魚類筋肉における鮮度低下および色変の温度依存性による動力学的特性値

誌名	日本水産學會誌
ISSN	00215392
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巻/号	50巻2号
掲載ページ	p. 281-285
発行年月	1984年2月

Bulletin of the Japanese Society of Scientific Fisheries 50(2), 281–285 (1984)

Kinetic Parameters of Freshness-lowering and Discoloration Based on Temperature Dependence in Fish Muscles*[1]

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(Accepted May 23, 1983)

The rate of freshness-lowering (k_f) in fish muscle of a few species (skipjack, mackerel, and sea bream) and the rate of discoloration in skipjack muscle (k_c) during storage were investigated by using the chemical indexes (K values; freshness, metMb%; discoloration). An attempt was made to express the temperature dependence on these quality-changes during storage by kinetic parameters (Ea=activation energy, A=frequency factor).

Consequently, the relationships of log (100−K value) or log (100−metMb%) versus storage-time indicated the first-order reaction, so that the values of k_f and k_c in sample fishes were obtained from these relationships at the storage temperatures between −40 (or −20) and +20°C. Therefore, the kinetic parameters (Ea, A) on the freshness-lowering or the discoloration of fish muscles were obtained from the ARRHENIUS's plot of k_f or k_c values in each sample respectively.

Fisheries products are exposed to various temperatures for different durations during their distribution from fishing places to consuming places, and the processes like handling, freezing, storage, transportation, and thawing etc. bring about the changes in quality of these products. The rates of these changes generally are found to have a temperature dependence.

If informations on kinetics of quality deteriorative reactions are obtained, quality changes in food systems under fluctuating temperatures could be simulated and predicted by computer. However, very little attention has been given to the feasibility of predicting and simulating the quality changes in fish muscles, based on kinetic studies. Moreover, little information is available regarding the kinetic data for quality changes in fish muscles.[1,2] Especially, kinetic studies spanning above and below freezing temperatures are not abundant.[3] Freshness-lowering and discoloration of fish muscle has been predicted in our previous studies[4,5] to exhibit an ARRHENIUS-type dependence on temperature.

Therefore, the purpose of this study was to investigate the rates of freshness-lowering and discoloration in fish muscles by using chemical indexes (i.e. K value[6] and metmyoglobin formation=metMb%[7]), and to determine their kinetic parameters (i.e. Ea: activation energy and A: frequency factor) as affected by storage temperatures from −40 to +20°C. This paper deals with the skipjack muscle mainly, which is relatively deteriorative.

Materials and Methods

Fish Sample

Skipjack *Katsuwonus pelamis*, mackerel *Scomber japonicus* and sea bream *Evynnis japonica* were obtained in fresh condition from a local fish store, and used to prepare fillets for experimental procedures. These fillets were kept at −70°C before preparation for storage tests and analysis.

Storage Test

Fillets were wrapped individually with the polyethylene films and stored at the temperatures of −40, −20, −10, −5, −3, 0, 10, and 20°C in the refrigerated show-case (HITACHI RC-3907LE) controlled within ±1°C. However, the storage temperature of −40°C was not used for the freshness-lowering tests of mackerel and sea bream fillets. After samples were equilibrated to a constant storage temperature, about 3.0 g dorsal muscles in duplicate were taken out at different intervals for chemical analysis.

*1 Orally presented at the annual meeting of the Japan. Soc. Sci. Fish., on October in 1979 (Hakodate) and on April in 1980 (Tokyo).

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Chemical Analysis

The *K* value, a freshness-estimation index was measured by column chromatography using the method of KOBAYASHI *et al.*[6] The ionexchanger used was Dowex 1×4, Cl^- type with a mesh of 50 to 100.

The metMb% for a discoloration estimation index of red muscles was measured by BITO's method.[7]

