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STUDIES ON MECHANISMS OF MANUFACTURING ALGIN

Part V. Amended Theory on Mechanism of Manufacturing Algin*

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Algin was first extracted by Stanford[1] from bladder wrack with sodium carbonate. His process may be described as follows: Drift-weed is macerated, with or without heating, for twenty-four hours with one-tenth of its weight of sodium carbonate. At the end of this period, the plants are completely disintegrated and a very viscous, semi-gelatinous mass is obtained. The alginic acid is precipitated from the filtrate by addition of either sulfuric or hydrochloric acid.

Takahashi[2] reported a new method: he extracted algin with oxalate the same as in the case of extracting pectin because alginic acid fairly resembles pectic acid regarding chemical configuration. It was explained that insoluble alginates such as calcium or aluminium alginate in brown algae were dissolved into soluble alginate by the following double decomposition (1):

$$\text{Ca-Alginate} + \text{M Oxalate} = \text{Ca-Oxalate} + \text{M-Alginate} \quad \cdots\cdots\cdots\cdots (1)$$

where M presents alkali metals or ammonium radical.

He did not accomplish further theoretical investigation. There are available only a few theoretical works regarding the procedure for manufacturing algin, although some improvements of manufacturing method have been reported.

It is usual for algae to be pretreated with water, hydrochloric acid or other solutions for the purpose of extracting potassium salts, iodine, mannit and pigment or other impurities and for algae to be made easy to macerate by treatment with sodium carbonate; however little consideration has been given to converting algin into certain definite form. A report was made in a previous paper[3] on the significance of converting algin into some definite forms e.g., free alginic acid or calcium alginate, pretreating algae with some solutions.

The process of manufacturing algin from brown algae and the theory thereof were reported under the condition of converting algin into free alginic acid and calcium alginate pretreating the plants with hydrochloric acid or calcium chloride solution, in previous papers.[4]-[6] However it is now necessary to amend the theoretical discussion of the mechanism of manufacturing as is described in this paper.

On some modifications in the theoretical discussion or the process of manufacturing algin and the correction of ionization constant of alginic acid, this paper makes a report.

In a previous paper,[4] it was considered that alginic acid was a sort of fairly strong acids and, therefore, its dissolution into soluble alginate was accomplished through a double decomposition between alginic acid and the alkali salt of weaker acd. But it is proved in recent investigation that cation exchange between alginic acid and even the salt of strong acid viz., NaCl or KCl occurs, and the ionization constant of alginic acid reported in the previous paper[4] has to be corrected the order of 10^{-4} to 10^{-5} for the saturated alginic acid solution. It is necessary to amend the theory of the manufacturing mechanism of algin; however, there is no amendment needed respecting the previously reported methods of manufacturing algin from brown algae.[4,5]

Amended theory of manufacturing algin from brown algae is as follows: The cation exchange between electrolytes and alginic acid or insoluble alginates should occur partly or almost completly in any case, and the dissolution of algin proceeds as a peculiar case of the cation exchange reaction.

On the Dissociation of Saturated Alginic Acid Solution

The dissociation degree of alginic acid was determined for the first time by Pauli and Sternbach.[7] Their obtained dissociation degrees of alginic acid were 0.169 to 0.270 in the concentrations of alginic acid 59.7 to 1.6×10^{-3} mol. Seiyama[8] determined the pK values and dissociation degrees of alginic acid. His obtained pK values were 2.87 to 4.60, dissociation degres were 0.285 to 0.316, respectively in the concentration of alginic acid, 11.88 to 0.19×10^{-3} mol. He calculated the above mentioned values from the values of pH; however he calculated the values from the electric conductivities too and the values obtained by both methods were fairly agreed. The author determined the dissociation degree, pH, ionization constant and pK of the saturated solution of alginic acid prepared by his own method[6] and well purified by the ordinary process.

The concentrations of the solutions were determined through the titration curves with 0.01 n NaOH solution. The dissociation degrees were calculated from the values of hydrogen ion concentrations obtained from pH values and the above obtained dissolved concentrations of alginic acid. The pH values were measured by glass electrode pH meter made by MITAMURA SHOTEN. The ionization constants were calculated from pH values as alginic acid consisting of mono-mono-valent mannuronic acid, and the values of pK were obtained from ionization constants.

