High Viscous Alginic Acid

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Introduction

Algin industry is a chemical industry newly developed in postwar Japan, and is regarded as a promising export industry in which seaweed is used as its raw material.

Many problems; however, remain to be solved. Especially maintaining the high viscosity of alginate through manufacturing processes is of great importance since this is the property to be utilized in most practical applications. The purpose of the present research is, by studying some properties of pure alginic acid and its salts, to confirm what causes the high viscosity and thus to make a contribution to the algin industry.

Alginie acid is a highly polymerized mannuronic acid in which the aldehyde groups of *d*-mannuronic acid are linked in β-glucoside bindings. The characteristic of this compound is the fact that in that one carboxyl group on each unit of monomer is free to react.

Owing to the various characteristics of alginic salts, this substance has lately been most effectively put in practical uses extensively in many fields, as foodstuffs, industrial and medical uses, toilet articles, etc.

Viscosity Measurement

A new viscosimeter of constant shearing force type (modified type of Ostwald's capillary viscosimeter) has been designed for a solution of alginate by Dr. Hajime Okada, and universally used in the algin industry of Japan. Experiments with various solutions revealed the fact that a viscosimeter of this type was suitable for measuring the viscosity of non-Newtonian fluid such as alginate. This apparatus is shown in Fig. 1. The liquid level head can be adjusted to obtain the desired shearing force, by moving up or down the capillary tube.

In this viscosimeter, the maximum shearing force is taken to be 27.6 dyne/cm. and in accordance with the length and diameter of capillary, the level head is determined as follows and the mark is graduated on the capillary tube

$$\text{Maximum shearing force}=27.6=PR/2L$$
$$=H\cdot g\cdot R/2L=980\cdot H\cdot R/2L \qquad (1)$$

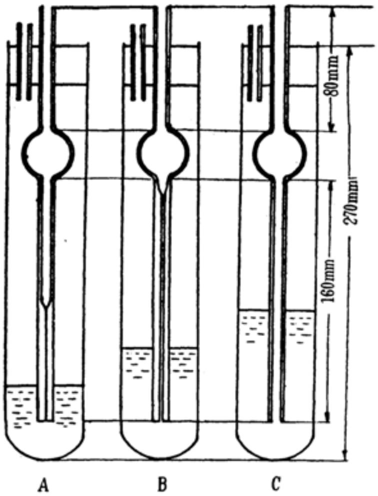

Fig. 1. A new viscosimeter of constant shearing force.

Each tube (A, B, C) should have a definite level head, which can be calculated from diameter and length of capillary.

$$H=27.6\times(2/980)\times L/R=0.05633\,L/R\text{ cm.} \qquad (2)$$

here, P=pressure

H=head of level

R=radius of capillary

L=length of capillary

Since the magnitude of viscosity of alginate solution changes from a few centipoises to poises, the viscosimeter tubes with different diameter of capillary are necessary. In such cases, each tube should have a definate level head, which can be calculated from diameter and length of capillary according to the above equation (2).

Viscosity Characteristics

Sodium alginate is a typical heteropolar high-molecular electrolyte having the following viscosity characteristics:

(1) The viscosity of the aqueous solution of alginate becomes maximum at the vicinity of neutral point. According to E. Heen[1], the electric charge of colloidal particles becomes maximum, so that the polar adsorption, hydrating property and viscosity suc-

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[1] E. Heen, *Koll. Z.*, **83**, 204 (1938).

cessively increase. This is the theory which explains the enormous viscosity due to "Elektroviskosen Effect".

Otherwise, H. Staudinger[2] estimated the phenomenon to be "Poly-ionische Viskositätserscheinung", i.e., by electrostatic action of high-valency colloidal ions, they agglomerate and viscosity increases.

(2) In the relation between reduced viscosity and concentration, the minimum point occurs at a certain diluted concentration. This phenomenon is not found on the homopolar high-molecular substance, so that it is due to the effect of ionized ions.

(3) If low-molecular electrolyte such as sodium carbonate or sodium chloride is added, the above minimum vanishes. This example is shown in Eig. 2. According to W. Kern[3], reduced viscosity increases in the region of sol and gel, and then at the boundary becomes minimum. In the sol region "Ionaler Faktor" and in the gel region "Makromolekular Faktor" act powerfully.