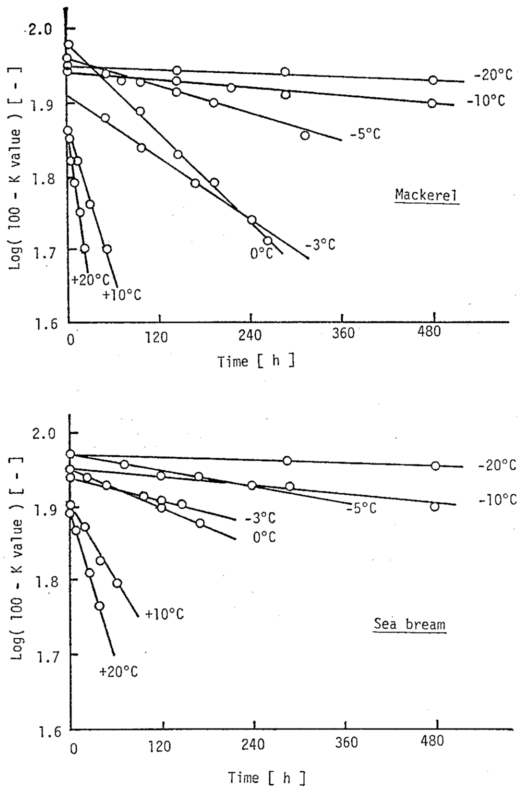

Fig. 1. Changes in *K* value of mackerel and sea bream during storage at different temperatures.

Results and Discussion

Rate of Freshness-lowering

K value is usually used as the index of freshness in a fish muscle, but the value of (100−K value), which indicates the ratio of remaining amount of (ATP+ADP+AMP+IMP) to total amount of ATP related compounds* and decreases with the increase of storage times, has been used in the present study. The plot of logarithms of (100−K value) versus time (h) in the muscle of mackerel, skipjack, and porgies yielded straight lines as shown in Figs. 1 and 2. These lines of freshness-lowering indicated the first-order reactions. These rate constant of k_f were obtained from the slope of straight lines by the least squares method and have been shown in Tables 1 and 2. The differences in quality changes in whole fish samples or different parts of the body among the same species was found to be negligible. In pre-tests of sampling mackerel muscles, there were no problems as above mentioned.

Rate of Discoloration

Usually metMb% has been used as the estima-

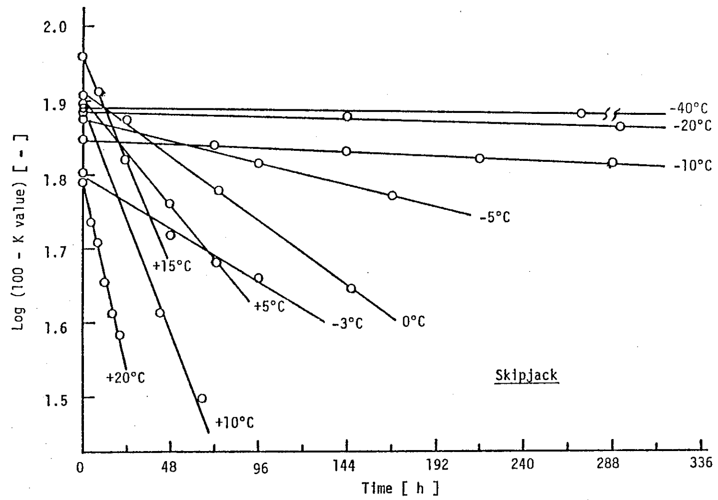

Fig. 2. Changes in *K* value of skipjack during storage at different temperatures.

* ATP related compounds: ATP (adenosine 5′-triphosphate)+ADP (adenosine 5′-diphosphate)+AMP (adenosine 5′-monophosphate)+IMP (inosine 5′-monophosphate)+HXR (inosine)+Hx (hypoxanthine).

Table 1. Rate constant of freshness-lowering in the muscles of mackerel and sea bream during storage at different temperatures

Species	Rate constant $k_f \times 10^3$ [h]						
	−20°C	−10°C	−5°C	−3°C	0°C	10°C	20°C
Mackerel	0.094	0.192	0.695	1.630	2.351	7.590	17.270
Sea bream	0.053	0.110	0.397	0.585	0.960	3.915	6.955

Table 2. Rate constants of freshness-lowering and discoloration in the muscles of skipjack during storate at different temperatures

Rate constants	Storage temperatures [°C]										
	−40	−30	−20	−10	−5	−3	0	5	10	15	20
$k_f \times 10$ [h^{-1}]	0.050	0.100	0.150	0.265	1.44	3.41	4.17	6.60	13.7	14.0	24.1
$k_c \times 10$ [h^{-1}]	0.030	0.132	0.288	1.170	2.21	5.18	16.30	35.90	96.7	230.0	270.0