The above mentioned values obtained from saturated alginic acid solutions are shown in Table 1, where, every solution is prepared being saturated 0.2 g of alginic acid in 100 cc of redistilled water, A represents the solution allowed to stand

Table 1

Solution	Concentration 10^1 mol	2	pH	K	pK
A	2.776	0.102	3.55	3.55×10^{-5}	4.45
B	16.790	0.095	2.80	1.64×10^{-4}	3.78

solution allowed to stand for an hour at 25°C after boiling for three hours.

The titration curve of the A solution is shown in Fig. 1. As the figure shows, the titration curve of alginic acid solution is very characteristic. This fact would be dependent upon the colloidal effect of high molecular electrolyte or upon the existence of carboxylic radicals having various dissociations although that point should be investigated further. For the above mentioned reason, the ionization constants described in Table 1 mean only the average ionization constants of saturated alginic acid solutions. At all events, it may be said that alginic acid is a fairly weak acid. Alginic acid is dissolved to a fair extent in water, that is

Fig. 1. The titration curve of alginic acid solution saturated by boiling for 30 minutes and allowed to stand for 20 hours

to say, about 0.3 g is dissolved in 100 cc of water with boiling for three hours, and this concentrated solution is not transparent but a protein-solution-like opalesque solution.
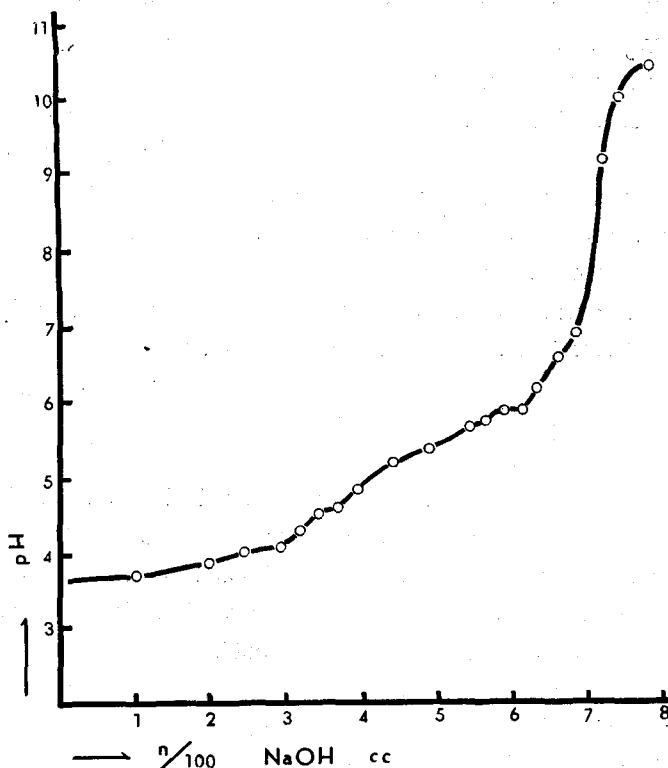
Cation Exchange Reaction of Alginic Acid

Alginic acid is a rather weak acid as described, however sometimes it behaves like a strong acid as follows : Alginic acid dissolves into soluble alginate reacting with many sorts of salts through double decomposition as described in a previous paper, [4] alginic acid liberates iodine from the mixed solution of potassium iodide

and sodium nitrite as a strong acid does and also it liberates sulfur from the solution of sodium thiosulfate, all of which should be explained that the cation exchange between hydrogen ion of carboxylic radical of alginic acid and the cation of the salts takes place in the above-described solutions.

The corresponding acid of the salt would be produced if the cation exchange reaction would occur between alginic acid and a salt following reaction(2):

$$Alg-COOH + KA \rightleftharpoons Alg-COOK + HA \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where K represents a cation, A represents an anion.

A preliminary examination of above-mentioned theory was made as follows: Alginic acid 0.2 g and the equivalent amount of various salts were put into 100 cc of redistilled water and the changes of pH values were measured after duration of an hour, pH value without salts was 4.5. Several results are shown as in Table 2.

Table 2

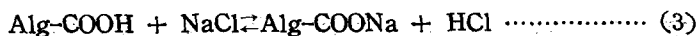| Salt	pH	Remarks
CH₃COONa	4.2	Alginic acid is dissolved entirely within half an hour.
Na₂HPO₄*	4.4	Alginic acid is dispersed into small particles and partly dissoved.
C₄H₄O₄Na₂*	4.1	Same as above.
NaF	4.0	Almost insoluble.
HCOONa*	4.1	Alginic acid is dispersed into small particles and partly dissoved.
C₄H₄O₆KNa	4.0	Alginic acid is dissolved entirely within half an hour.
K₂CrO₄*	4.4	Alginic acid is dispersed into small particles and slightly dissolved.
C₂O₄Na₂*	3.8	Alginic acid is dispersed into very small particles and partly dissolved.
NaASO₂	4.4	Almost dissolved.
Na₂B₄O₇	4.8	Alginic acid is dissolved entirely within half an hour.
NaCl	3.3	Apparently insoluble.
KCl	3.4	Apparently insoluble.

