Colloid Chemical Studies on Starching Materials. I. Structural Viscosity of Poly-Vinyl Alcohol Solution[*]

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As a starching material for clothes, poly-vinyl alcohol has recently been used. The colloid chemical studies interest as from both scientific and practical stand-points. As for the solution of high polymers, it has been already known that the structural viscosity is observed even for fairly dilute solutions. It has also been known that the poly-vinyl alcohol solution has structural viscosity, at least for concentrated solutions. If an anomalous viscosity named as structural viscosity is the result of the viscoelastic properities of the solution, then, it is desirable to separate the observed apparent viscosity into two parts, viscosity part and elasticity part, and to consider, e.g., intrinsic viscosity about the pure viscosity part.

Experimental

As samples of poly-vinyl alcohol, six pure specimens provided by Nippon Gosei Kagaku Kogyo K.K. are used; that is, Gohsenol GH–20, GM–14, GL–05, NH–20, NM–14 and NL–05. In them, G means that the saponification value is 90±2%, and N means that the saponification value is 99–100%. They are white powder. The purity was 98% or better. The mean polymerization degree was determined by viscosity method using Sakurada's equation. About 0.8 g. of the specimen was warmed with 100 cc. of distilled water and dissolved in it and set alone for eight hours. 10 cc. of supernatant solution was put into the Ostwald's viscometer, and viscosity was measured at 20°C. On the other hand, 20 cc. was heated until dry, and the concentration C (g./l.) was measured. Using Sakurada's equation[1]:

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[1] Sakurada, *J. Chem. Soc. Japan* (*Engineering Sec.*), **47**, 135 (1944).

$$[\eta]=2.303 \log \eta_r/C$$

$$\log \rho=1.613 \log\left(\frac{[\eta]\times 10^4}{8.87}\right) \quad (1)$$

the average polymerization degree ρ was obtained. The average polymerization degree was 2,000 for H–20, 1,400 for M–14 and 500 for L–05.

Gohsenols were dried for one hour in an electrical drying oven at 110°C and cooled and kept in deisccator. It is said that four hours' warming at 40–50°C is necessary, in order to dissolve them completely in water. In this paper, however, the following method of dissolution was adopted, considering the practical method of dissolution of starching materials. A specimen weighed accurately was kneaded with a small amount of distilled water, hot water of 90°C was added under constant stirring, and the volume was made up to a nearly necessary amount. This was warmed on a water bath at 90°C for five minutes with continuous stirring. Then the volume of the solution was accurately made up, after it was kept at room temperature to cool. The concentration range measured was 0.2–5.0%.

The structural viscosity was measured with an Ostwald type over-flow viscometer, which was used before by one of authors[2]. It was a vertical type viscometer having a capillary of 21.2 cm. in length and 0.67 mm. in inner diameter. The amount of flow, Q (cc./sec.), was measured for each hydrostatic pressure difference, P (cm. H_2O). For liquids without structural viscosity, Poiseille's law has been verified for this viscometer. As stated in the previous paper, the viscosity coefficient is calculated by the equation,

$$\eta=2.57\times 10^{-5}\times P/Q \text{ (g./cm./sec.)} \quad (2)$$

The range of the pressure difference measured was 4–23 cm. H_2O.

As shown in the previous paper, the viscosity coefficient obtained from Eq. (2) shows a linear relation to the reciprocal of the rate of flow, $(1/Q)$, for some solutions having structural viscosity, such as V_2O_5-sol and Hg-sulfosalicylate-sal. For the apparatus used, the linear relation is expressed:

$$\eta=\eta_N+2.57\times 10^{-5}\times P_0/Q \quad (3)$$

where η_N(g./cm./sec.) and P_0 (cm.H_2O) are constants. P_0 is thought to be a pressure to destroy the net-work structure in the solution, and corresponds to a yield value. η_N corresponds to a Newtonian viscosity of distroyed structure. η_N depends pronouncedly on the history of the solution, while η_N does not depend on the history.

Results and Discussion

The same structural viscosity as cited above was observed also for poly-vinyl alcohol solution. Fig. 1 is an example of data for 2% solution of NH–20, where the variation of apparent viscosity by the history of solution is shown. For example, a solution used to measure its viscosity has been kept for some days, and again the viscosity is measured. Then a different value is obtained. In the case shown in Fig. 1, it seems that the viscosity gradually increased, but in other cases, the viscosity decreased. Curve 3 was obtained after stirring the sample of curve 2 for thirty minutes at room temperature. The distinct increase of viscosity by stirring was observed.

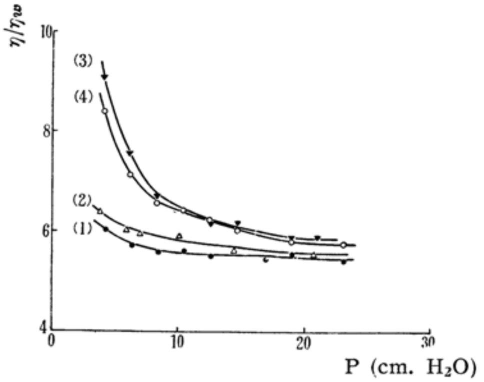

Fig. 1. The stractural viscosity of 2% Gohsenol NH-20. after the preparation of solution: (1) 1 hr (2) 72 hrs: (3) 72 hrs (stirred 30 min.): (4) 96 hrs.

