Colloid Chemical Studies on Starching Materials. II. Intrinsic Viscosity of Polyvinyl Alcohol in Soap Solutions

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In the preceding paper[1], the structural viscosity of aqueous solutions of polyvinyl alcohol was studied. In this paper, some results will be reported on the viscometric behavior of polyvinyl alcohol in soap solutions. This study has been made in order to see whether there exists any interaction between polyvinyl alcohol and soap. The interaction of non-ionic high polymer molecules and anionic detergent molecules will be of some interest in the field of both polymer and surface chemistry. It may, further, be of some interest in the field of textile industry, since experiments of this kind will give some fundamental information on the process of removing starching material from the surface of textile fibers.

Experimental

Polyvinyl alcohol.—Two materials provided by Nippon Gosei Kagaku Kogyo K. K., Gohsenol NM-14 and GM-14, were used[2]. The degree of polymerization of both NM and GM is about 1400. The degree of saponification of NM is 99~100%, while that of GM is 90±2%. Two grams of the polymer was dissolved in water by heating at 90°C for 15 min. After being cooled, it was transferred into a volumetric flask and made up to 100 cc. in a thermostat at 40°C. This solution, to be used after volumetric dilution, was prepared on the day when measurements were made, because the viscosity would slightly increase day by day. The method of dissolving the polymer affects the viscosity of the solution as discussed in the preceding paper. Heating for 15 min. is not long enough so that the molecules are probably not fully extended in the solution. This is one of the reasons for the increase of viscosity by aging. The above described method was, however, adopted considering the practical method of preparation of starching solution. Water used throughout the experiments was for the electric conductivity measurement.

Soap.—Sodium laurate was used. Lauric acid (m. p., 44.95°C) was neutralized with sodium hydroxide (extra pure reagent grade, rods) in conductivity water at 90°C. Sodium hydroxide was always used in 2% excess, in order to prevent the hydrolysis of the soap.

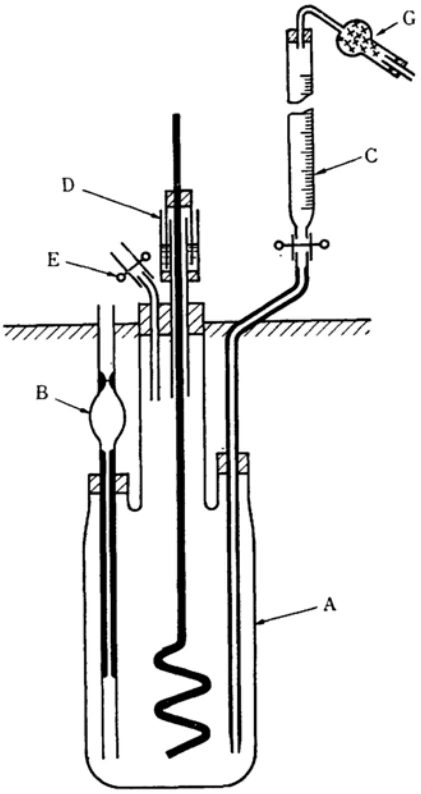

Fig. 1. Viscometer

Viscometer.—A viscometer illustrated in Fig. 1 was used. This is a flask of cylindrical shape (A) with three openings, equipped with a viscometer (B), a burette (C) with a soda lime tube (G), a stirrer (D) and a glass and rubber tubing closed with a pinchcock (E). In the flask (A), 50 cc. of soap solution containing or not containing polyvinyl alcohol was placed and a solution of the same soap concentration and of a different polyvinyl alcohol concentration was added from the burette. After being stirred with D, viscosity was measured with B, with E opened during the measurement. Thus the viscosity of the solution of various concentration of polyvinyl alcohol in a certain soap concentration was measured. The time for distilled water to flow down the viscometer was measured in advance for each

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[1] M. Nakagaki and A. Shimazaki, This Bulletin, **29**, 60 (1956).

[2] Gohsenol contains a small amount (probably less than 1%) of sodium acetate, but the writers do not believe this affects the results essentially.

amount of water in the flask, on the basis of which the viscosity of the solution relative to distilled water was calculated. Dividing this by the relative viscosity of the soap solution of the same concentration, the viscosity of the solution relative to the soap solution as the solvent was calculated and designated by η_r. All experiments were made in a thermostat at 40°C.

Results and Discussions

Treatment of the Experimental Values.—On treating the experimental values there are several points to be considered. At first, the effect of velocity gradient should be taken into account. Solutions of Gohsenol usually show structural viscosity. The apparent viscosity is, then, a function of the rate of flow, Q(cc./sec.), as shown in the preceding paper¹⁾. The quantity Q or $1/Q$ is, however, not very adequate to compare the effect of velocity gradient in two capillaries of different radius. On the basis of Poiseuille's law, the largest velocity gradient, G_m, that is the velocity gradient on the wall of the capillary, is

$$G_m = (4/\pi a^3)Q \tag{1}$$

The average velocity gradient, $\bar{G}$, defined by

$$\bar{G} = \int_0^a G(r) 2\pi r \,\mathrm{d}r / \pi a^2 \tag{2}$$

is related to the largest velocity gradient by

$$\bar{G} = (2/3)G_m \tag{3}$$

where a is the radius of the capillary and r is the distance between the axis of the capillary and the point where the velocity gradient is being considered. Either G_m or $\bar{G}$ may be used to discuss the effect of velocity gradient.

