CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
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DOI: 10.3303/CET1124080

Dynamism of the Water Species as a Probe Molecule in Food

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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 these different kinds of food. All four parameters evaluated for the five kinds of food 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 was divided into two regions discriminating two different water species as water species-A_1 ($0.1\sim0.8\times10^{-8}$s $< C\tau_C$, a weakly restricted water species) and water species-A_2 ($1.0 \sim 10\times10^{-8}$s $> C\tau_C$, a strongly restricted water species).

A forced cyclic-temperature-change operation between 30 and -30°C for the five kinds of food 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 caused by the cyclic-temperature-change operation. The amplitude (α) of the oscillation obtained was differently evaluated depending on three components, the food structure matrix and the water species-A_1 and -A_2, indicating a clear discrimination among the three.

The 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 the dynamic change from water species-A_1 to -A_2 due to a progress of the dehydration of food.

1. Introduction

In the biochemical (Takaoka *et al.*, 2009), biomedical, and organic- and inorganic-catalysis (Kobayashi *et al.*, 1997) fields, a probe molecule has been conveniently used to clarify the detailed mechanism of the dynamic process in their complicated systems. The same technique should be applied to the food technology field because the food system includes a biological dynamism influenced by environmental changes derived from the food production processes as dehydration, hydration, heating, mechanical crashing, and evacuation. In their processes, although isotope molecules have conveniently been used as a probe molecule, water species retained in food 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 food, five parameters can be chosen as effective moisture diffusion coefficients, *De* (Konishi *et al.*, 2001), activation energy of *De*, E_D, pre-exponential factor of *De*, PF, hardness of food, N_P, and

Please cite this article as: Konishi Y. and Kobayashi M., 2011, Dynamism of the water species as a probe molecule in food, Chemical Engineering Transactions, 24, 475-480
DOI: 10.3303/CET1124080

correlation time of water species, τ_C (Konishi *et al.*, 2003) evaluated by the NMR-technique. In particular, the mobility parameter, τ_C, can conveniently visualize an interesting oscillating dynamism that occurs in food 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).

The objectives of this study are (1) to demonstrate the dynamic behavior of the five parameters (De, E_D, PF, N_P, and τ_C) specified by the kinds of food 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, and (3) to characterize the oscillating behavior of $1/\tau_C$ derived from the self-organization of water species.

2. Experimental

Five kinds of food, salmon, squid, sardine, beef (produced in Australia, B_A, and Hokkaido, B_H), and pork (produced in Hokkaido, P_H) were used as typical examples; all of them had the initial moisture content of 230~280%-d.b. (dry base, W_D). The sample weight was continuously recorded by the output of a strain-gage transducer using a data-logger. Under 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 kinds of food, a nuclear magnetic resonance (NMR) technique was effectively applied to measure the molecular mobility (correlation time τ_C) by 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 90° 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±0.5°C. The spin-spin relaxation times were obtained by the spin-locking method, and, from the times obtained, the correlation time of a water proton, τ_C, was evaluated.

The forced cyclic-temperature-change operation used in this study was conducted in a specified temperature region at which hysteresis behavior appeared 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 of the temperature to evaluate the relaxation time for the NMR technique was included into the cyclic 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.

3. Results and Discussion

3-1. A critical τ_C value appeared in the physicochemical parameters

As 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 is a useful tool to analyze food materials (Ruiz-Cabrera *et al.*, 2004). Each of the parameters, *De*, E_D, *PF*, and N_P, for the five kinds of food demonstrates a characteristic dynamism as a function of the mobility parameter, τ_C, derived from the NMR method. Figure 1 illustrates the three parameters, *De*, E_D, and N_P, as a function of τ_C. The τ_C-value (designate as $C\tau_C$) at which the three parameters commonly indicate an anomalous change is clearly evident. This anomalous change at $C\tau_C$ possibly contributes to a drastic change of water species from species-A_1 to species-A_2 derived from the dehydration operation. This dehydration process produces a drastic change in the restriction strength of water species retained in the food tissues accompanying a growth of τ_C. Focusing on the E_D curves in Fig.1, two food groups were recognized: the group of squid, salmon, and sardine increased in the region of water species-A_2, whereas the group of P_H, B_A, and B_H decreased, even though the data obtained were widely scattered. This opposite tendency between the two food groups would result from a difference in the structure change of food tissues induced from the dehydration operation. The physicochemical meaning of this phenomenon is discussed in the next section.