These data are recalculated and plotted in Fig. 2 as a relation between (η/η_w) and and $(1/Q)$. The linear relation of Eq. (3) is certified. Moreover, Fig. 2 shows that the variation of apparent viscosity with the history of the specimen is due to the variation of the apparent yield value, P_0, while the Newtonian viscosity, η_N, does not change. The apparent yield value of the specimen of curve 2 was 0.59 cm. H_2O, which increased to 1.65 cm. H_2O by stirring for thirty minutes as shown in curve 3. This suggests the growth of net-work structure. Anyway, the treatment (e.g. stirring) is more effective than the duration of time.

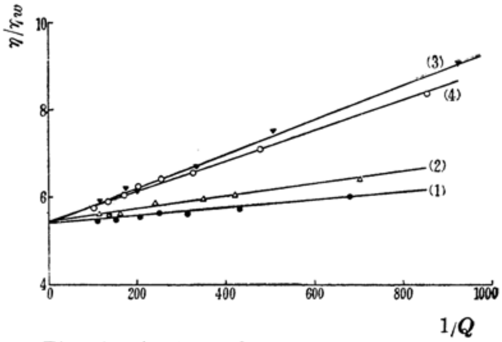

Fig. 2. $(\eta/_w)-(1/Q)$ relation recalculated from Fig. 1.

For each Gohsenol specimen, structural viscosity is measured at various concentra-

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[2] M. Nakagaki and S. Sakata, *Bull. Chem. Soc. Japan*, **27**, 548 (1954).

tions. Every data showed the linear relation of Eq. (3). Values of two constants of Eq. (3), Newtonian relative viscosity (η_N/η_w) and apparent yield value P_0, are shown in Figs. 3 and 4. (η_N/η_w) increases monotonously with the increase of concentration, while P_0 shows no definite trend for concentration. This is reasonable, since P_0 is a sensitively dependent quantity on the history of a specimen.

On the viscosity of poly-vinyl alcohol solution, E. Tsuruta and M. Takeda[3] found the following relation:

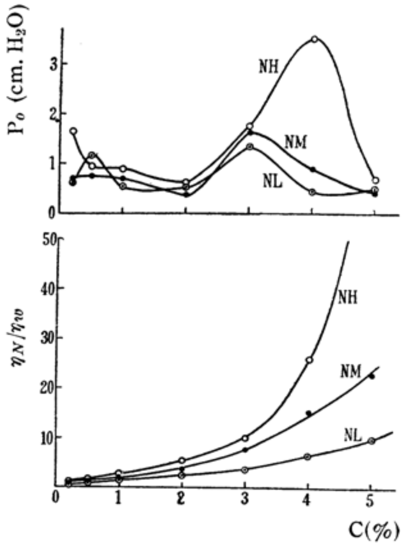

Fig. 3. (η_N/η_w) and P_o for Gohsenol N.

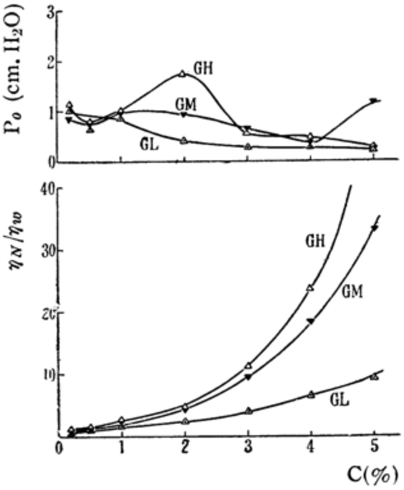

Fig. 4. (η_N/η_w) and P_o for Gohsenol G.

$$\eta_{sp}/C=[\eta]+k'[\eta]^2C \qquad (4)$$

for the concentration range of 0.1–1%. The Present experiment, shown in Figs. 3 and 4, covers wider concentration range, and does not satisfy Eq. (4). While, the value of $[\eta_N]$ calculated by the following equation:

$$[\eta_N]=\ln(\eta_N/\eta_w)/C \qquad (5)$$

is constant in the range of 0.2–5.5%. The constancy of Eq. (5) has been already stated by Sakurada[1] and others[4]. The mean value of $[\eta_N]$ obtained is shown in Table I.