In the present experiments, the value of G_m was in the range between 1000 to 4000 (sec.$^{-1}$), which corresponds to the range of $(1/Q)$-value between 8 and 35 for the viscometer used in the preceding paper. Because of this low value of $1/Q$, it is clear according to the results of the preceding paper¹⁾ that the viscosity data in the present paper is very close to the value of η_N, that is the viscosity value extrapolated to zero of $1/Q$. Therefore, the effect of the velocity gradient may be neglected in the present experiments.

The viscometer used in this experiment is suitable to study the concentration dependence of the viscosity. However, the data should be extrapolated to zero concentration in order to obtain the value of the intrinsic viscosity. There are two well known equations for this purpose, that is Huggins' equation,

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c \tag{4}$$

and Staudinger's equation,

$$\ln \eta_r/c = [\eta] - k_2[\eta]^2 c \tag{5}$$

where c is the concentration of polymer. It was pointed out by Heller³⁾ that the simultaneous use of these two equations can appreciably reduce the arbitrariness in the extrapolation. For this purpose, both η_{sp}/c and $\ln \eta_r/c$ are expressed by $f(c)$ and plotted on the same figure. Three typical pairs of curves thus obtained are shown in Fig. 2. The upper curve of a pair corresponds to η_{sp}/c and the lower to $\ln \eta_r/c$.

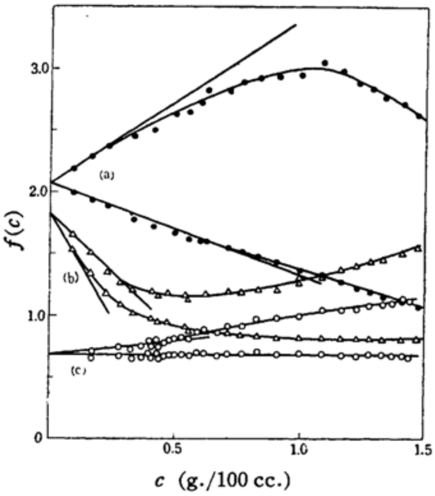

Fig. 2. Three types of $f(c)$-plot.
(a) Gohsenol NM in 0.1 N soap
(b) Gohsenol GM in 0.025 N soap
(c) Gohsenol NM in water

Experimental Results.—The value of the intrinsic viscosity, $[\eta]$, and the limiting slope of $f(c)$ curves, $k_1[\eta]^2$ and $k_2[\eta]^2$, are shown in Table I. In this experiment, the concentration of soap, c_s, shown in the first column is kept constant and the concentration of polymer, c, was changed.

At first, experiments were made using Gohsenol NM. As shown in Table I, the intrinsic viscosity increases when the soap concentration exceeds 0.025 N, which is close to the critical micelle concentration of sodium laurate⁴⁾. This agrees with the experimental observation by Saito⁵⁾ that the viscosity of polyvinyl

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3) W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).

4) On the critical micelle concentration of sodium laurate, many investigators gave values between 0.02 and 0.028 N, the most probable value being 0.0255 N.

5) S. Saito, *Kolloid-Z.*, **133**, 12 (1953).

alcohol solution increases by addition of sodium oleate or some other detergents. The detailed behavior of the system in soap solutions near the critical micelle concentration will, therefore, be of some interest. This was studied by using Gohsenol GM, which is a little easier to handle than NM.

TABLE I

CONSTANTS IN HUGGINS' AND STAUDINGER'S EQUATIONS

Soap concn.	Gohsenol NM			Gohsenol GM		
c_s(N)	$[\eta]$	$k_1[\eta]^2$	$k_2[\eta]^2$	$[\eta]$	$k_1[\eta]^2$	$k_2[\eta]^2$
0	0.68	0.22	0	0.71	0.24	0
0.005	0.70	0.27	0	—	—	—
0.01	0.68	0.22	0	0.73	0.27	0
0.02	—	—	—	0.71	0.26	0
0.025	0.73	0.27	0	1.16	−0.62	1.24
0.03	—	—	—	1.82	−1.90	3.40
0.04	—	—	—	2.24	−0.84	3.13
0.05	1.62	0.55	0.76	1.98	0.99	0.94
0.1	1.80	0.88	0.69	2.07	1.33	0.84
0.15	1.76	0.81	0.71	—	—	—

The results are also shown in Table I. In this concentration range, the intrinsic viscosity has a maximum.

