68

VIII

ЕВРОПЕЙСКИЙ КОНГРЕСС РАБОТНИКОВ
НИИ МЯСНОЙ ПРОМЫШЛЕННОСТИ

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Kazuhiro Okamura

AQUIFEROUS CAPACITY OF RAW FISH AND RELISHABILITY OF PUDDINGY FISH PRODUCTS INFLUENCED BY CONCENTRATION OF SALT ADDITION

№ 46

МОСКВА 1962г.

Aquiferous Capac[illegible] of Raw Fish and Relishability of Puddingy Fish Products Influenced by Concentration of Salt Addition

By Kazuhiro OKAMURA

Japan, being a narrow, overpopulated cuntry, has been dull in stock-raising. Everyday life of her nation as Buddhist might have surely been another reason of her great tardiness in industrial development of meat products as foodstuff. However, as Japan is a sea-girt country, she is on the other hand highly developed in fishery. Animal protein demanded in dietary life of nation is hence supplied in Japan chiefly as fish meat or products thereof.

This state of things in Japan may be seen, for instance, from the fact that, while her output of ham and sausage as representative groceries of processed meat amounted in 1960 only to about 80,000 tons, particular types of puddingy product, "neriseihin ", which are prepared by thermally fixing a raw fish preliminarily processed into a state of paste and stand comparison perhaps with the ham and sausage consumed in countries in Europe and America, attained in the same year even to 500,000 tons and above.

Thus, in Japan, "neriseihin" or said sort of puddingy products of fish being a very important kind of food, studies about this grocery are in its various aspects now being actively pushed forward.

As representative kinds of "neriseihin" of fish, there may be mentioned rather traditional products such as "kamaboko" (boiled or steamed fish cake), "satsumaage" (fried fish cake) and "chikuwa" (a sort of cylindrically formed kamaboko) and rather modern ones such as fish sausage. These various types of product, however, are in common with one another in respect of that they are manufactured by grinding the raw fish in the presence of common salt added by about 3% of the fish to give rise a smooth paste and heating the paste into an elastic jelly. As the elasticity or masticatory response constitutes a most distinct reflex of the quality of fish "nerisaihin", it is general in criticizing the grade of these groceries to assign the higher rank to the more elastic product. Perhaps for this reason, among studies on fish "neriseihin", those aiming to increase the elasticity are most often met with.

It is known that meat processing into ham or sausage can be accomplished appreciably with ease by using a raw meat having a strong tendency to water retention and a great ability of self-binding. In manufacturing fish "neriseihin", in turn, it is rather a matter of absolute necessity to employ a raw fish truly excellent in water retention tendency as well as in self-biding ability. In general, the so-called white flesh of fish is far stronger in water retention as compared with meat.[1,2]

As regards the method of improving the water retention of raw meat, some kinds of phosphate were disclosed about 10 years ago of their efficacy and are in these days employed in manufacturing various types of meat product.

The authore, examining in these past years the effect of addition of some phosphates on the elasticity of "Kamaboko" prepared from raw fish added with these salts, arrived at the confirmation of that some phosphates can be effectively used also with the aim of preparing finished products of "kamaboko" appreciably increased in elasticity.[3~5]

In the author's opinion, "kamaboko", which is an apparently quite homogeneous, highly elastic jellied product prepared by thoroughly grinding white fish flesh into a paste and subjecting the paste to heat treatment, provides a splendid test material fitted for studying the rheological properties of fish flesh by following their changes induced by adding the raw fish with various phosphates at various concentrations.

Referring to the nature of some phosphate that effectively enhances the water retention of meat on the one hand and increases the elasticity of finished "kamaboko" on the other, it was expected that a certain positive correlation can be found between the water retention of raw fish and the elasticity of the "kamaboko" made thereof. In this point of view, the auther, carrying out a few circumstantial inquiries into the influences of several kinds of raw fish and the jelly strength of finished product of "kamaboko", obtained some results suggestive of very interesting facts, which will now be reported in the following.

I. Effect of concentration of added salt on water retention of raw fish

i) Method of measuring the factor of water intake of fish.