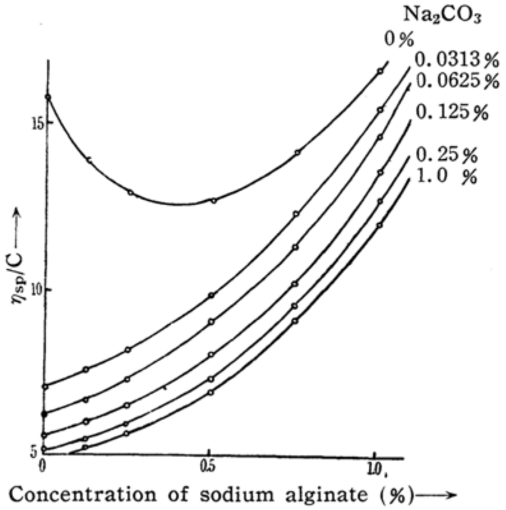

Fig. 2. Effect of addition of sodium carbonate on the relation between reduced viscosity and concentration.

Reduced viscosity=("Ionaler Faktor")
×("Makromolekulaler Faktor")

In the existence of low-molecular electrolyte, the "Ionaler Faktor" approaches to one, so that "Makromolekulaler Faktor" controls all the region.

The critical viscosity (at the transition point between sol and gel) of the aqueous solution of sodium alginates of different origin was measured and found to be about 3.5 to 3.6 c.p. The fact verifies the Staudinger's theory that the critical viscosity has the same value in lower-molecular as well as in high-molecular compound, if the compounds belong to the same homologue,

When the sodium carbonate is added until its concentration attains to 0.031%, the aqueous solution of sodium alginate shows no more minimum point in reduced viscosity-concentration curve. The reason is that the electric charge of the alginate particle is discharged by sodium ion added and has no characteristics of heteropolar high-molecule.

Viscosity and Temperature

Generally, according to Andrade[4], the viscosity of fluid has a relation against temperature as following equation:

$$\eta = Ae^{Q/RT} \tag{3}$$

here, η=relative viscosity
T=absolute temperature
R=gas constant
Q=activation energy

$$\log \eta = \log A + Q/4.574T$$

The viscosity measurement of an aqueous solution of sodium alginate at various temperature shows that the relation between the viscosity and temperature of such a non-Newtonian fluid may be expressed by Andrade's equation. The Fig. 3 shows the examples.

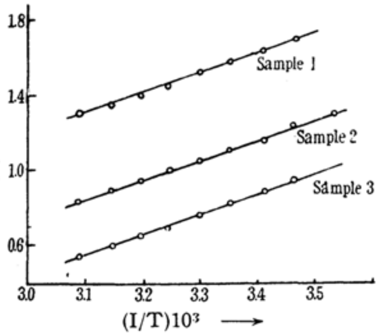

Fig. 3. Relation between log η and I/T. From inclination of staight line against abscissa, the activation energy can be calculated.

The activation energy (Q) for the fluidity of 1% solution of sodium alginate, when computed from the above equation, is approximately 5,000 cal. with some variations according to the concentration and viscosity of the solution.

Viscosity and Concentration

Many equations had been proposed by Einstein, Mark and Fikentscher, Arrhenius[5],

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[2] H. Staudinger, *Ann.*, **502**, 201 (1938).
[3] W. Kern, *Z. Phys. Chem.*, A, **153**, 391 (1931).
[4] Andrade, *Nature*, **125**, 580 (1930).
[5] Arrhenius, *Z. Phys. Chem.*, I, 285 (1887).

Baker, Philippoff and Hess, Bredee Bergenand Booys, etc.

When applied to sodium alginate solution, Arrhenius' equation (4) gives value appropriate only at a high concentration. Especially when the alginate solution does not contain low molecular electrolyte, the deviation from the Arrhenius' equation becomes conspicuous.

$$\log \eta = k \cdot c \tag{4}$$

The Arrhenius' equation can not express the relation of viscosity and concentration (c) of the solution of heteropolar high-molecule such as sodium alginate, of which the viscosity is due to the ionic high molecule.

The Baker's equation⁶⁾,

$$\eta = (1+ac)^k \tag{5}$$

gives values that agree fairly with observed ones. However, the Baker's equation is not satisfied at a high concentration, contrary to Arrhenius' equation.

