#### THE COLLOIDAL BEHAVIOUR OF SERICIN. I.

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#### Introduction.

The crude silk fiber spun by the silk-worm, consists of a filament of fibroin surrounded by a glue-like coating known as sericin. Sericin, also called silk-glue, is one of the proteins secreted from the silkgland by the silk-worm. It swells in cold water, and is readily soluble when boiled. The relative proportion of these two components, fibroin and sericin in crude silk differs considerably with different varieties of cocoons, but generally sericin occupies about 25 per cent. of the raw fiber. Mulder gave formula  $C_{15}H_{25}N_5O_8$  to sericin, the elementary composition being C: 43, H: 6, N: 16, and O: 35 per cent.

Sericin is commonly accompanied by small amounts of colouring and mineral matters as well as of fatty and waxy substances. The physicochemical behaviours of sericin have a great influence on the facility in reeling the raw silk from cocoons. For this reason I have studied some colloidal properties of sericin in its various states and varieties.

To the chemical investigation of silk fiber, especially of the amino acids obtained from it, R. Inoue<sup>(1)</sup> has contributed, and according to his estimation the percentages of the known constituents of silk-glue are as follows:

	Inner layer (per cent.)	Outer layer (per cent.)
Glycocoll	5.77	2.99
Alanine	8.49	9.24
Tyrosine	5.25	2.85
Serine	2.56	6.33
Phenylalanine	2.66	2.60
Leucine	0.73	2.30
Proline	0.35	_
Aspartic acid	6.81	2.74
Glutamic acid	_	0.94

<sup>(1)</sup> R. Inoue, Reports Seric. and Silk Ind. Science, 1929.

E. Hiratsuka<sup>(2)</sup> studied completely the properties of liquid silk in the silk-worm. We shall understand by "fine structure" the molecular and micellar constitution of the proteins as revealed or indicated by chemical investigations, by X-ray spectroscopy, and by other investigations.

It is confirmed by the chemical investigations of Fischer that the proteins consist of long chain-like molecules of condensed or peptide amino acids. The natural proteins consist of more or less uniformly oriented crystallites of parallel polypeptide-type chains. Brill (1923),<sup>(3)</sup> Herzog and Jancke (1927)<sup>(4)</sup> state that, under X-ray investigation, fibroin has a crystalline character and that it is a mixture of at least one crystalline and several amorphous compounds, the nature of the mixture varying with the sources of the silk.

Meyer and Mark (1928)<sup>(5)</sup> believe that fibroin consists of four principal valence chains of glycyl-alanine, the length of the micellæ being 150 A. U. and corresponding to a polypeptide of at least twenty glycylalanyl groups. But very little work has been conducted to elucidate the chemical constitution of sericin and it is generally believed that it has an amorphous structure. To the study of its chemical composition Abderhalden and his co-workers<sup>(6)</sup> have made much contribution. Karrer made a fermentative investigation on fibroin and examined the partial decomposition of sericin by the proteolytic enzymes secreted by some bacteria. E. Furuya has been studying along a similar line in our college. I report here a study of some colloidal behaviours of sericin existing on the cocoon layer and separated from it by boiling in water or by precipitation with an electrolyte.

#### PART I.

### Sec. I. The Solubility of Sericin on the Cocoon Layer.

(1) The Solubility of Sericin in Water. Generally, "kaijo" of cocoons is represented by the weight of raw silk reeled per hour under the same condition. The state and colloidal properties of the sericin particles of the cocoon change in a remarkable manner with the external factors during their gelatinization, drying process or their preservation, and the internal

<sup>(2)</sup> E. Hiratsuka, Bull. Imperial Seric. Exp. Station, Japan, Vol. 1 (1918), 203-224.

<sup>(3)</sup> Brill, "Ein Beitrag zur chem. Konstitution des Seidenfibroins," 1923; Naturwissenschaften, 18 (1930), 622.

<sup>(4)</sup> Herzog and Jancke, Z. Physik, 3 (1920), 196; Helvetica Chim. Acta, 11 (1928), 529.

<sup>(5)</sup> Meyer and Mark, Ber., 61 (1928), 1982; Z. physik. Chem., 2 (1929), 115.