As it had been found that peculiar high affinity to water of fish flesh makes it impossible to employ the known procedure for meat[6~7] in determing the water retention of fish flesh, the auther worked out as already published[1] a new method of measuring the water retention of raw fish. This method comprises estimation of a term named by the author as "factor of water intake". This new method proved to be conveniently usable also in the case of meat. Now, the estimation of factor of water intake may be carried out as follows: A definite amount (Mg) of raw fish is added with a known quantity (Wg) of either plain water or aqueous salt solution amounting to 2—20 times the weight of raw fish and treated in a homogenizer strictly for 3 minutes. As soon after this time as possible, a 100g portion of the homogenized mixture is transferred into a centrifuge tube of 100ml capacity and treated at 3400—3800r.p.m. for 15 minutes. The temperature of the sample should throughout the centrifugal treatment be kept below 20°C. When the supernatant liquor thus appearing is measured as Cg, the factor of water intake, Q(%), of the raw fish can be calculated by means of the following equation:

$$Q = \frac{W}{M}(100 - C) - C$$

Q thus calculated, standing for the quantity of water or aqueous solution coming held by 100 grams of raw fish, corresponds numerically to the newly fixed amount of aqueous medium represented as percent of the weight of fish.

ii) The factor of water intake variable with salt concentration.

Now, presenting the results obtained according to the above-explained method in Figs. 1~9, a brief discussion will be given about the effect of environmental salt concentration on the factor of water intake.

In using a phosphate capable of developing a basic reaction in water, the salt solution has to suitably be neutralized before use, since the factor of water intake is sharply influenced by pH.

In most of the experiments that led to these results, fish flesh previously well rinsed with water was employed as sample. In preparing such a rinsed sample, minced fish was placed in plain water of 5 times the weight of fish. After thorough stirring, the fish was settled and drained. Through repeating this operation a few times, there was obtained a sample of rinsed fish.

As seen from the results presented in Figs. 1~9, which contain for the sake of reference also a few data for pork as an example of meat, fish shows a very large factor of water intake in plain water; however, a notably small factor of water intake in a salt solution of low concentration. As seen in Fig.1, on the other hand, a fish sample not rinsed with water showed a small value of the factor of water intake even when placed in plain water. As raw fish inherently contains various kinds of ionizable matter, they were perhaps ionized in the added water and gave rise to an environment similar to that prevailing when a rinsed fish was placed in a dilute salt salution. Therefore, to make clear the influence of a salt existing at a low concentration, the fish sample to be used must have previously been well rinsed with plain water.

It may be remarked, in this connection, that, in the practice of "kamaboko" manufacture, it is recommendable for obtaining a highly elastic, dense product to subject raw fish, as practised by some makers, to final rinsing in a dilute salt solution. According to the kind of raw fish, the usual bleaching with water alone often makes the raw fish turn out to be too water.

Fig. 1 ~ Fig. 9

From the above data, it may be given as a conclusion that:

Raw fish recedes in the presence of a small amount of neutral salt in its ability of water retention. The factor of water intake of fish attains thus to a minimum at a certain low value of environmental salt concentration. Saying further, the salt concenttion corresponding to the minimum factor of water intake is considered to be dependent on the ionic strength and the type of dissociation of the salt concerned. When the salt is to be assigned with m stages of electrolytic dissociation, there will appear m minimus on the curve of water intake drawn against salt concentration.

It has further been disclosed that the salt concentration at the minimal water intake approximalely satifies the following relation:

$$\frac{1}{2}\sum_i V_i Z_i^2 \times \frac{1}{2}\sum_i |Z'_i| = 0.1$$

wherein V_i stands for the molar concentration, Z_i for the valency of the i-th ion produced by complete dissociation of the salt and Z'_i represents the valency of the i-th ion present in a dissociation stage of the salt in which the minimum water intake makes its appearance. This relation is referred to by the author as the equation of salt concentration at minimum water intake.

For reference, the values of concentration calculated and proved to satisfy this equation are listed in Table 1 for several kinds of salt.

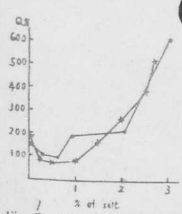


Fig. 1 Effect of NaCl addition on the factor of water intake (Q') of fish flesh.
● lean pork meat; × mixed fish flesh (sea-eel: Nibea = 4 : 6
For the pork meat : NaCl solution 1 : 9; for the fish flesh : NaCl solution 1 : 5.

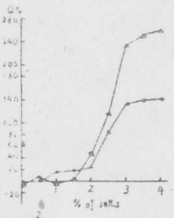


Fig. 2 Effect of NaCl addition on the factor of water intake Q'.
Flesh : NaCl solution = 1 : 4; ●, "sarokawa", Makaira mazara; ○, "kibada", Neothunnus macropterus

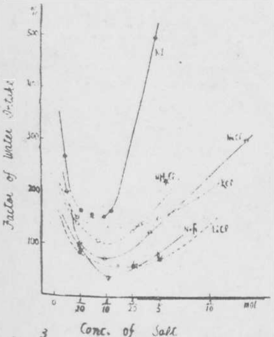


Fig. 3 Factors of water intake of a fish flesh (sea-eel) previously washed with water are shown as variable with the concentration of added salt solution.
Salt: Both cation and anion are of mono valency.