From the point of view of the two regions of sol and gel, there is no identical equation applicable through high and low concentration.

According to the author⁷⁾, in the lyophile colloidal solution such as alginate or carrageen, of which the viscosity is due to hydration with water, the viscosity may behave against concentration such as the depression of surface tension versus concentration. According to Freundlich's equation, it is able to express as following:

$$\eta_{sp} = \eta - 1 = \alpha \cdot c^{1/n} \tag{6}$$

$$\log \eta_{sp} = \log \alpha + (1/n) \cdot \log c \tag{7}$$

Schematically the relation between viscosity and concentration has two equations of the same type, only the value of constant, being different, as shown in Fig. 4.

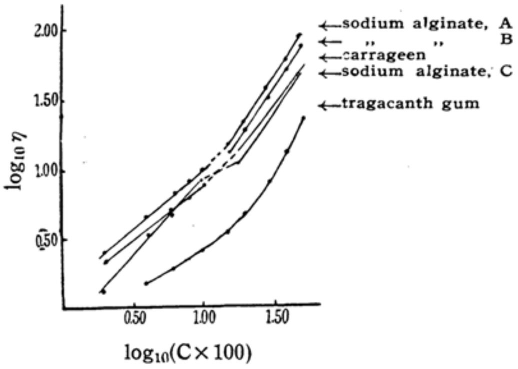

Fig. 4. Relation between viscosity and concentration has two equations of the same type, only differing the value of constants.

The critical concentration, which divides the equation into two, is about 0.15% and it coincides with the concentration, at which the hydration of alginate reaches maximum.

Recently Tetsuro Seiyama⁸⁾ proposed the following equation:

$$\eta = 1 + (a \cdot \phi \cdot c + A \cdot c^{1/2})/(100 - a \cdot c) \tag{8}$$

In this equation, the viscosity is assumed to be a linear function of $c^{1/2}$ under the assumption that the ionic atmosphere of high-molecular electrolyte is like that of low molecular electrolyte.

Colloidal State of Sodium Alginate in Aqueous Solution

In an aqueous solution of sodium alginate, the colloidal particle hydrates and swells. The Einstein's equation is derived dynamically from volume occupied by the solute particle, so that conversely, the specific volume of solute in solution can be computed theoretically from the equation.

According to Ichiro Sakurada⁹⁾, it follows by expansion of Baker's equation,

$$\eta = (1+ac)k = 1 + akc + [k(k-1)/2]a^2c^2 + \tag{9}$$

In diluted concentration, it may be allowed to neglect the term c^2 and follows,

$$\lim_{c\to0} \eta = 1 + akc \tag{10}$$

also from Einstein's equation,

$$\lim_{c\to0} \eta = 1 + 2.5\ (fc/100) \tag{11}$$

so that it follows,

$$ak = (2.5/100) \cdot f, \text{ or } f = 40 \cdot a \cdot k \tag{12}$$

By applying the equation (12) on alginate solution, the authors calculated the specific volume (f), which is shown in Fig. 5. The value of f decreases radically until the concentration of sodium carbonate approaches

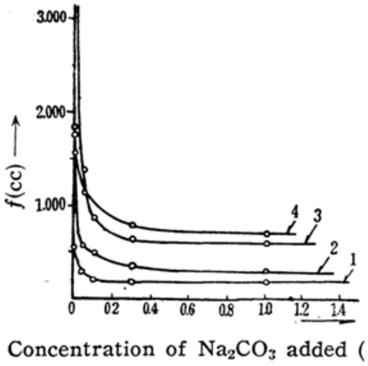

Fig. 5. Relation between specific volume and concentration of Na_2CO_3.

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6) F. Baker, *J. Chem. Soc.*, **103**, 1653 (1913).

7) T. Takahashi, *Report of Imperial Industrial Research Laboratory*, **28**, No. 5 (1933).

8) T. Seiyama, *J. Ind. Chem. Japan*, **52**, 300 (1949).

9) I. Sakurada, *J. Ind. Chem. Japan*, **35**, 1103 (1932).

0.3% and then takes the constant value, differing with the polymerization degree.

Computing from the above value, we know that 1 g. of pure highly-polymerized sodium alginate can fix water of about 3,500 cc. in volume.