<sup>(6)</sup> Abderhalden, Z. physiol. Chem., 178 (1928), 253; ibid., 207 (1932), 141-146; ibid.,
210 (1932), 246; Biochem. Z., 211 (1929), 395; ibid., 226 (1930), 209.

conditions of the liquid silk. It will, therefore, lead to the different solubilities of sericin in water.

R. Inoue<sup>(7)</sup> measured already "kaijo" of cocoons by obtaining the curves of the amounts of nitrogen dissolved into the solution in a definite time. Further, he and T. Watanabe found that sericin on the outer layer of cocoons was more soluble in water than that on the inner layer. I confirmed fully their results and further found that the sericin solution obtained from cocoons having good "kaijo" or from the outer layer of cocoons had a stronger power of gelatinization and that this would lead to difficult conglomeration at the contact point of silk fiber on the cocoon.

When the cocoon layer containing the natural sericin is boiled with some distilled water in a flask with a reflux condenser, the sericin particles mostly disperse into the solution and form a hydro-philic colloid containing very small amounts of fatty and colouring matters.

The natural sericin is apt to denature to some extent by heat, alcohol, dialysis, and other external factors, so I used the sericin solution in that condition as the material to be examined. In general the solubility of sericin in water varies with the kinds of cocoons, with its total amounts existing on the cocoon fibers, with the amount of salts in water, and also with the temperature of the water.

The sericin is not a simple compound, but a mixture of similar proteins as described later. By the difference in the proportions of the mixtures in compliance with varieties of cocoons, the solubility in water will be affected, because each component has a different solubility in water.

The author determined some physico-chemical properties of aqueous solutions of the cocoon layer and observed that the solubility of sericin particles in dilute solutions is proportional to their relative viscosities, indices of refraction, or lowering of surface tension, and that the logarithm of solubility is also proportional to turbidity.

From these relations I was able to determine the solubility of sericin by measuring its physico-chemical properties. As already described, the solubility of sericin on the cocoon layer varies with its "kaijo." This will be caused mostly by the different proportions of two kinds of sericin, but it will also be affected by the different pH values of sericin solutions.

I have determined electrically the pH values of the sericin solutions, allowing them to stand for two hours after preparation. The results are shown in Table 1.

<sup>(7)</sup> R. Inoue, Rep. Seric. and Silk Ind. Science, 1 (1926), Vol. 1.

Table 1.

Cocoons h		Cocoons having middle "kaijo"			
conc. (%)	pH	pH conc. (%)		conc. (%)	pH
0	4.88	_	_	_	_
0.05	4.96	0.07	5.09	0.07	4.92
0.09	5.70	0.10	5.29	0.11	5.09
0.11	5.79	0.14	5.38	0.14	5.30
0.16	5.89	0.16	5.81	0.16	5.62
0.20	5.96	0.19	5.86	0.24	5.73
0.26	6.01	0.22	5.97	0.29	5.78
0.35	6.21	0.31	6.05	0.38	5.98
0.40	6.20	0.42	6.11	0.48	6.08

Though the pH value of the sericin solution is a function of its concentration, a solution from cocoons having better "kaijo" shows the greater value in the same concentration. In order to clarify the cause of this difference of pH I made the following experiment.

A diaphragm with 0.1 g. cocoon layer was made at the middle point of an U-tube, 20 c.c. of distilled water free from carbon dioxide were poured into it, then the platinum electrodes were inserted at the ends of the tube, and an electric current of 110 volts was passed through. After an hour pH of each solution around the electrodes was measured.

The cathodic solution showed weak basicity (pH 7.43-7.81) and the anodic moderate acidity (pH 3.37-3.73). I detected qualitatively a minute amount of ammonia in the cathodic solution, and glycocoll, tyrosine, bitartrate. etc. in the anodic solution. It seemed to me that these compounds existed originally in the cocoon layer before the electric treatment and caused the change of pH.

Even for the same cocoon pH values of the solutions obtained by boiling it with water vary with the position of the layers.