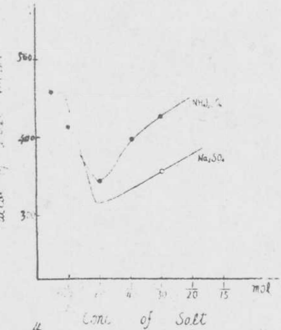


Fig. 4 The same as in Fig. 3 but that the salts consist of mono-valent cation and di-valent anion.

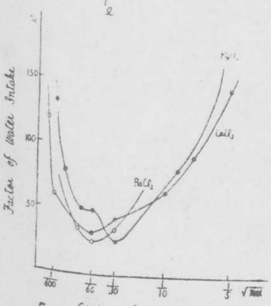


Fig. 5. The same as in Fig. 3 but that the salts consist of di-valent cation and mono-valent anion.

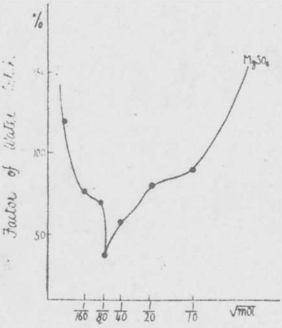


Fig. 6. The same as in Fig. 3 but that the salt consists of di-valent ions.

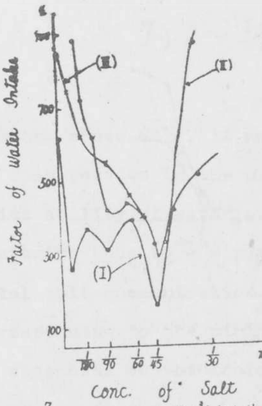


Fig. 7. The same as in Fig. 3 but that the salt is potasium phosphate.

(I): Available salt solutions were prepared from 1/10 mol K_2HPO_4 solutions by neutralization to pH 7.0 with HCl and dilution to specified concentrations with 1/2 mol KCl.

(II): K_2HPO_4 solutions were used without neutralization and KCl addition.

(III): The same as in (II) but that a fish flesh washed with water was used after storage for 2 days at 3°C.

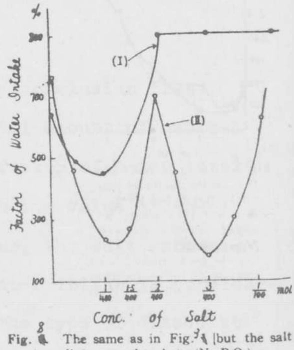
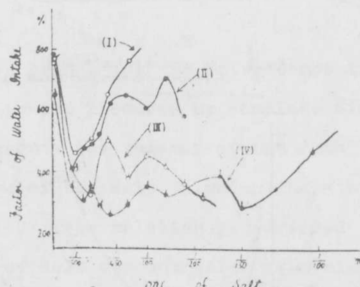


Fig. 8. The same as in Fig. 3 but the salt is sodium pyrophosphate ($Na_4P_2O_7$).

(I): Sodium pyrophosphate.

(II): 1/20 mol solution of $Na_2P_2O_7$ was neutralized to pH 7.0 with HCl and used after dilution with 1/2 mol NaCl.



(I): Comparatively fresh fish was used without washing; the phosphate was used as dissolved in 1/2 mol NaCl.

(II): The same as in (I) but that the washed flesh was kept at 3°C for 3 days before the test.

(III): The salt solutions were prepared from 1/20 mol $Na_5P_3O_{10}$ by neutralization to pH 7.0 with HCl followed by dilution with 1/2 mol NaCl. Fish flesh was used in the day of its washing with water.

(IV): The same as in (III) but that the washed fish was brought into contact with salt solution after storage of 24 hours at 3°C.

Fig. 9. The relations between water intake and environmental concentration of sodium tripolyphosphate ($Na_5P_3O_{10}$) as variable with the freshnes of fish flesh (washed or not washed with water.

Table 1. Calculation of V_i, the salt concentrations at which the fish flesh shows minimum water intakes, for various salts.

