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Calorimetric measurements on the swelling of seaweed

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Abstract

Heat of swelling of the eight kinds of seaweed Arame (*Eisenia bicyclis*), Hiziki (*Hizika fusiformis*), Asakusanori (*Porphyra tenera*), Tengusa (*Gelidium amansii*), Wakame (*Undaria pinnatifida*), Aonori (*Enderomorpha profifera*), Mafunori (*Gloiopelfis tenax*) and Kombu (*Laminaria japonica*), which are used for food in Japan, were measured. The swelling of seven types was exothermic. However, that of Kombu was endothermic. The dependence between water content and the heat of swelling of Kombu showed a concave upward curve, with a minimum value at $\approx 0.1\,\mathrm{g\,g^{-1}}$ of water content. The dissolution of Kombu extracts was endothermic and the swelling of "Kombu ghost" (Kombu grounds) was exothermic. From the dependence on the water content of the heats of the dissolution of the Kombu extracts and the swelling of the Kombu ghost, we conclude that the endothermic phenomenon for the swelling of Kombu is derived from the sum of the heats of dissolution of water-soluble components in Kombu and the heat hydration of the insoluble skeleton.

Keywords: Kinetics of swelling; Swelling of seaweed; Heat of swelling

1. Introduction

The swelling of dried foods in water is a very complex phenomenon because it must be considered from the viewpoints of adsorption, absorption, permeation, diffusion, hydration, Donnan equilibrium, osmotic pressure, and other factors. It is thus difficult to analyze the thermal data of swelling. Even though thermal measurements of swelling

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have such shortcomings thermal behavior may reflect the chemical and physical changes of swelling.

It is generally accepted [1, 2] that the swelling of dried foods in water involves an exothermic reaction because of the accompanying hydration of hydrophilic groups in food substances. In practice, however, the heats of swelling of rice grain, starch, gelatin, agar etc. are exothermic [1–4]. No literature has been found on the heat of swelling of dried seaweeds.

In the present studies, heats of swelling of some dried seaweeds were measured, and a discussion is presented on the swelling of Kombu (*Laminaria japonica*).

2. Experimental

The dried seaweeds Arame (*Eisenia bicyclis*), Hiziki (*Hizika fusiformis*), Asakusanori (*Porphyra tenera*), Tengusa (*Gelidium amansii*), Wakame (*Undaria pinnatifida*), Aonori (*Enderomorpha profifera*), Mafunori (*Gloiopelfis tenax*) and Kombu (*Laminaria japonica*) are used for food in Japan. The dried seaweeds were secured from The Fisheries Institutions of Kagawa and Nagasaki prefectures and The Fisheries Section of Hokkaido Prefecture. The seaweeds were washed with tap water for a short time to clean their surfaces, then air dried, and cut into 10 mm lengths except for Kombu.

As for Kombu, because the amounts of components, such as amino acids, are not evenly distributed in the Kombu leaf, we selected the center parts of the leaves and cut them into pieces 10 mm × 1 mm to be able to enclose them in glass ampoules "Kombu ghost" was prepared by boiling the leaf in a large amount of water for 30 min to remove the water-soluble components, and was then air dried.

An extract of Kombu was prepared from the above extracted broth by freeze drying.

The water contents of the samples were adjusted over different concentrations of various salts or dried over silica gel or under phosphorus pentoxide. Final water contents were measured after drying at 105°C.

Heats of swelling were measured with a twin conductive calorimeter (Tokyo Riko Model TCC-21). The symmetrical twin cells are housed in an aluminum block, which has a large thermal capacity. One of the cells is for the reference, which is water of the same weight as the materials, and the other is for the sample. About 50 mg of sample was enclosed in the glass ampoule. After the system had reached thermo-equilibrium at 25°C, the sample was introduced into 20 cm^3 of distilled water by breaking the ampoule.

Because the calorimeter is a conductive rather than an adiabatic type, an exotherm coincides with cooling. If we define $g(t)$ as the observed calorimeter signal which is proportional to the temperature difference between the sample and reference cells at time t, and $Q(t)$ as the real heat process in the system at t, we get the equation

$$\frac{\mathrm{d}g(t)}{\mathrm{d}t}=\frac{1}{A}\frac{\mathrm{d}Q(t)}{\mathrm{d}t}-Kg(t) \tag{1}$$

where A is the calorimeter sensitivity at the steady state and K is the cooling constant of the system. Integration of Eq. (1) gives

$$Q(t) = A\left[g(t) + K\int g(t)\,\mathrm{d}t + g_0\right] \tag{2}$$

where g_0 is an integration constant which is reduced to zero by the nature of the problem. When the thermal reaction is complete, $g(t)$ is zero. Then Eq. (2) is expressed as follows

$$Q = A\mathrm{K}\int_0^{\infty} g(t)\,\mathrm{d}t \tag{3}$$

where Q is the total integral heat of the thermal process. If we calculate K from the cooling process of calibration heat and A from the steady heat evolution of calibration heat, Q will be obtained.