The outer cocoon layer showed generally the greatest pH value, next the inner layer, and the middle layer the smallest, the difference in the values for these layers depending on "kaijo" of the cocoon. The swelling and the solubility of sericin increased greatly with the rise in temperature and two cases are expressed by the same equation.

$$W \times 100 = S = At^K \quad (A = 1.0)$$

where W represents the quantity of dissolved sericin in g. when 5 g. cocoons are boiled with 100 c.c. of distilled water in a flask for 30 minutes, t the temperature in centigrade, A and K constants.

The value of constant K depends not only on the temperature, but also on "kaijo" of the cocoon (Table 2).

" kaijo "	K(20-50°C.)	K(60-90°C.)	K(100°C.)
good	0.55	0.85	0.84
middle	0.43	0.71	0.77
bad	0.42	0.67	0.75

Table 2.

This leads to the conclusion that the sericin dispersed from the cocoon fibers having good "kaijo" contains more sericin A which is comparatively easily soluble even in cold water. And at the neighbourhood of  $60^{\circ}$ C. the solubility of sericin, that is constant K, increases rapidly.

- 2. The Solubility of the Natural Sericin in Salt Solutions. The neutral salts have generally a solvent action on proteins and under nearly all conditions exert a recognizable influence on proteins in solution. Denis (1856) noticed that the solubility of a certain protein increased by the addition of neutral salts and it is also known that in dilute solutions (less than 2 or 3 normal) neutral salts of the alkalies, or of alkali earth metals, increase the solubility of the protein in water. Cohen (1924) showed that the rate at which solubility is raised by increasing quantities of a salt is characteristic of each individual protein, and gave formula  $S/S_0 = a\mu^{\beta}$ , where  $S_0$  is the solubility of the protein in water, S the solubility in a salt solution with an ionic strength  $\mu$ ,  $\alpha$  and  $\beta$  constants.
- A. A. Green  $(1931)^{(8)}$  also examined the solubility of hæmoglobin in salt solutions and showed that the solubility in concentrated solutions at constant pH and temperature was represented by an equation of the type:

$$\log S = \beta - K_s' \mu$$
 ,

where S is the solubility,  $\mu$  the ionic strength,  $\beta$  an intercept constant which in the case of non-electrolytes is  $\log S_0$ , and  $K'_s$  the salting out con-

<sup>(8)</sup> A. A. Green, J. Biol., Chem., 93 (1931), 495-541; ibid. 95 (1932), 47-66.

stant apparently independent of temperature and of pH but varying with salts. He obtained later the following experimental equation:

$$\log S - 1.6 \sqrt{C} = 1.30 - k_0 C$$
,

where C is the concentration of the salt and  $k_0$  is a constant which varies with electrolytes.

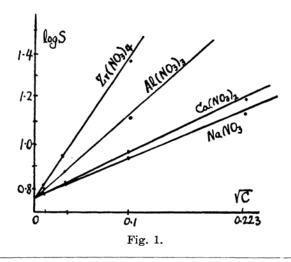
The solubility of sericin on the cocoon in dilute salt solutions has been qualitatively investigated by R. Inoue<sup>(9)</sup> and he showed that the solubility of sericin increased in the presence of a small amount of salts (chlorides, sulphates, carbonates, etc.) and, on the contrary, decreased in concentrated salt solutions.

I also examined the solubility of sericin on the cocoon in salt solutions and obtained the following data: Cocoon layer 2.2 g. (Nichi  $110 \times \text{Shi } 103$ , 1931) were boiled with 100 c.c. of distilled water in a flask with a reflux condenser for 30 minutes, the solution was filtered, and then the solubility of sericin was estimated by the determination of nitrogen contained in the filtrate.

Log  $(S/S_0)$  is not proportional to the square root of concentration,  $\sqrt{C}$ , but it decreases gradually with increasing salt concentration.

$$\frac{\log{(S/S_0)}}{\sqrt{C}} + K_0C = \text{const.} = K \text{ or } \log{(S/S_0)} + K_0C^{\frac{3}{2}} = K_1\sqrt{C},$$

where S is the solubility of sericin in pure water,  $K_0$  and K constants.



<sup>(9)</sup> R. Inoue, loc. cit.