Equation and Solution / Salt	$\frac{1}{2}\cdot\sum_i V_i Z_i^2 \times \frac{1}{2}\sum\lvert Z_i^1\rvert = 0.1$	V_i (mol)
NaCl, KCl, NH_4Cl, NaF, KI, LiCl	$\frac{1}{2}\cdot\{V_i\times(+1)^2+V_i\times(-1)^2\} \times\frac{1}{2}\{\lvert+1\rvert+\lvert-1\rvert\}=0.1$	$\frac{1}{10}$
$(NH_4)_2SO_4$, Na_2SO_4	$\frac{1}{2}\cdot\{V_i\times(+1)^2\times2+V_i\times(-2)^2\} \times\frac{1}{2}\{\lvert+1\rvert\times2+\lvert-2\rvert\}=0.1$	$\frac{1}{60}$, $\frac{1}{30}$
$CaCl_2$, $BaCl_2$, $MgCl_2$	$\frac{1}{2}\{V_i\times(+2)^2+V_i\times(-1)^2\times2\} \times\frac{1}{2}\{\lvert+2\rvert+\lvert-1\rvert\times2\}=0.1$	$\frac{1}{60}$, $\frac{1}{30}$
$MgSO_4$	$\frac{1}{2}\{V_i\times(+2)^2+V_i\times(-2)^2\} \times\frac{1}{2}\{\lvert+2\rvert+\lvert-2\rvert\}=0.1$	$\frac{1}{80}$, $\frac{1}{40}$
K_3PO_4※, Na_3PO_4※, Tri-sodium citrate	$\frac{1}{2}\{V_i\times(+1)^2\times3+V_i\times(-3)^2\} \times\frac{1}{2}\{\lvert+1\rvert\times3+\lvert-3\rvert\}=0.1$	$\frac{1}{180}$, $\frac{1}{120}$, $\frac{1}{60}$
$Na_4P_2O_7$※	$\frac{1}{2}\{V_i\times(+1)^2\times4+V_i\times(-4)^2\} \times\frac{1}{2}\{\lvert+1\rvert\times4+\lvert-4\rvert\}=0.1$	$\frac{1}{400}$, $\frac{1}{300}$, $\frac{1}{200}$, $\frac{1}{100}$
$Na_5P_3O_{10}$※	$\frac{1}{2}\{V_i\times(+1)^2\times5+V_i\times(-5)^2\} \times\frac{1}{2}\{\lvert+1\rvert\times5+\lvert-5\rvert\}=0.1$	$\frac{1}{750}$, $\frac{1}{600}$, $\frac{1}{450}$, $\frac{1}{300}$, $\frac{1}{150}$

※ : These salts are ~~neutralised~~ used after neutralization to pH 7.0

In this table, only the calculation formulae for V_i are presented, which are usable under the complete dissociation of the salt concerned. However, in the case of a salt having a polyvalent ion and hence to be assigned with plurality of dissociation stages, the value of Z_i varies with the stage of dissociation of the salt. For example, for sodium triphosphate to which five stages can be assigned in respect of electrolytic dissociation, five values of $\frac{1}{2}\sum_i\lvert Z_i\rvert$ can also be considered as 1/750, 1/600, 1/450, 1/300 and 1/150 (mol/l).

II. Influence of kind and concentration of added salt upon the elasticity (jelly strength) of finished product of fish "neriseihin".

Now, the author shall present the results he obtained in studying as to how the environmental salt consentration influences the kamaboko-forming ability of raw fish kept exposed thereto. To make clear the feature of this influence reflected in the elasticity or jelly strength of finished product of kamaboko, there were prepared a number of specimens of the latter by grinding a previously minced fish together with common salt added in an amount of 3% of the weight of fish, dividing the there produced fish paste into a number of lots, adding the respective lots with various kinds of salt in various amounts and solidifying these lots of fish paste by cooking for 25 minutes at 95~100°C. Salt concentrations thus established in kamaboko specimens were expressed as the number of mols of salt added to 1Kg fish paste.

Jelly strength measurement: In judging the elasticity or jelly strength, each kamaboko specimen was chewed and organoleptically estimated of its elastic response to teeth. Grading of specimens according to thus estimated jelly strength was carried out by the following procedure:

Kamaboko specimens of various salt contents prepared as above are first designated A, B, C,8------. They are then brought into pairs. Changing the combination of pendant members as many in kind as possible, comparative jelly strength is represented according to the degree of distinction found between these pendants, for example, as $A \doteqdot B$, $A \geqq C$, $A > D$, $A \not> E$, $A \gg F$ and so on. The symbols $\doteqdot$, $\geqq$, $>$, $\not>$ and $\gg$ being estimated as 0, 0.5, 1.0, 1.5 and 2.0 marks, respectively, the total marks to be given to a particular specimen are obtained after completing the comparison of every one of specimens with all the other ones, while a specimen found always to be inferior to others remins getting no marks at all.