The mixed solutions signed,* in the table, do not form true transparent colloidal solutions because they retain small particles of algin, however, they precipitate fibrous alginic acid gel by adding hydrochloric acid as the case of usual soluble alginate. It is considered that if the cation exchange would proceed and if the reaction is almost or partly reversible the dissolution would not occur, however, alginic acid or algin replaced its cation would be dispersed into small particles. That is to say, the ion exchange reaction between hydrogen ion of carboxylic radical of alginic acid and cation of the salt proceeds until equilibrium is reached.

On the cation exchange reaction concerned with calcium alginate, one of the commonest insoluble alginates, a report has previously been made.[6]

It was also previously reported how the dissolution of alginic acid by the salts of weak acid assumes the reaction of simple double-decomposition.[4] The facts described in that paper are well-established, however, they may be explained by the theory of cation exchange.

The cation exchange equilibrium between alginic acid and NaCl or KCl was

studied as follows. The cation exchange equilibriums may be written respectively following formulas (3) and (4).

$$Alg\text{-}COOH + NaCl \rightleftarrows Alg\text{-}COONa + HCl \quad \cdots\cdots\cdots\cdots\cdots (3)$$

$$Alg\text{-}COOH + KCl \rightleftarrows Alg\text{-}COOK + HCl \quad \cdots\cdots\cdots\cdots\cdots (4)$$

If above mentioned cation exchange reactions occur, hydrochloric acid ought to be produced. Produced hydrochloric acid is determined by neutralization with sodium hydroxide or by titration of Cl ion. Carefully purified alginic acid powder, prepared after the author's method, 0.2 g, and the equivalent amount of NaCl or KCl was put into conical flask and 20 to 80 cc of redistilled water was added. After standing for 20 hours at 20°C, the cation exchange equilibrium was determined following two methods: A) The equilibrium mixtures themselves were distilled by steam till distillate reached 400 cc, and distillates were titrated with 1/40 n NaOH solution to determine acidity and on the other hand Cl ion in distillates was determined by titrating with 1/100 n AgNO₃ solution after MOHR's usual method. B) After removal of matter left after filtration, acidity and Cl ion of the filtrate were determined respectively in same way as above.

The purpose of these two experiments was as follows: Experiment A was done to learn whether the titrable acid was truly hydrochloric acid or not. Experiment B was done to calculate the amount of absorbed electrolyte. The absorbed electrolyte was then calculated
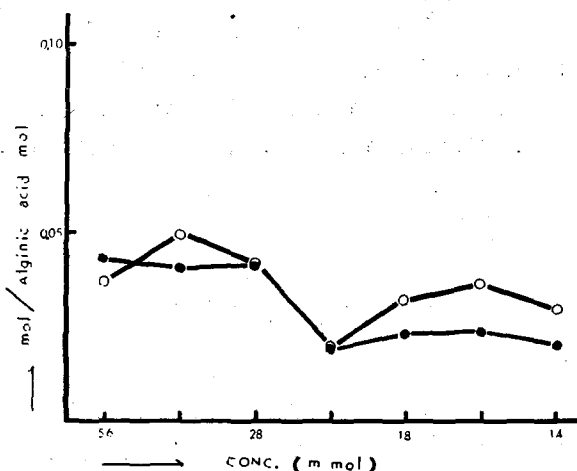

Fig. 2. Produced acid by steam distillation after method A using NaCl
O—O ; calculated from neutralization
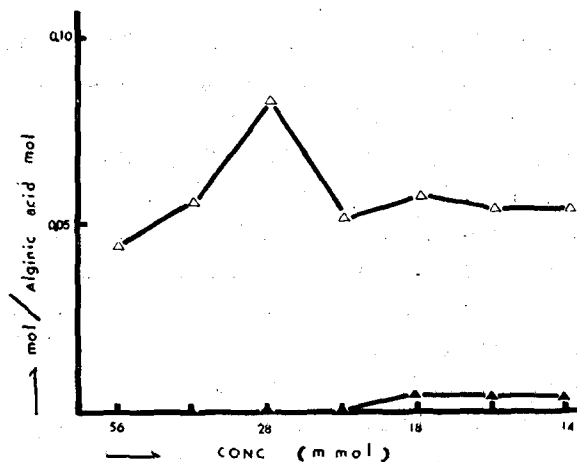●—● ; calculated from the amount of Cl ion