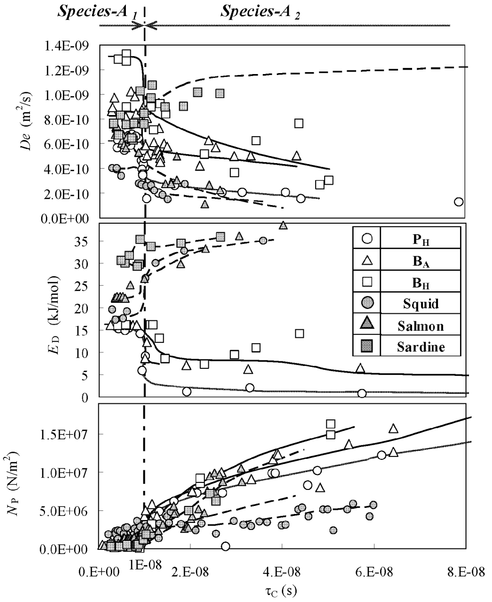

Fig. 1 Physicochemical parameters, De, E_D, and N_P, as a function of τ_C.

3-2. Physicochemical meaning of the $C\tau_C$ value

The apparent diffusivity, *De*, is generally expressed by Equation (1) (Butt, 1980).

$$De = \left(\frac{\varepsilon}{\chi}\right) \cdot D = \delta \cdot D_0 \cdot exp\left[\frac{-E_D}{R \cdot (T_D + 273)}\right] \tag{1}$$

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*. The pre-exponential factor (PF), δD_0, can easily be evaluated by the E_D- and *De* values estimated from the mathematical model analysis (Konishi *et al.*, 2001) of the dehydration curves of foods. Figure 2 illustrates PF as a function of τ_C for the five kinds of food. The five curves obtained demonstrate again the existence of $C\tau_C$ in all the kind of food by dividing them into two water species regions, -A_1 and -A_2 regions. In addition, there are two food groups, as the group of B_A and P_H demonstrates a steep decay whereas the group of squid, salmon, and sardine indicates a steep increase in the water species-A_2 region. This extra-ordinal difference strongly indicates an opposite variation of ε, χ, and D_0 between the two food groups. The values of ε and D_0 increase and the value of χ decreases for the former, whereas inverse variations are realized for the latter. This inverse variation induces the characteristic E_D curves in Fig. 1, indicating a clearer discrimination of water diffusion mechanisms between the two food groups.

3-3. Hysteresis dynamism derived from the self-organization of water species retained in different kinds of food

The physicochemical parameter, τ_C, can conveniently be used to evaluate the mobility of water species retained in the different kinds of food. Since $1/\tau_C$ (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 3 (a) and (b) illustrate an Arrhenius plot for 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 $1/\tau_C$ resulted from a self-organization of water species-A_1 and -A_2 at a specified temperature lower than 0°C. The self-organization observed at the different values of $1/\tau_C$ can again propose an Arrhenius plot, as shown by the broken lines in Figs. 3 (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 of 182 and 116kJ/mol, respectively. The same analysis of the Arrhenius plots was applied for squid, salmon, beef, and pork, and the evaluated values are summarized in Table 1. Comparing the values among the different kinds of food, beef and pork have larger E_{SO} for water species-A_2 than for water species-A_1, whereas E_{SO} for salmon, squid, and sardine are larger for water species-A_1 than 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

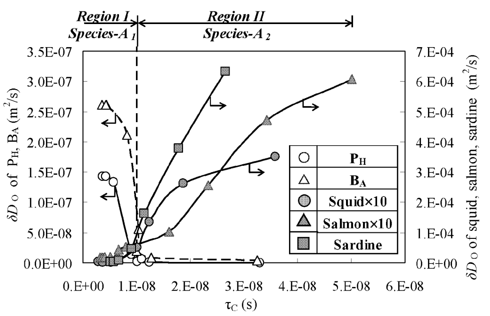

Fig.2 PF dynamism as a function of τ_C to recognize $C\tau_C$.

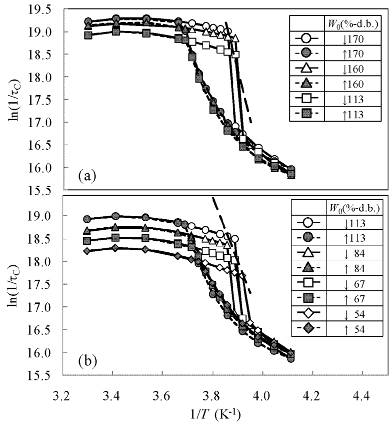

Fig. 3 Arrhenius plot of $1/\tau_C$ for sardine to recognize the self-organization of water species-A_1 (a) and -A_2 (b).