As regards the method of measuring kamaboko jelly strength, there has been presented by Shimizu and Simidu a Gelometer,[8~9)] an instrument specially designed for this purpose. This instrument is very elaborate and allows the jelly strength to be calculated from the strength and elongation at break measured therewith. The present author, however, through his repeated employing this instrument, takes it as somewhat unsatisfactory in its demanding a long time of measurement and a great bulk of specimen. The above introduced procedure contrived by the present author, on the other hand, proved as strikingly suited to be used in estimating relative jelly strength of Kamaboko specimens. Only defect assignable to this method is its incapability of allowing one to get an absolute value of jelly strength.

Now, for kamaboko specimens with various salt contents, jelly strength represented as the marks they acquired through the above procedure of examination is given in Figs. 10~16.

Fig. 10 ~ Fig. 16

As seen from the data in these Figs., raw fish is caused by the addition of salt to exhibit a minimum jelly strength at a certain low concentration of the salt. As to the salt concentration corresponding to this minimum of jelly strength, further, a relationship has been discovered that it agrees with the salt concentration which provides raw fish with a minimal value of the factor of water intake.

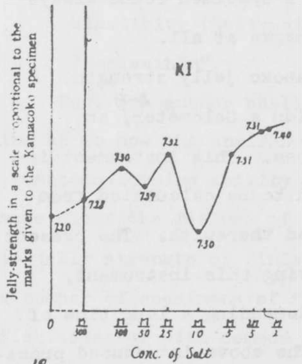


Fig. 10. Organoleptically marked jelly-strength of Kamaboko plotted against the concentration of the KI added to a raw fish paste prepared from *nibea argentata*. The numerals along the curve show the pH values of Kamaboko specimens.

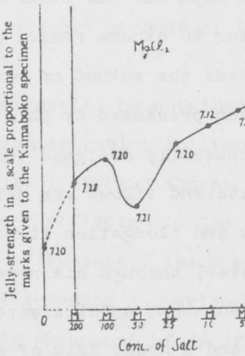


Fig. 11 Organoleptically marked jelly-strength of Kamaboko plotted against the concentration of the $MgCl_2$ added to a raw fish paste prepared from *nibea argentata*. The numerals along the curve show the pH values of Kamaboko specimens.

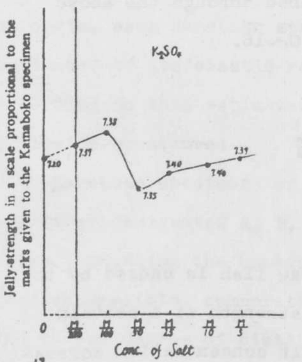


Fig. 12 Organoleptically marked jelly-strength of Kamaboko plotted against the concentration of the K_2SO_4 added to a raw fish paste prepared from *nibea argentata*. The numerals along the curve show the pH values of Kamaboko specimens.

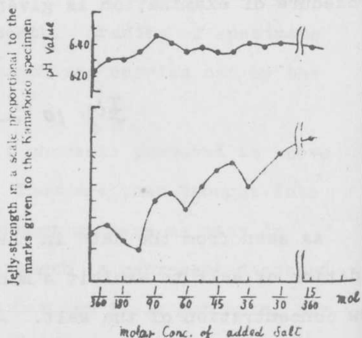


Fig. 13 Values of pH and organoleptically estimated jelly-strengths of Kamaboko specimens from sea-eel flesh by addition of various amounts of equimolar mixture of KH_2PO_4 and K_2HPO_4.

75

6.80

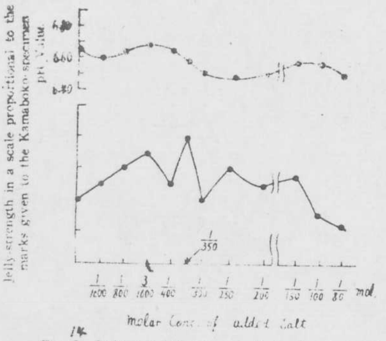


Fig. 14 Values of pH and organoleptically estimated jelly-strengths of Kamaboko specimens prepared from sea-eel flesh by addition of various amounts of equimolar mixture of $Na_4P_2O_7$ and $Na_2H_2P_2O_7$.