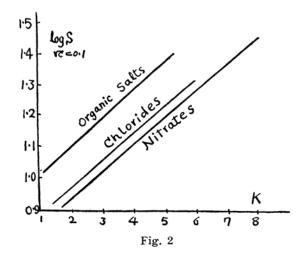
The value of constant K depends on the nature of the cation of the inorganic salt, and it increases with increasing valency of the cation (Table 3 and Fig. 1).

Table 3

Nitrate	K	K <sub>0</sub>	Chloride	K	K <sub>0</sub>
NaNO <sub>3</sub>	1.86	4	NaCl	1.85	10
Ca(NO <sub>3</sub> ) <sub>2</sub>	2.11	4	CaCl <sub>2</sub>	2.34	20
$Al(NO_3)_3$	6.00	50	$AlCl_3$	5.93	60
Zr(NO <sub>3</sub> ) <sub>4</sub>	7.58	50	_		_
		1			

Solutions of sodium salts of organic acids

	K	$K_0$		K	$K_0$
Formate	1.74	2	Oleate	4.52	4
Acetate	1.75	2	Benzoate	1.65	2
Propionate	1.72	2	Benzene- sulphonate	1.60	2
Butyrate	1.715	2	Bitartrate	1.63	2
Valerate	1.706	2	Citrate	2.50	2



The solubility of sericin increases in the presence of small amounts of nitrates, chlorides, or sodium salts of organic acids, and the relation

between the solubility and the concentration is expressed by the same equation:

$$\frac{\log \frac{S}{S_0}}{\sqrt{C}} + K_0 C = K.$$

At the same salt-concentration the values of constant K for salts used are proportional to the logarithm of the solubility of sericin as shown in Fig. 2. In the case of the sodium salts of lower fatty acids the solubility of sericin diminishes slightly with increasing number of carbon atoms in the molecule. The sodium salts of organic acids have stronger dispersing power for sericin than those of inorganic acids and the effect of anions of sodium salts on the solubility of sericin is reversed to the effect of anions on the solubility of fibroin (chloride<bitartrate<acetate<citrate).

## Sec. II. The Relative Viscosity of Colloidal Solutions of Sericin.

There is one property in which hydrophilic colloids like sericin sol differ characteristically from water which acts as their dispersion medium. That is viscosity, and it is found that it increases with, but at a greater rate than, the concentration, showing that there is always some association.

For the measurement of the relative viscosity I used the well known Ostwald viscosimeter with a capillary tube of the inner diameter 0.08 cm.

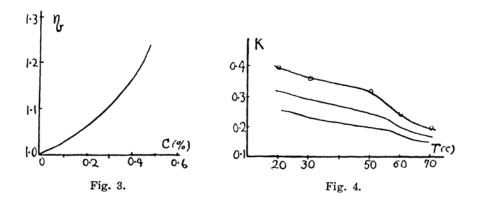
The sericin sol was obtained by boiling about 5 g. of cocoon layers with 200 c.c. of distilled water in a flask with a reflux condenser for 30 minutes. After filtration it was immediately cooled to 20°C. in cold water, and then I measured its relative viscosity after leaving it to stand at 20°C. for 15 minutes.

(1) Variation of Viscosity with Concentration. The viscosities of sericin sols at varying concentrations are shown in Table 4. All these viscosities are expressed in the term of the viscosity of water at 20°C. which is taken as unity.

The slope of the viscosity-concentration curve as shown in Fig. 3 is an indication of the extent to which association between the solute and the solvent has occurred. The rise in viscosity with increasing concentrations is very rapid in solutions of sericin. The viscosity-concentration constant K or  $\frac{\ln \eta r}{C}$  is not strictly constant and increases gradually with increasing concentration of sericin and is given by the equation K = aC + b, where a and b are constants. But K can be considered to be constant in a narrow range of concentration.

Table 4
Relative Viscosity at 20°C., (good "kaijo").