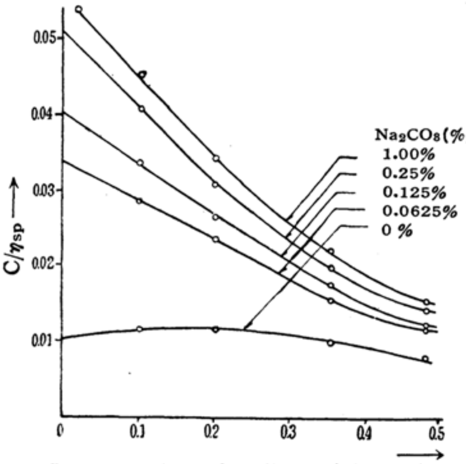
Fikentscher's equation⁽¹⁰⁾,

$$\eta=1+a\cdot\phi\cdot c/(100-\phi\cdot c) \qquad (13)$$

is transformed as follows:

$$c/\eta=100/a\phi-c/a \qquad (14)$$

From the $c/\eta-c$ curve shown in Fig. 6, the values of $100/a\phi$ and $1/a$ can be calculated respectively.



Concentration of sodium alginate (%)

Eig. 6. Relation between reciprocal of reduced viscosity and concentration.

As a result, the value of a takes 6.5 to 8 at 1% of sodium carbonate, even if the polymerization degree of alginate differs greatly. If the particle is a spherical and non-electric body, the value of a is 2.5, according to Einstein's equation. This result shows distinctly that the particle of alginate must be in a bar shape.

Kuhn's equation (15)⁽¹¹⁾ refers to a bar molecule.

$$\eta=1+[2.5+(1/16)(1/d)^2]\cdot\phi\cdot c/100 \qquad (15)$$

here, 1 = length of a bar particle

d = longitudinal diameter in cross section of a bar particle

Placing

$$a=2.5+(1/16)\cdot(1/d)^2 \qquad (16)$$

or $\qquad 1/d=4\sqrt{a-2.5}$

and putting the above value of a into equation (16), the value of $1/d$ of sodium alginate becomes 8 to 9. The colloidal particle of alginate, therefore, seems to change its shape into a spheroid with major axis about 8 to 9 times the minor axis, if electrolyte, for example sodium carbonate, is added by 1% to the solution.

Electric Conductivity

The high molecular electrolyte is polyvalent as well as colloidal, and therefore its behaviour differs from the common electrolyte. The dissociation property can be studied by measuring either hydrogen ion concentration or electric conductivity, but on the high molecular electrolyte such as sodium alginate, the electric conductivity is the only method for investigation of dissociation.

On the purification of sodium alginate for measurement of conductivity, the method of coagulation by methanol is the most effective in removing the foreign minerals and other impurities. It takes at least three times of operation for purification to obtain alginate pure enough for electric conductivity measurement.

From the observed conductivity, the equivalent conductivity is computed according to the following formula:

Equivalent conductivity $=1{,}000\ k/c$

here, k = specific conductivity

c = equivalent concentration

The examples of experiments are shown in Fig. 7. Alkali metals and ammonium salts of alginate in aqueous solution were found to show the typical characteristics of poly-valent colloidal electrolytes, i.e., the equivalent conductivity (λ) increases with the dilution of the solution, while, if furthermore diluted, it becomes constant or decreases.

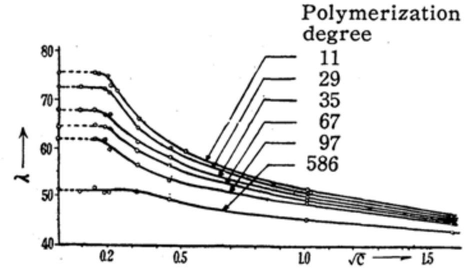


Fig. 7. Relation between equivalent conductivity and square root of concentration of sodium alginates having different polymerization degree.

The above phenomenon was already indicated as showing characteristics of high molecular electrolyte such as sodium alginate by Pauli and Sternbach⁽¹²⁾ and Seiyama⁽¹³⁾.

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10) H. Mark and H. Fikentscher, *Koll. Z.*, **49**, 135 (1929).

11) W. Kuhn, *Z. Phys. Chem.*, *A*, **158**, 78 (1931).

12) W. Pauli and Sternbach, *Koll. Z.*, **84**, 291 (1938).