3. Results

3.1. Heats of swelling of dried seaweeds

About 50 to 100 mg of the dried seaweed was enclosed in a thin glass ampoule. After thermal equilibrium had been reached, the sample was thrown into 20 cm^3 of water at 25°C. Some of the thermograms (those of Wakame and Kombu) are shown in Figs. 1 and 2.

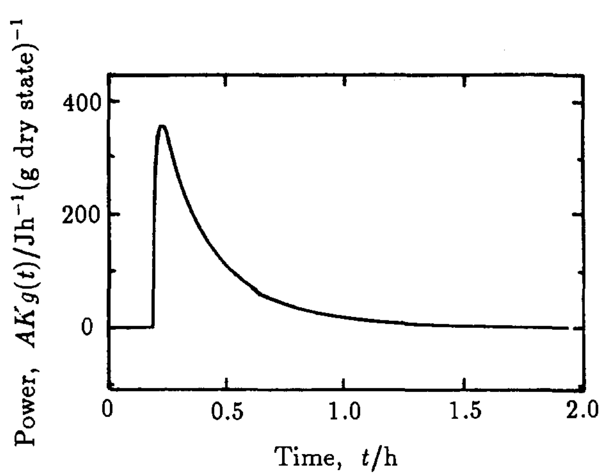

Fig. 1. Thermogram of swelling of Wakame (*Undaria pinnatifida*). 29.9 mg (as dry weight) of Wakame sample, water content 0.105 g g^{-1}, were enclosed in a glass ampoule. After the system had reached thermo-equilibrium at 25°C, the sample was thrown into 20 cm^3 of distilled water by breaking the ampoule. Values of A and K were 8.00 mJ μV^{-1} and 4.133 h^{-1}, respectively.

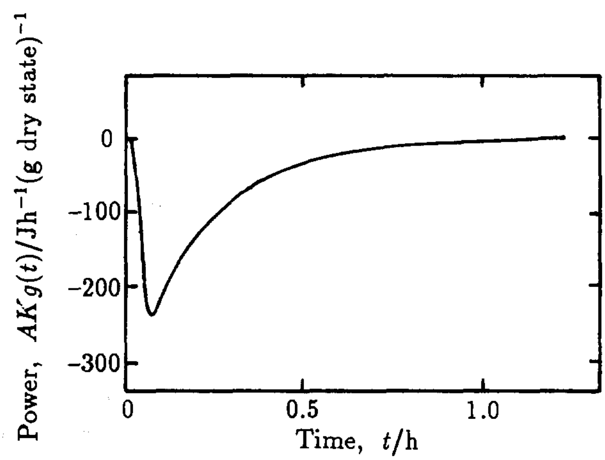

Fig. 2. Thermogram of swelling of Kombu (*Laminaria japonica*). 76.2 mg (as dry weight) of Kombu sample, water content 0.1136 g g^{-1}, were enclosed in a glass ampoule. After the system had reached thermo-equilibrium at 25°C, the sample was thrown into 20 cm^3 of distilled water by breaking the ampoule. Values of A and K were 13.30 mJ μV^{-1} and 4.890 h^{-1}, respectively.

Heats of swelling of the samples were calculated by Eq. (2) from the obtained thermograms, and are listed in Table 1.

As shown in Table 1, the swelling of seaweeds apart from Kombu was exothermic. By contrast, the swelling of Kombu was endothermic.

3.2. *Heat of swelling of Kombu and dependence on moisture contents*

To clarify the above apparently abnormal properties of the heat of swelling of Kombu, more detailed information was needed. The effects of the moisture content of

Table 1
Heats of swelling of some seaweeds[a]

Seaweed	Q/J (g dry state)$^{-1}$
Arame	52.7
Hiziki	42.4
Asakusanori	29.9
Tengusa	43.3
Igisu	42.7
Wakame	62.3
Aonori	41.7
Mafunori	32.7
Kombu	−25.1

[a] Water content 0 g g^{-1}.