Conc. C(g./100 c.c.)	flow. time t (sec.)	rela. visc. $\eta_r = rac{td}{t_0 d_0}$	visc.—conc. const. $\frac{\ln \eta_r}{C} = K$
0.59	10.34	1.320	$0.2043 \times 2.3 = 0.4699$
0.47	9.74	1.233	0.1935 ,, $= 0.4451$
0.40	9.47	1.185	0.1843 ,, $= 0.4239$
0.38	9.40	1.171	0.1804 ,, $= 0.4149$
0.30	9.00	1.122	0.1666 ,, $= 0.3832$
0.28	9.05	1.115	0.1688 ,, $= 0.3882$
0.107	8.40	1.037	0.1474 ,, = 0.3380
0.00	8.12	1.000	_



Sericin forms molecular aggregates in the aqueous solution and the value of the viscosity coefficient is a function of the volume of the molecular aggregates. For the polymeric organic materials Duclaux proposed the following equation:

$$M = \frac{\ln \eta_r}{C} \times 10^4 = K \times 10^4 \,,$$

where M is the molecular weight of a polymeric material. Staudinger gave the following equation:

$$M = \frac{1}{K_{cm}} \cdot \frac{\ln \eta_r}{C} = \frac{K}{K_{cm}},$$

where  $K_{cm}$  is the molecular weight-concentration constant having a mean value  $5 \times 10^{-4}$ .

$$M = \frac{1}{5}K \times 10^4 \qquad (M > 50000)$$

If the equation of Duclaux holds also for sericin sol, its molecular weight would be 4026 in concentration of about 0.35 per cent. This molecular weight is ten times as great as the value calculated for the empirical formula  $C_{15}H_{25}N_5O_8$  ( = 403.0) of Bowmann.

	а	ь	α	M(C=0.35%)
good "kaijo"	0.2711	0.310	0.0735	4026
middle "	0.2544	0.230	0.0647	3320
bad "	0.2075	0.161	0.0431	2382

Table 5.

$$rac{\ln \, \eta_r}{C} = aC + b \; , \qquad rac{\ln \, \eta_r}{C\Big(C + rac{b}{a}\Big)} = a^2 = a$$

It can be seen from Table 5 that the degree of aggregation of sericin particles obtained from a cocoon having good "kaijo" is greater than that of sericin micellæ obtained from a cocoon having bad "kaijo."

Though the calculated molecular weight depends on the diameter of capillary tube of the viscosimeter used, all correspond nearly to 403 n, where n may be any integer.

Staudinger considered that such an anomalous increase of viscosity would be due to the existence of long chain particles.

Fikentscher<sup>(10)</sup> recently proposed an equation containing a single arbitrary constant, which, although empirical, appears to be superior in general applicability to any hitherto used, namely

$$\frac{\ln \eta_r}{C} = \frac{ak^2}{1 + bkC} + k,$$

where C is the concentration in grams per  $100 \, \text{c.c.}$  of the solution, a, b, and k constants, the last constant k being the arbitrary one, which

<sup>(10)</sup> H. Fikentscher and H. Mark, Kolloid-Z. 49 (1929), 135.

Fikentscher calls "Eigenviskosität." The values of constant k obtained from his equation for hydroxydecanoic acid polymeride are shown in Table 6.

Table U	$\mathbf{T}$	a	bl	e	6	•
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mol. wt.	k	mol. wt.	k
780	0.020	9330	0.058
1710	0.025	16900	0.071
5670	0.042	20600	0.081

Table 7.

temp.	go	od "kaij	o ''		middle			bad	
(C.)	C	K	$k_p$	C	K	$k_p$	C	K	$k_p$
20	0.34	0.4025	0.067	0.34	0.3144	0.059	0.33	0.227	0.049
30	0.35	0.3536	0.063	0.34	0.2860	0.055	0.33	0.246	0.051
50	0.34	0.3200	0.060	0.33	0.239	0.051	0.32	0.211	0.044
60	0.34	0.2301	0.049	0.32	0.202	0.046	0.34	0.188	0.044
70	0.33	0.1925	0.045	0.35	0.1535	0.039	0.38	0.132	0.036

 $(k_p \text{ proper viscosity}).$ 

Both the viscosity-concentration constant K and proper viscosity  $k_p$  decrease with rising temperature (Table 7) and the value of  $\frac{\mathrm{d}K}{\mathrm{d}\,t}$  changes suddenly near 60°C. as shown in Fig. 4. As already described sericin forms molecular aggregates in association with water molecules and this tendency to aggregate diminishes as temperature rises.