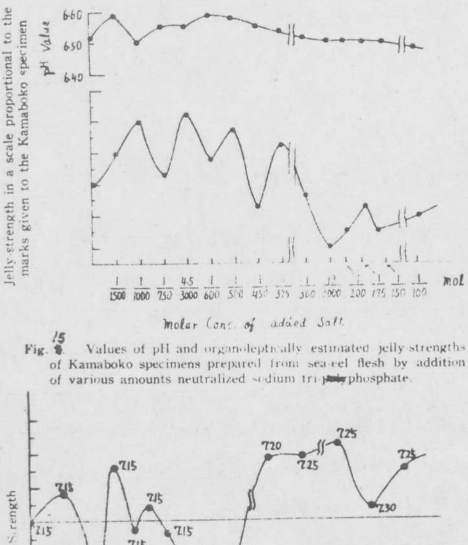


Fig. 15 Values of pH and organoleptically estimated jelly-strengths of Kamaboko specimens prepared from sea-eel flesh by addition of various amounts neutralized sodium tri-polyphosphate.

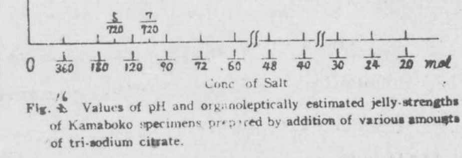


Fig. 16 Values of pH and organoleptically estimated jelly-strengths of Kamaboko specimens prepared by addition of various amougts of tri-sodium citrate.

Accordingly, from the combination of the results of Experiments I and II, there may be drawn the fallowing conclusion:

A neutral salt or a salt suitably neutralized behaves rather as impeditive against kamaboko-forming tendency of raw fish and in fact to an extreme extent when it is present at a certain low concentration. The salt concentration corresponding thus to an elasticity minimum of finished kamaboko is identical with that which induces the raw fish to be minimized in its factor of water intake. Denoting this particular value of salt concentration as v_i (mol/liter) in reference to its i-th ion, v_i is connected with Z_i, the valency of the i-th ion produced by complete dissociation of the salt, and also with Z_i', the valency of the i-th ion in a dissociation stage of salt just producing said two kinds of minimums, and indeed by way of the following equation:

$$\frac{1}{2}\sum_i v_i Z_i^2 \times \frac{1}{2}\sum_i |Z_i'| = 0.1$$

From the fact that the salt concentration making a raw fish show a minimal factor of water intake agrees entirely with that which imposes the corresponding kamaboko product with a minimal jelly strength, it may well be deduced that the elasticity of finished kamaboko is closely connected with the factor of water intake of raw fish, though the routine process of kamaboko manufacture is carried out in the presence of common salt at a concentration far remote from that minimizing the elasticity of the product.

Summary

The feature of the influence of various kinds of added salt on the moisture retention of raw fish was experimentally studied in detail under varying the environmental salt concentration. The results indicate that raw fish attains in its affinity to water as estimated in the term of factor of water intake to a minimum at a certain low

concentration of added salt. When the salt can develop m stages of dissociation, there appear m minimal values of factor of water intake with varying salt concentration. The salt concentration just at which a minimal factor of water intake makes its appearance is independent of the kind of salt and depends only upon the ionic strength and the ionic valency realized by the existing electrolytic dissociation of the salt, the relation being represented by the equation

$$\frac{1}{2}\sum_i V_i Z_i^2 \times \frac{1}{2}\sum_i |Z'_i| = 0.1$$

wherein V_i stands for the molar concentration, Z_i for the valence of the i-th ion produced through the complete dissociation of the salt, and Z'_i represents the valency assignable to the i-th ion present at the salt concentration that produces the existing minimal factor of water intake. Thus, the environmental salt concentration that imposes raw fish with a minimum water retention seems likely to be a reflex of the electrolytic peculiarity of the fish itself.

When specimens of kamaboko as a typical fish "neriseihin" are prepared in the presence of an added salt varied in concentration, a minimum or minima in jelly strength make their appearance at a concentration or concentrations of salt which agree with those that produce minimal values of factor of water intake, the ionic condition concerned being represented by the above equation.

Acknowledgment

Now, in closing the explanation of the present study, the author extends his hearty thanks to Professor Dr. Wataru Shimizu at Kyoto University and Professor Dr. Hiroshi Hirano at Tokyo University of Fisheries for their giving constant encouragements and invaluable suggestions in carrying out this work.

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VIII