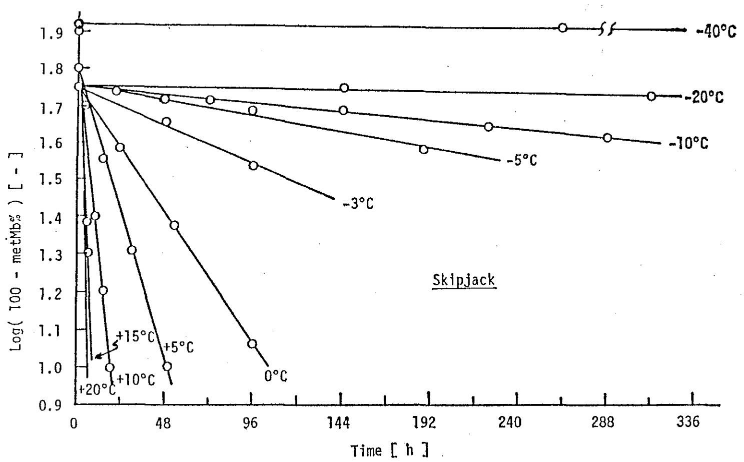

Fig. 3. Changes in metMb% of skipjack during storage at different temperatures.

tion index of discoloration in red muscled fish, but the value of (100−metMb%), which indicates the ratio of remaining amount of MbO_2 (oxymyoglobin) to total Mb (myoglobin) and decrease of this ratio with the storage time, has been used in the present study. The plot of the logarithms of (100−metMb%) versus storage time yielded straight lines (Fig. 3), these indicating a first-order reaction. The first-order rate constants (k_c) of skipjack muscles were determined at various storage temperatures in the same manner as the rate of freshness-lowering and shown in Table 2. These results indicated that the rate of discoloration increased with rising storage temperature as the same manner as that of freshness-lowering. MATSUURA et al.[8] reported that autoxidation of myoglobin isolated from fish muscle followed the first-order reaction. These results showed similar tendencies in their report[8] and our previous report.[4]

Temperature Dependence on the Rates of Quality Changes

On the basis of rate constants of freshness-lowering and discoloration rate, ARRHENIUS's plots were used for comparing the freshness-lowering rate among the fish species under a study (Fig. 4), and for comparing the freshness-lowering rate with the discoloration rate in skipjack muscles (Fig. 5). From Fig. 4 it appears that changes in kinetics of freshness-lowering occurred at temperatures close to the freezing point (−2.0°C) and at −10°C. In case of discoloration, the change of kinetics occured near at −5°C besides a freezing point. These fact are evident from the breakes in the lines of Figs. 4 and 5. These results may

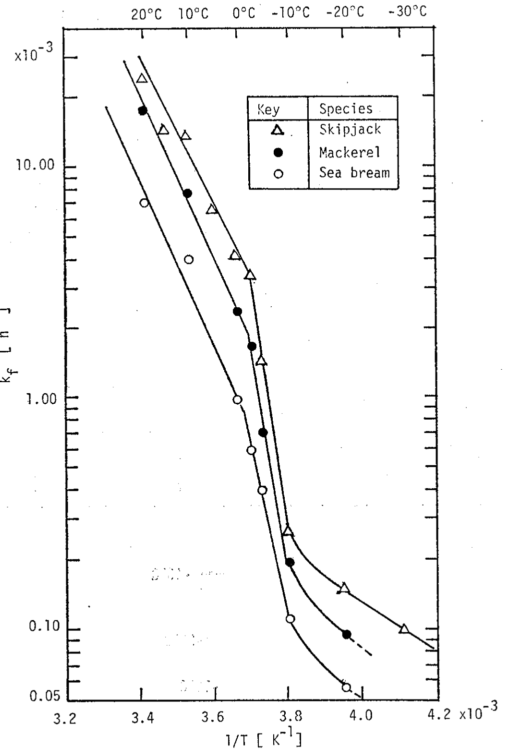

Fig. 4. Effect of temperature on the rate constant of freshness-lowering in muscles of skipjack, mackerel and sea bream. k_f=Rate constant of freshness-lowering, T=Absolute temp.