Fig. 3. The amounts of the cation exchange and the absorption of NaCl
△—△ ; the amount of the cation exchange
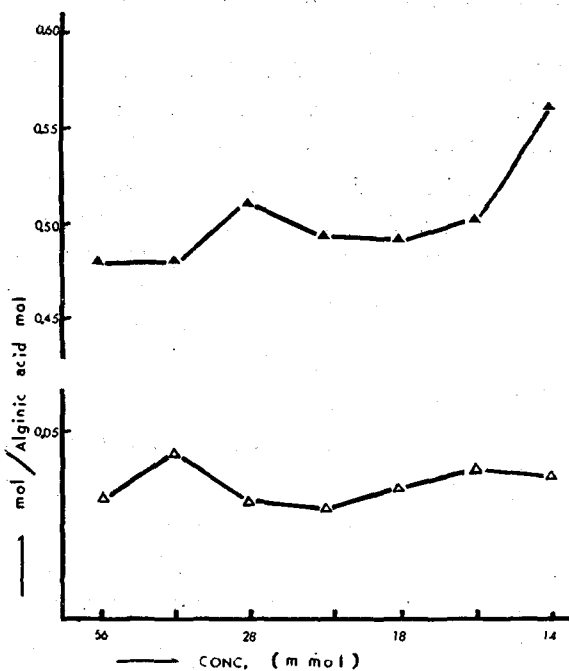▲—▲ ; the absorption of NaCl

Fig. 4.   The amount of the cation exchange
and absorption of KCl

△—△ ; the amount of the cation exchange
▲—▲ ; the absorption of KCl

by subtracting titrated Cl ion of filtrate from total added Cl ion. The results are illustrated in Figs. 2, 3 and 4.

It may be said that produced acid is hydrochloric acid on the agreement of titrated acidity with Cl ion content of distillate as shown in Fig. 2, however the amount of distilled acid is less than that obtained from filtrate directly as shown in Fig. 3. Under the experimental condition, H ion of alginic acid is exchanged with Na or K of NaCl or KCl even in small amount. That is to say, in NaCl solution about 0.45 to 0.08 mol of H ion of alginic acid replaces for 1 mol of alginic acid and in KCl solution about 0.03 to 0.04 mol by cation exchange respectively. The absorbed amount of electrolyte differs in the two cases, NaCl and KCl, as shown in Figs. 3 and 4. In NaCl solution, alginic acid scarcely absorbs the salt, although in KCl solution it does to the amount of about 0.48 to 0.55 mol for 1 mol of the acid.

It is evident that the cation exchange between alginic acid or its insoluble salts and electrolyte does occur. The amended theory regarding the mechanism of manufacturing algin may be described as follows.

Theoretical Discussion on the Mechanism of the Manufacturing Algin

The dissolution of alginic acid or insoluble alginates is considered as special cases of the cation exchange reaction between algin and electrolyte.

The cation exchange between free alginic acid and electrolytes occurs under the equilibrium of formula (2) as above mentioned.

As alkali metal–, ammonium– or magnesium–alginates are soluble, if K, written as M hereafter, is one of these cations the reaction would proceed to dissolve alginic acid into soluble M–alginate when the reactions are completely or nearly irreversible. The electrolytes, MA, which make the reaction (2) completly or nearly

irreversible are those having anion OH$^-$ or fairly weak acid radical as described in previous paper. [4]

The cation exchange between insoluble alginates and electrolytes occurs under the equilibrium of following reaction which is based on the same principle:

$$\text{Alg--COOX} + \text{K'A'} \rightleftarrows \text{Alg--COOK'} + \text{XA'} \quad \cdots\cdots\cdots\cdots\cdots (5)$$

where Alg--COOX presents insoluble alginate, K' and A' present respectively cation and anion. If K' is one of M and the ion exchange reaction is completely or nearly irreversible, the insoluble alginate is dissolved into soluble M--Alginate. These electrolytes are shown in previous paper. [3] The recommendable methods of manufacturing algin are described later.