The value of K or  $k_p$  for sericin obtained from cocoons having good "kaijo" is always larger than that for sericin obtained from cocoons having bad "kaijo."

The sericin sol which has been obtained from cocoons having good "kaijo" and will have larger aggregation and higher hydration is more easily influenced by the temperature change. The solvation volumes of  $1\,\mathrm{g}$ . sericin, b, calculated from Fikentscher's formula, are also a function of temperature (Table 8). B is the degree of solvation and is equal to b/v, where v is the specific volume.

Table 8.

temp.	goo	od "kaij	o ''		middle			bad	
(C.)	C	b	В	C	b	В	C	b	В
20	0.34	16.2	21.22	0.34	12.6	16.44	0.33	8.1	10.53
30	0.34	14.0	18.34	0.35	12.1	15.79	0.32	8.5	11.05
50	0.36	13.4	_	0.36	9.2	_	0.36	7.1	_
60	0.33	8.2	_	0.36	8.5	_	0.36	7.7	_
70	0.32	6.5	_	0.33	5.2	_	0.33	4.1	_

It can be presumed that above 60°C. the sol form of sericin is present, while below 20°C. the gel form occurs. Between these temperatures both forms will be present in a ratio depending on the temperature and the age of the solution. Hardy considered that the ionized protein had a greater effect on the viscosity of water than the unionized, and, with Pauli and Samec (1909), he attributed this to a greater association between the ionized protein and water.

2. Variation of Viscosity with Time. The viscosity of the sericin solutions in which the formation of colloidal micellæ occurs is not constant, but changes with time, showing there is a gradual change in structure. The increase of viscosity of sericin solutions with time, which ultimately leads to gelatinization, is probably due to separation of finely dispersed precipitate throughout the system.

The effect of time on viscosity is the greatest between 20° and 60°C.. Below 20°C., or above 50°C., the variation of viscosity with time is very small for a few hours (Table 9).

Table 9.

time	0°C.	10°C.	20°C.	50°C.	70°C.
(min.)	0.35 %	0.32 %	0.32 %	0.27 %	0.43%
15	22.21	12.35	9.07	5.94	5.98
30	21.93	12.30	9.36	6.09	6.04
45	21.73	12.50	9.45	6.30	6.17
60	21.64	12.43	9.47	6.66	6.20
120	22.50	12.45	9.50	8.96	6.17
180	22.89	12.50	9.28	9.80	6.23

Above 60°C. the curve runs practically parallel to the time axis; at lower temperatures, an increase in viscosity with the time is clearly noticed. (Fig. 5).

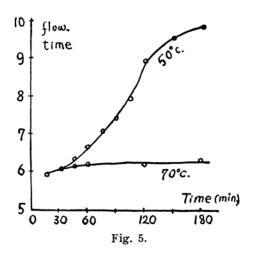
# 3. Variation of Viscosity with Time and Temperature.

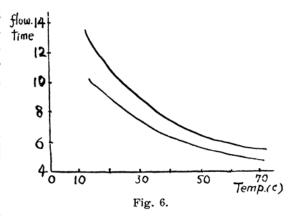
In making a solution of sericin by heating cocoons in distilled water, the sericin dissolved entirely in sol form, which was cooled immediately, and viscosity measurements were made after 15 minutes.

The logarithm of flowing time in sec. of sericin solutions is a linear function of the logarithm of temperatures in centigrade;  $\ln t = \ln \alpha - \beta \ln T$  or  $t = \alpha T^{-\beta}$ , where  $\alpha$  and  $\beta$  are constants (Table 10).

Table 10.

"kaijo"	α	β	conc.	
good	14.1	0.20	0.45%	
middle	12.2	0.18	0.26%	
bad	12.2	0.18	0.28%	





Constant  $\alpha$  depends on the concentration of the sericin solution and constant  $\beta$  on the aggregation of sericin particles.