In Sakurada's Eq. (1), the concentration C is given in g./l., so it is recalculated to %, and

$$[\eta_0]=8.87\times10^{-4}\times\rho^{0.62} \qquad (6)$$

is obtained. As shown in Table I, the value of $[\eta_0]$ from this equation are greater than the values of $[\eta_N]$ cited above. It is generally accepted that the intrinsic viscosity is proportional to the volume occupied by the solute in the solution. For example, the molecular extension is greater and intrinsic viscosity is greater in a good solvent than in a poor solvent[5]. It is assumed that Sakurada's intrinsic viscosity $[\eta_0]$ of Eq. (6) corresponds to a completely dissolved state. Then, the smaller value of $[\eta_N]$ than $[\eta_0]$ means the incomplete dissolution or incomplete molecular extension; e.g. some parts of high polymer may not be dispersed to molecular dissolution but they may suspend as crystallites. In the present experiment, solution is heated only fifteen minutes at 90°C, while it is generally said that four hours warming at 40–50°C is necessary to obtain a complete dissolution[3]. Then it is assumed that y (%)

$$y=\left(\frac{[\eta_0]-[\eta_N]}{[\eta_0]}\right)\times100\ (\%) \qquad (7)$$

TABLE I

Specimen Marks	Specimen ρ	Temp (°C)	$[\eta_N]$
NH	2000	14.0±0.9	0.828±0.010
NM	1400	14.1±1.7	0.627±0.013
NL	500	18.4±1.1	0.454±0.009
GH	2000	12.6±2.1	0.857±0.024
GM	1400	14.4±2.5	0.717±0.017
GL	500	15.8±1.3	0.456±0.014

	$[\eta_0]$ Eq. (6)	y (%)	After 4 hr'. warming $[\eta_N]$	After 4 hr'. warming y (%)
NH	0.985	15.9	0.838	14.9
NM	0.800	21.7	0.783	2.1
NL	0.426	~0	—	—
GH	0.985	13.0	—	—
GM	0.800	10.4	—	—
GL	0.426	~0	—	—

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[3] E. Tsuruta and M. Takeda, *J. Chem. Soc. Japan (Pure Chem. Sec.)*, **74**, 191 (1953).

[4] For example, K. Hirabayashi, "Poval" (1952), p. 54.

[5] K. Yoshioka, "Review of Recent Colloid Science", (1950) Vol. 2, p. 36.

corresponds to the fraction of incomplete dissolution. These values are also shown in Table I. It is shown that the low molecular weight specimens, NL and GL are nearly completely dissolved, but the other high molecular specimens are incompletely dissolved, as far as 10–20%. According to E. Tsuruta and M. Takeda[3], the intrinsic viscosity decreases with the increase of temperature. Considering this fact, the value of y should be somewhat greter than that cited in Table I, since Eq. (6) is derived by Sakurada at 20°C.

To discuss the effects of acetyl group, completely saponified specimens, N–series, and 90% saponified specimens, G–series, are compared. The hydration of acetyl group is weaker than the hydroxyl group, so the acetyl group left in G–series will decrease the extension of molecules, just as in a poor solvent. This expectation is not realized, since the incomplete dissolution degree, y (%), of G–series is smaller than that of N–series. To explain this, it is assumed that the existence of 10% of acetyl groups hardly change the solvation of the polymer molecule as a whole, while they decrease the mutual interaction of hydroxyl groups in a crystallite to increase the solubility and molecular extension. This assumption is also adequate to explain the difference of apparent yield values of G– and N–series. Though the apparent yield values are highly dependent on the history of the solutions, the value of P_0 for 90% saponified specimens (GH, GM, GL) are about 1 cm. H_2O, while for completely saponified specimens (NH, NM, NL) it is rather greater than that of G–series. This is also explained by the idea that the formation of intermoleular bonding of hydroxyl groups are easier and the net-work structure is stronger when the saponification is more complete and molecular weight is higher.

If the value of $[\eta_N]$ is smaller than $[\eta_0]$ by the season cited above, then the value of $[\eta_N]$ should increase by more complete dissolution. To certify it, the following procedure are tried. The solutions, made after the method cited before, are put into a flask with a rubber stopper and warmed at 45°C for four hours. The results obtained for these solutions are also cited in Table I. It is shown that the value of $[\eta_N]$ has increased by four hours warming. The fration of incmplete dissolution, y, was about 2% for NM, therefore, it has been nearly completely dissolved. However, the dissolution of the higher molecular weight specimen, NH, was not yet complete and y was about 15%.

Summary

The structural viscosity is measured for the aqueous solutions of poly-vinyl alcohol. The relative viscosity, (η/η_w), shows linear relationship to the reciprocal of the rate of flow, Q:

$$\eta=\eta_N+2.57\times10^{-5}\times P_0/Q$$

where η_N and P_0 are constants. P_0 corresponds to the pressure to destroy a net-work structure in the solution, or an apparent yield value, and η_N corresponds to the viscosity coefficient of the destroyed structure, which is assumed to flow as Newtonian.

As for the Newtonian viscosity η_N of polyvinyl alcohol solutions, $[\eta_N]$ defined by

$$[\eta_N]=\ln(\eta_N/\eta_w)/C$$

is independent on concentration, as far as measured. Comparing the intrinsic viscosities of specimens of the same polymerization, degree, the completely saponified specimen shows smaller value than partly saponified one. This may be explained by the decrease of molecular extension due to the strong intramolecular interaction of OH groups. The apparent yield values P_0 is 0.5∼3.5 cm. H_2O and is highly dependent on the history of the solution. The completely saponified specimen shows greater P_0 value. It will also be explained by the strong intermolecular interaction of OH groups to form net-work structure.

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