The Methods of Manufacturing Algin

It is desirable to convert algin in brown algae into definite form manufacturing algin as above described, because algin in brown algae exists in various types of combination, such as insoluble salts and other complex compounds. It is a practically useful method to pretreat algae with hydrochloric acid or calcium chloride solution converting algin respectively into free alginic acid or calcium alginate. The outline of the recommendable manufacturing methods employing thus pretreated algae are described again although these methods were previously reported in Japanese. [4)6]
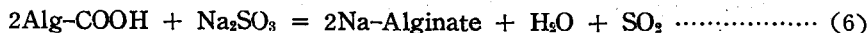
A) The manufacturing process pretreating with diluted hydrochloric acid

Alginic acid is dissolved into soluble alginate by hydroxide or carbonate of alkali metals, ammonium or magnesium and a number of salts of fairly weak acid as described in Table 3 because the cation exchange equilibrium between these electrolytes and free alginic acid are completely or nearly irreversible. A new recommendable process of manufacturing algin has been found as follows: Alginic acid is dissolved into Na--alginate by Na_2SO_3 because produced SO_2 escapes out of the system and the equilibrium of the reaction proceeds completely following reaction (6).

Table 3

M_2SO_3; $MHSO_3$; $M_2S_2O_3$; Rochelle salt; CH_3COOM; M_2CO_3; $MHCO_3$; $MAsO_2$; $M_2S_2 + x$; MBO_3; $M_2B_4O_7$; MCN etc.

$$2\text{Alg--COOH} + Na_2SO_3 = 2\text{Na--Alginate} + H_2O + SO_2 \quad \cdots\cdots\cdots\cdots\cdots (6)$$

The reaction proceeds keeping the acid, and the filtration is very easily done because of decreasing viscosity of macerated solution. Furthermore, because of the formation of SO_2, the solution is prevented from decomposition by microorganism and algin is bleached.

Practical application of manufacturing algin from brown algae with Na_2SO_3 is briefly described as follows.

In order to convert various types of algin in brown algae into free alginic acid, the algae are treated with 0.1 n HCl solution for 15--30 minutes at 50--60°C. After

removal of acid solution, 15% of Na_2SO_3 by weight of dried algae and 30 times that weight of water are added to remaining algae and heated for an hour at 60–70°C; then the bodies of the algae are completely disintegrated.

B) The manufacturing process by pretreating with $CaCl_2$ solution

Calcium alginate is dissolved into solube alginate when the following reaction (7) is completely or nearly irreversible.

$$Ca-Alginate + MA \rightleftharpoons M-Alginate + CaA \quad \cdots\cdots\cdots\cdots\cdots (7)$$

Several examples of these electrolytes are shown as in Table 4. A new recommendable process pretreating algae with $CaCl_2$ solution is described as follows: Brown algae are treated with boiling water for 15–30 minutes to swell the plants and to remove soluble matter and other impurities. After removal of water, the plants are treated with 0.5% $CaCl_2$ or saturated $Ca(OH)_2$ solution for 15–30 minutes at 80–100°C to convert algin in brown algae into Ca-alginate and to fix the pigment of the cortex, making it insoluble. Rejecting the extract the plants are treated with 0.5% NaCl solution for 30–60 minutes at 80–100°C. Within this period, Ca-alginate swells and Na-alginate is partly produced by cation exchange reaction, while the pigment is left in the plants. Without drawing off the extract, plants are macerated with Na_2CO_3 in the quantity of 10% weight of dried algae for 10–20 minutes with gentle stirring. Allowing to stand for several hours, produced sodium alginate is dissolved into solution although the pigment is left in the epidermis without dissolution. The colour of the algin thus obtained is almost white without any bleaching process and its viscosity is very high owing to the weak attack of alkali solution. The filtration of macerated algae is very easy because epidermis and other mucilages are scarcely dissolved. The author proposed to name this "SUZUKI's Method" in previous paper.

Table 4

M_2CO_3; MHCO$_3$; M_2HPO_4; M_3PO_4; M_2SO_3; (COOM)$_2$; MF; M-silicate etc.

Summary

1) Under several conditions, the solubilities, ionization constants, dissociation degrees, pH values and pK values of saturated alginic acid solutions are determined. It is proved from the detemations of above mentiond values that alginic acid is a fairly weak acid.

2) The titration curve of alginic acid with sodium hydroxide is very characteristic, however, the reason of these phenomena is not cleared yet.

3) The amended theory of manufacturing algin from brown algae is described from the viewpoint of the cation exchange reaction.

4) Recommendable processes for manufacturing algin in actual are described.

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