13) T. Seiyama, *J. Ind. Chem. Japan*, **53**, 122 (1950).

According to the present authors[14] the equivalent conductivity decreases with increase of polymerization degree. If the equivalent conductivity takes a constant value at very much diluted solution, the ultimate equivalent conductivity (λ_0) may be extrapolated. When the λ_0 is plotted against a logarithm of polymerization (n), as shown in Fig. 8, the linear relation exists between equivalent concuctivity and logarithm of polymerization degree.

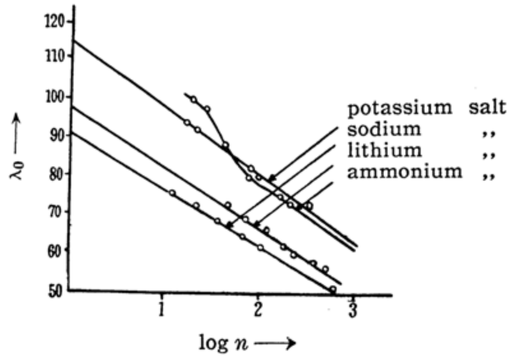

Fig. 8. Relation between equivalent conductivity at infinite dilution and logarithm of polymerization degree.

$$\lambda_0^n = \lambda_0^1 - k\log n \tag{17}$$

Here λ_0^n, λ_0^1 are equivalent conductivities at infinite dilution of alginate of polymerization degree n and 1, and k is the constant.

The above relation fits in case of alkali metals as well as magnesium and triethanolamine alginates.

Dissociation of Alginate

The equivalent conductivity decreases as the polymerization degree increases. This fact is to be interpreted as a result of change of ionic activity in high molecular electrolyte. Generally, the high molecular electrolyte has numerous ionic valency, so that it dissociates step by step, and it is impossible to apply the mass action law to dissociation of high molecular electrolyte as in the case of low molecular electrolyte.

According to Pauli and Valko[15], the dissociation degree is defined as average dissociation degree, and it is varied by distance between ionic radicals, i.e., density of ionic radicals in yarn-like molecule.

Furthermore, the ionic activity has a great role in dissociation of high molecular electrolyte. The alginate particle is not in the shape of a straight bar, but may dissolve in form of " Knäuel ". As the polymerization degree increases, the density of ionic radicals increases and ionic activity decreases. This relation is shown in Fig. 9.

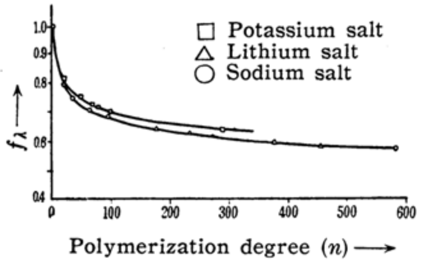

Fig. 9. Relation between coefficient of ionic activity (f_λ) and polymerization degree.

The sodium ion may be restricted in inner structure of colloidal ion of alginic acid, and as the polymerization degree increases, the activity of sodium ion decreases.

The ionic activity of alkali alginates decreases with increases of n, and this relation may be represented by equation (18):

$$f_\lambda^n = f_\gamma^l - K\log n \tag{18}$$

here f_λ^n and f_λ^l denote the coefficients of ionic activity when $n=n$ and $n=1$ respectively, and K is a constant that depends on the concentration.

Furthermore, by measuring ashes in sodium alginate, the relation between the degree of ionization and n of alginic acid was also proved to be represented by an equation similar to the above.

The alginic acid dissociates partially in the aqueous solution and its chain molecule forms a " Knäuel ". In its central part, the ionic radical is suppressed to ionize under the influence of ionic charge on the surrounding part, and retains the form of its inactive state.

When alkali acts upon alginic acid, at first the neutralization occurs on free and active ionic radicals in the outer part of alginic acid. As the neutralization proceeds, the ionic radical which formed salt, dissociates completely and the molecule expands owing to repulsive action among the negatively charged ions. Thus, the molecule decreases its ionic density, and approaches to the complete dissociation.

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[14] T. Takahashi and K. Kimoto, *Rep. of the Institute of Industrial Science* (Tokyo Univ.), **1**, No. 4 (1951).

[15] W. Pauli and Valko, *Elektrochemie der Kolloide*, 73 (1929).