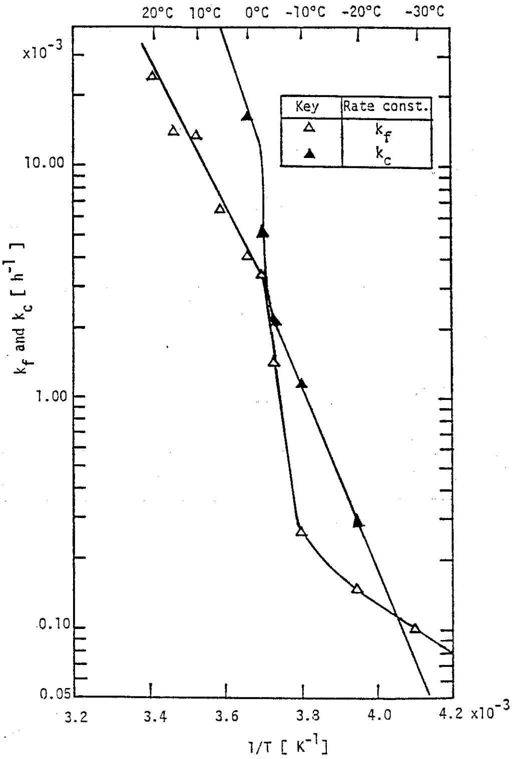

Fig. 5. Effect of temperature on the rate constant of freshness-lowering and discoloration in skipjack muscles. k_f=Rate constant of freshness-lowering, k_c=Rate constant of discoloration, T=Absolute temp.

be happened due to the phase-change of water in fish muscles during freezing and thawing. FENNEMA[3] described that many reactions in both cellular and non-cellular systems for both enzymatic and non-enzymatic reactions, either increased or declined in rate during the early stages of freezing, and then he summarized that the cause of these accelerations (or rate enhancements) were believed to be due to freeze-concentration effect.

From Fig. 4, it is ascertained that the freshness-lowering of skipjack was faster than that of mackerel, and the freshness-lowering of red muscle fish (skipjack and mackerel) was faster than that of white muscle fish (sea bream). These results were in agreement with the generally accepted opinions. On the other hand, it has been indicated in Fig. 5 that rate of discoloration was faster than that of freshness-lowering in skipjack muscle in the range above −25°C. Effect of the initial concentration of chemical substances on the rates of quality changes are not discussed here, because K value and metMb% are relative values as generally known.

ARRHENIUS's equation is often used to account for temperature effect on reaction rate. On the basis of rate constant of quality changes, ARRHENIUS's plots were prepared in Figs. 4 and 5. If these lines are derived by linear regression, the most common and generally valid assumption is that temperature-dependence of the deterioration rate will follow the ARRHENIUS-type equation, namely:

$$k=A \exp(-Ea/RT)$$

in which k (here k_f or k_c) is the reaction rate

Table 3. Apparent activation energy (Ea) and frequency factor (A) in the muscles of mackerel and sea bream

Species	Temp. range	Ea (Kcal/mol)	A [h^{-1}]
Mackerel	Abov −2°C	16.231	2.269×10^{10}
	−2 to −10°C	41.445	4.886×10^{30}
Sea bream	Above −2°C	15.819	4.852×10^{9}
	−2 to −10°C	33.615	7.178×10^{11}

Table 4. Apparent activation energy (*Ea*) and frequency factor (*A*) of the rate of freshness-lowering and discoloration in muscles of skipjack

Rate constant	Temp. range	*Ea* [cal/mol]	*A* [h^{-1}]
Freshness-lowering (k_f)	Above −2.0°C	1.399×10^4	7.294×10^8
	−2.0 to −10.0°C	5.092×10^4	5.272×10^{38}
	Below −10.0°C	5.478×10^4	8.024×10
Discoloration (k_c)	Above −2.0°C	2.521×10^4	2.239×10^{18}
	−2.0 to −5.0°C	9.054×10^4	1.321×10^{71}
	Below −5.0°C	1.829×10^4	1.836×10^{12}

constant of freshness-lowering and discoloration. T is the absolute temperature, R is gas constant, Ea is often defined as the energy of activation, an apparent quantity characteristic of the reaction of quality change, and A is frequency factor. Kinetic parameters of activation energy and frequency factor were obtained from the slopes of straight lines in Figs. 4 and 5 using the ARRHENIUS's equation above described. The kinetic parameters of k_f on the range from −10 to +20°C, in mackerel and sea bream muscles were shown in Table 3 and those of k_f and k_c in skipjack muscles were shown in Table 4. (on the range from −40 to +20°C).

Acknowledgements

Authors wish to thank emeritus prof. Dr. F. OHTA, Kagoshima University for useful suggestions, and to thank prof. Dr. D. NOMURA, Kyushu University for reading the manuscript. Furthermore, we are grateful to Messrs. A. ONO, K. KOBA and M. SHIMOMURA for their experimental assistances.

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