited the existence of a critical τ_C ($C\tau_C = 1.0\times10^{-8}$s) at which a drastic change was appeared.

(2) Water species-A_1 and -A_2 clearly demonstrated a typical self-organization indicating the characteristic hysteresis on the Arrhenius plot of $1/\tau_C$.

(3) The forced cyclic temperature change operation (FCTCO) between the two temperatures, Ts_1 and Ts_2, demonstrated a characteristic oscillation of $1/\tau_C$. The oscillation clearly discriminated between water species-A_1 and -A_2 and among salmon, squid, and beef, indicating a different amplitude (α) of the oscillation.

(4) The water activity of water species-A_1 and -A_2 as a probe molecule gave a different linear line as a function of τ_C discriminating among the various kinds of foods.

5. ACKNOWLEDGEMENT

This work was financially supported by the Cooperation of Innovation Technology and Advanced Research in Evolution Area (City Area) from the Japanese Ministry of Education, Culture, Sports, Science, and Technology. The authors wish to thank Associate Professor Koichi Miura, Kitami Institute of Technology, for their effective assistance with the proton NMR analysis.

Nomenclature

B_A	*beef meat produced in Australia* (-)
B_H	*beef meat produced in Hokkaido, Japan* (-)
$C\tau_C$	*critical value of correlation time of water proton* (s)
a_w	*water activity(-)*
D	*moisture diffusion coefficient* (m^2/s)
D_0	*frequency factor of D* (m^2/s)
De	*effective moisture diffusion coefficient* (m^2/s)
E_D	*activation energy of moisture diffusivity* (kJ/mol)
Eso	*activation energy of the self-organization of water species-A_1 and -A_2* (kJ/mol)
$FCTCO$	*forced cyclic temperature change operation* (-)
I	*nuclear spin quantum number of water proton* (= 0.5) (-)
N_P	*Hardness of food products* (Newton/m^2)
P_H	*pork meat produced in Hokkaido, Japan* (-)
PF	*pre-exponential factor, δD_0, (m^2/s)*
PUP	*poultice-up process* (-)
R	*gas constant* (=8.314J/K·mol)
r	*proton-proton distance of water molecule* (= 0.16 nm)
T_2	*spin-spin relaxation time of water proton* (s)
Ts_1	*temperature at which the self-organization of the water species was initiated* (K)
Ts_2	*temperature returned from the self-organization of the water species* (K)
T_D	*drying temperature* (°C)
T	*temperature given at the forced cyclic operation* (K)
t	*drying time(h)*
W	*moisture content at the drying time t* (%-d.b.)
W_D	*initial water content of drying flesh sample* (%-d.b.)
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})
ε	*porosity of the food tissue* (-)
π	*the ratio of the circumference of a circle to its diameter*(=3.14)
γ	*gyromagnetic ratio of proton* (=2.675×10^{8} rad·T^{-1}·s^{-1})
$\hbar$	*modified Plank's constant* (=6.63×10^{-34} J·s)
ω_0	*resonance frequency* (=3.14×10^{9} s^{-1})
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)

6. REFERENCES

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

Butt, J.B., 1980, Reaction Kinetics and Reactor Design, Prentice-Hall, Inc., Englewood Cliffs, New Jersey 07632.

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

Kobayashi, M., Kanno, T., Takeda, and Fujisaki, S., 1997, Reaction pathway design and optimization in heterogeneous catalysis: II. Oscillating partial oxidation of propene on Pt/SiO2 designed by widely varying dispersion, Applied Catalysis, 151, 207-221.

Konishi, Y., Horiuchi, J., and Kobayashi, M., 2001, Dynamic evaluation of the dehydration response curves of foods 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., Miura, K. and Kobayashi, M., 2003(a), 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., and Kobayashi, M., 2003(b), Characteristic innovation of a food drying process revealed by the physicochemical analysis of dehydration dynamics, J. Food Eng., 59, 277-283.

Konishi, Y., and Kobayashi, M., 2009, Quantitative evaluation of the design parameters requested in a beef and pork drying operation, AIDIC Conference series, vol.9, 177-186.

Konishi,Y. & Kobayashi, M. (2010). Food design by using water species as a probe molecule. *Proceedings of the Annual Conference of the Japan Society for Food Engineering.*, 25.

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

Labuza, T.P., Tannenbaum, S.R., and Karel,M. 1970, Water content and stability of low moisture and intermediate moisture foods, Food Technol., 24, 543-550.

Ruiz-Cabrera, M.A., Gou, P., Foucat, L., Renou, J.P. and Daudin, J.D., 2004, Water transfer analysis in pork meat supported by NMR imaging, Meat Science, 67, 169-178.

Schmidt, S.J., Water and solids mobility in foods, 2004, Advances in food and nutrition research, volume 48, 2004, Edited by S.L. Taylor, Elsevier

Takaoka, Y., Sakamoto, T., Tsukiji, S., Narazaki, M., Matsuda., T., Tochio, H., Shirakawa, M., and Hamachi, I., Self-assembling nano-probes displaying off/on ^{19}F NMR signals for protein detection and imaging. Nature Chemistry, 1, 557-561, DOI:10.1038/NCHEM. 365.