Kombu were measured. As shown in Fig. 3, the heat of swelling of Kombu showed a minimum at $\approx 0.1 \text{ g g}^{-1}$ of water content.

From the above results, we suggest that the heat of swelling of Kombu is due not only to the hydration of hydrophilic components but also to some endothermic reactions which occur at the same time.

3.3. Heat of swelling of Kombu ghost

In Kombu, various amino acids, alginic acid and some other water-soluble substances are present in fairly large quantities [5–8]. Separation of the water-soluble substances (Kombu extract) and the insoluble ones (Kombu ghost) was carried out by boiling the Kombu gently for 30 min in a large amount of water. The insoluble "Kombu ghost" was dried, its moisture content was determined, then its heat of swelling was measured at 25°C.

As shown in Fig. 4, the solid line is the best fit curve obtained by least squares treatment with a single exponential function; the heat of swelling of the Kombu ghost showed an exothermic reaction, and the heat of swelling decreased with increasing water content.

3.4. Heat of dissolution of Kombu extract

Kombu was gently boiled in water, and water-soluble substances (Kombu extract) were obtained by the freeze drying method. After the evaluation of water contents, the heat of dissolution of Kombu extract was measured. As shown in Fig. 5, the solid line shows the best fit curve from least squares treatment with a quadratic function; the heat of dissolution was endothermic, and the negative value of the heat of dissolution became smaller with increase water content.

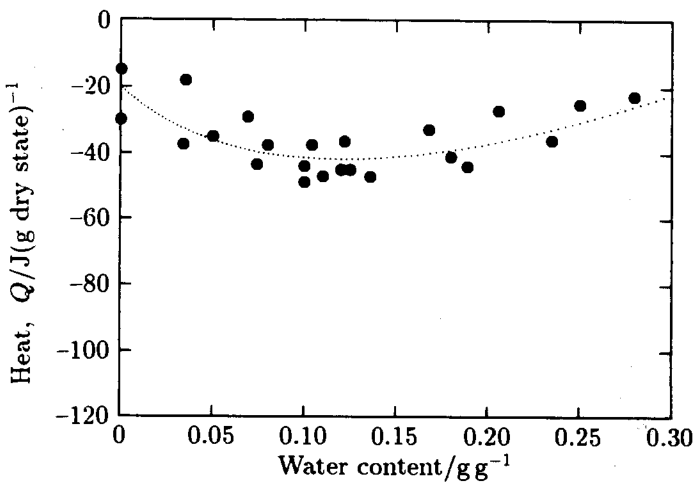

Fig. 3. Effects of moisture content on the heat of swelling of Kombu.

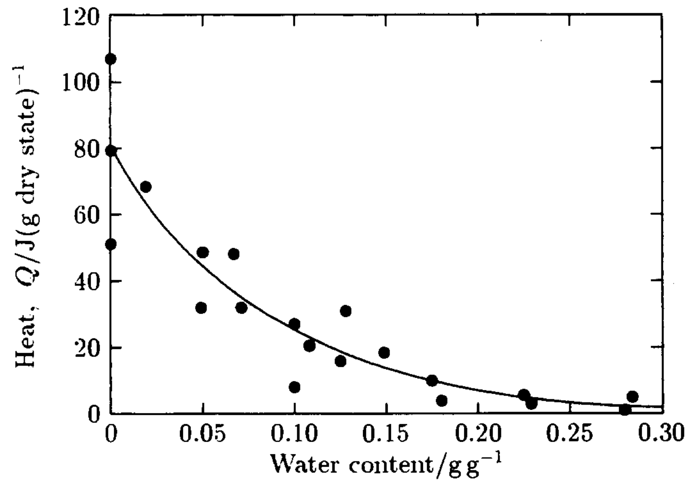

Fig. 4. Effects of moisture content on the heat of swelling of the "Kombu ghost" fraction.

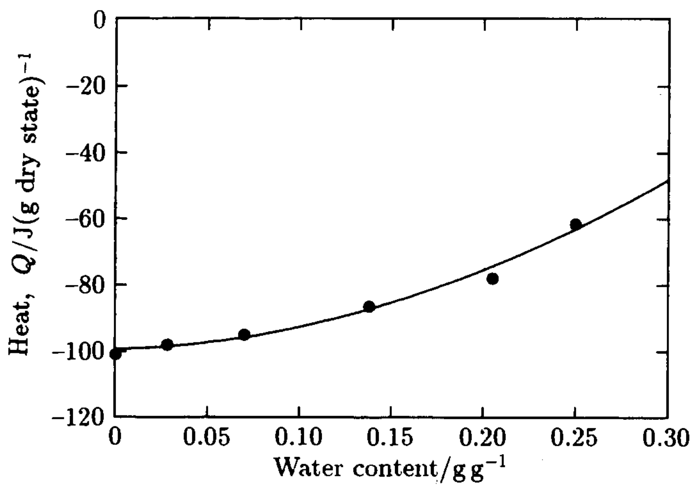

Fig. 5. Effects of moisture content on the heat of swelling of Kombu extract.