4. Effect of Acids and Alkalis on the Viscosity. The condition in which sericin dissolves has a considerable effect on the viscosity of the solution. At the isoelectric point the charge of sericin particles is zero, and, since the electro-viscous effect is necessarily minimum at this point, the viscosity must increase both with an increase and with a decrease of the hydrogen-ion exponent.

The relation between the viscosity and hydrogen-ion concentration are shown in Table 11.

Table 11.
Effect of HCl, (at 20°C.).

good (0.185%)		mid. (0.20%)		bad (0.175%)	
flow. time	$p\mathrm{H}$	flow. time	$p\mathrm{H}$	flow. time	pH
8.65	4.665	8.50	4.50	8.29	4.40
8.55	4.060	8.44	4.26	8.21	4.29
8.52	4.025	8.31	4.18	8.20	4.25
8.50	3.985	8.26	4.12	8.16	4.175
8.31	3.960	8.25	4.00	8.31	3.73
8.62	3.520	8.51	3.58	8.34	3.68
8.75	2.810	8.68	2.78	8.50	2.77
8.82	2.450	8.73	2.37	8.58	2.27

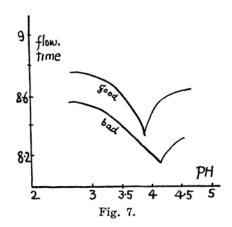


Table 12. Isoelectric point of sericin.

	_		
"kaijo"	0.2 %	0.12 %	
good	3.95	3.80	
middle	4.12	3.97	
bad	4.18	4.08	
I		1 1	

The influence of hydrogen-ion concentration on the viscosity of sericin is reproduced in Fig. 7. As shown in Table 11 the pH value has a much marked effect on the viscosity, the viscosity coefficient for 0.2 per cent. solution of sericin rising from 8.5 at pH 4.0 to 8.82 at pH 2.45. The point of minimum viscosity in sericin coincides with the isoelectric point.

For sericin sol the hydrogen-ion concentration of the isoelectric point varies with the concentration of the protein (Table 12).

Table 13.

vol. added	0.l <sub>N</sub> NaOH	0.ln NH4OH
in c.c.	0.22 %	0.29 %
0	1.080	1.110
0.05	1.130	1.130
0.1	1.105	1.183
0.2	1.085	1.210
0.3	1.071	1.225

The isoelectric point of sericin obtained from cocoons having good "kaijo" is always more acidic than that of sericin obtained from cocoons having bad "kaijo." The viscosity of sericin in alkaline solution increases with the concentration of alkali and attains to the maximum point and falls again with increased hydroxyl-ion activity (Table 13).

5. Effect of Inorganic Salts on the Viscosity. I investigated the effect of inorganic salts which are commonly contained in small amounts in the natural water on the viscosity of the sericin solution (Table 14).

Table 14. (10 c.c. sericin solution +x c.c. salt solution +(2-x)c.c. water).

$\frac{N}{100}$ salt solution added in c.c.	0.08 per cent. sericin solution (at 20°C), flowing time in sec.				
	NaCl	KNO <sub>3</sub>	$\mathrm{MgCl}_2$	CaCl <sub>2</sub>	$\mathrm{FeCl}_3$
0	9.7	9.7	9.7	9.7	9.7
0.1	9.8	9.2	10.2	10.4	10.0
0.3	9.8	9.3	10.8	10.5	10.2
0.5	10.1	9.6	11.2	10.8	10.6
0.7	10.4	10.0	11.6	10.6	11.0
0.9	10.8	10.2	11.8	10.4	10.9
1.1	10.9	10.5	12.2	10.3	10.6
1.5	12.0	10.7	13.5	10.2	10.6

When potassium nitrate is added to a sericin solution there is first a decrease in the viscosity. When more of the salt is added the viscosity continually increases. In the case of calcium chloride and ferric chloride the effect on the viscosity is contrary to the case of potassium nitrate. The viscosity, after passing through a maximum, goes on decreasing. When sodium chloride or magnesium chloride is added to the same solution the viscosity increases with increasing concentration of the electrolyte (Fig. 8).