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

	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

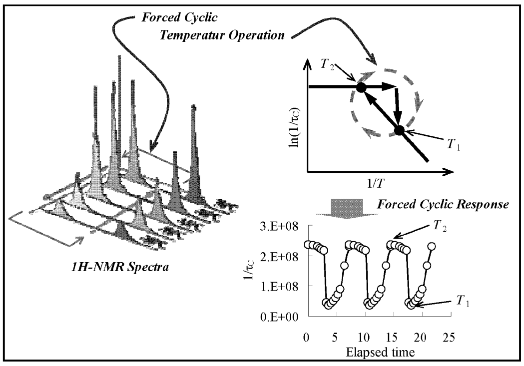

Fig. 4 Schematic visualization of the cyclic-temperature-change-operation, the NMR-spectra dynamism, and the $1/\tau_C$ –oscillation obtained.

structures, such as proteins and carbohydrates.

The hysteresis behavior of $1/\tau_C$ obtained in Fig. 3 visualizes an interesting oscillation of $1/\tau_C$. A cyclic-temperature-change operation between the two temperatures, T_1 (initiation temperature inducing the self-organization) and T_2 (the temperature after the self-organization), demonstrates a characteristic oscillating behavior, as schematically shown in Figures 4.

3-4. Oscillating behavior of $1/\tau_C$ derived from the self-organization state of water species in the course of the forced cyclic-temperature-change operation

Figure 5 illustrates typical examples of the oscillating behavior induced by the forced cyclic-temperature-change operation. As is evident from the figure, the oscillating behavior obtained clearly demonstrates a characteristic dynamism according to the kind of food and the water species. For all kinds of food, the amplitude (α) of the oscillation for water 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 that self-organization on water species-A_1 causes it to be larger than on water species-A_2. The amount of self-organized water species-A_1, conclusively, is larger than that of species-A_2.

kinds of food

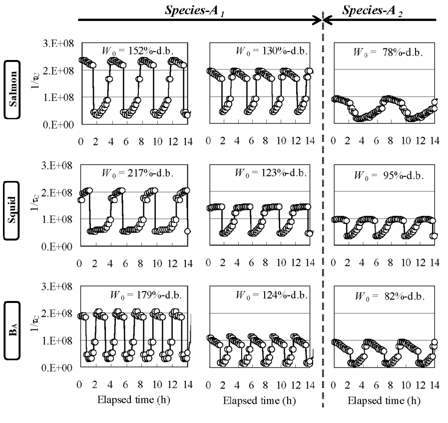

Fig. 5 Oscillation characterized by the

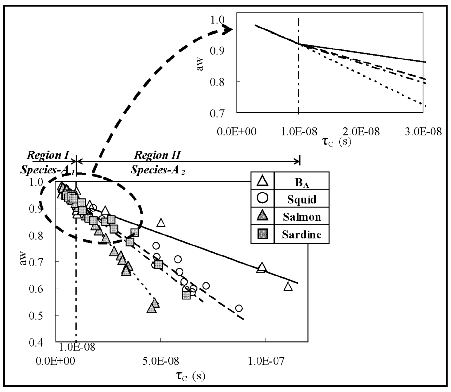

Fig. 6 a_w as a function of τ_C to discriminate the kinds of food

3-5. Discrimination of the water activity of food revealed by the τ_C-dependency

The molecular mobility parameter, τ_C, indicates characteristic behavior depending on the water species-A_1 and -A_2 regions, as shown in Figures 6. In the water species-A_1 region, the data for all food fall roughly on the same linear line, whereas, in the water species-A_2 region, each food has a different linear line, indicating a characteristic molecular mobility depending on the kind of food. At a_w =0.7, salmon had $\tau_C = 3.3\times10^{-8}$ s, while B_A gave $\tau_C = 8.7\times 10^{-8}$ s. This result indicates that the molecular mobility, τ_C, of beef is much higher than that of salmon even though both kinds of food have the same value of a_w.

4. Conclusions

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

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

(3) A cyclic-temperature-change-operation between the two temperatures, T_1 and T_2, demonstrated a characteristic oscillation of $1/\tau_C$ visualizing the discrimination of water species-A_1 and -A_2 retained in the different kinds of food.

(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 kinds of food.

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