4. Discussion

Woessner [9, 10], Aizawa [11, 12] and Hatakeyama et al. [13] reported from their NMR and DSC studies on agar, Sephadex and polyvinylalcohol that there are three kinds of water in gels of hydrophilic polymers; most of the water in gels is free water which does not interact with the polymers.

The main constitutents of seaweed are polysaccharides; these are hydrophilic polymers. Water may react with surface and internal polysaccharides of seaweeds by hydrogen bonding.

As listed in Table 1, except for Kombu, heats of swelling of the dried seaweeds are exothermic and of approximately the same magnitude, despite the fact that the samples differ greatly in the power of water absorption. From these results, it is assumed that the heat of swelling of the seaweeds, apart from Kombu, arises mainly from the interaction of polysaccharides with water, and the transfer of free water into the seaweeds may be very small or negligible.

In contrast, the swelling of Kombu is endothermic. Fig. 3 shows the dependence between water content and the heat of swelling; the curve bends upward with a minimum at ≈ 0.1 g g^{-1} water content.

Considerable amounts of water-soluble components (up to 50% by weight), for example amino acids, are contained in Kombu [14]. Two fractions, the water-soluble components (Kombu extract) and the Kombu ghost residue, were separated with hot water. As shown in Fig. 5, the dissolution of the Kombu extract was endothermic and the absolute value of the heat of dissolution decreased with increasing water content. In contrast, swelling of the Kombu ghost was exothermic and the heat of swelling decreased exponentially with increasing water content, as shown in Fig. 4.

In the process of swelling, hydration of the hydrophilic groups in Kombu and dissolution of water-soluble substances probably occur at the same time. Therefore, when 50% of the best fitting curves of Figs. 4 and 5 is combined, we get the solid line in Fig. 6. The two lines are quite similar. Accordingly, we may conclude that the heat of swelling of Kombu will be the sum of the endothermic reaction of hydration of its hydrophilic skeleton of insoluble material (Kombu ghost) and the exothermic reaction of dissolution of water-soluble material, such as amino acids and others, in Kombu.

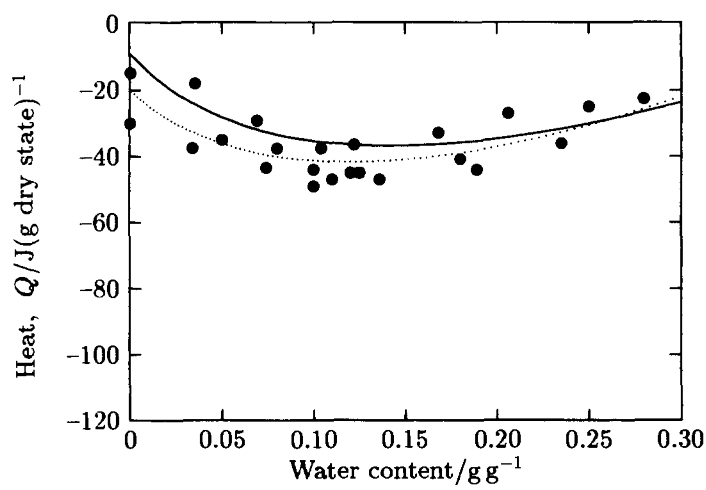

Fig. 6. Additivity of heats for the ghost fraction and the extracts of Kombu.

5. Conclusions

Except for Kombu, the heats of swelling of seaweeds are exothermic; that of Kombu is endothermic. A large amount of water-soluble materials such as amino acids are contained in Kombu. We can separate Kombu into two fractions; one is water-soluble and the other is the insoluble "Kombu ghost". The heat of dissolution of the water-soluble materials is endothermic and the heat of swelling of Kombu ghost is exothermic. From the addition of heats for the two separate fractions, we obtained the heat of swelling of Kombu. From the above results, we conclude that the endothermic reaction of dissolution of water-soluble materials in Kombu contributes greatly to the observed heat of swelling.

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