In a soap solution of low concentration, $\ln \eta_r/c$ is almost constant in the range of the polymer concentration studied here, as an example of the case is shown in Fig. 2 (c). Therefore, $k_2[\eta]^2$ is equal to zero. In a soap solution of high concentration, η_{sp}/c increases and $\ln \eta_r/c$ decreases with polymer concentration, c, at the range of low values of c. An example is shown in Fig. 2 by curve a. In this case, both $k_1[\eta]^2$ and $k_2[\eta]^2$ are positive. In a soap solution of intermediate concentration, both η_{sp}/c and $\ln \eta_r/c$ increases when the concentration of polymer approaches to zero. An example of this type of curves is shown by curve b in Fig. 2. In this case, $k_1[\eta]^2$ is negative and $k_2[\eta]^2$ is positive.

Examination of k_1 and k_2.—The values of k_1 and k_2 were calculated from data given in Table I and shown in Fig. 3, together with the value of $[\eta]$, as a function of the soap concentration c_s. The short vertical lines at c_s=0.025 N show the critical micelle concentration of the soap. At about this soap concentration, the intrinsic viscosity and k_2 increase while k_1 decreases abruptly. The curve of $[\eta]$ and k_2 has a maximum and the curve of k_1 has a minimum.

The relation between k_1 and k_2 is shown in Fig. 4. The straight line shows the well known relation,

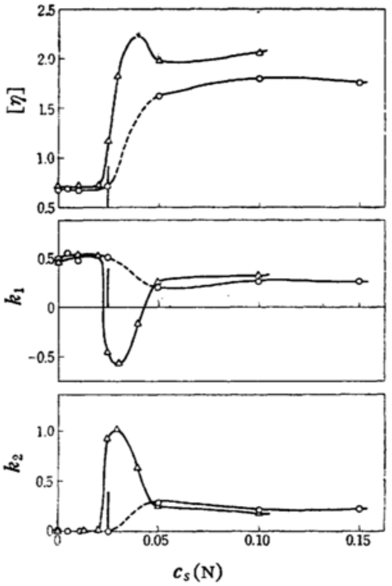

Fig. 3. The c_s dependence of $[\eta]$, k_1 and k_2. ○ Gohsenol NM; △ Gohsenol GM.

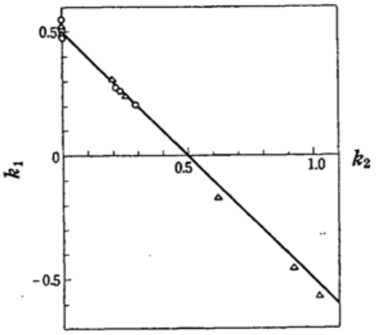

Fig. 4. Relation between k_1 and k_2.

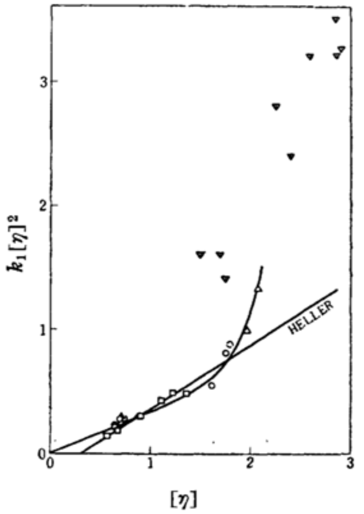

Fig. 5. Relation between $k_1[\eta]^2$ and $[\eta]$.
○ and △: Gohsenol
□ and ▽: Polystyrene

$$k_1 + k_2 = 0.5 \qquad (6)$$

which had been pointed out by Ewart[6]. Fig. 4 shows that this relation can be extended to the negative values of k_1. This is a natural consequence because Ewart's relation can be derived mathematically from Eqs. 4 and 5.

The relation between $k_1[\eta]^2$ and $[\eta]$ is shown in Fig. 5. Eirich and Riseman[7] proposed an empirical relation,

$$k_1[\eta]^2 = \alpha + \sigma[\eta] \qquad (7)$$

where α and σ are constants. Using data by Streeter and Boyer[8] on polystyrene ($\overline{M}_w=3.7\times10^5$) in various organic solvents, values $\sigma=0.50_7$ and $\alpha=-0.14_6$ were obtained by Heller[3]. This relation is shown in Fig. 5 by a straight line and individual data by □. On the other hand, the present data were plotted for Gohsenol NM by ○ and GM by △, except for three points of negative k_1 values. According to these data, $k_1[\eta]^2$ increases more rapidly than the straight line by Heller at large $[\eta]$ values. This is, however, not strange if we refer to the values given by Cragg[9], which are based on data by Bawn et al. on polystyrene ($M=1.6\times10^6$) in various organic solvents and shown in Fig. 5 by ▽. Therefore, the relation between $k_1[\eta]^2$ and $[\eta]$ of polyvinyl alcohol-soap-water system studied in this paper follows the same tendency as that of polystyrene in organic solvents, except the case for which k_1 is negative.

Interaction between Polyvinyl Alcohol and Soap.—On the basis of the experimental observations described above, polyvinyl alcohol is being dissolved in soap solution in three different states depending on the concentration of soap.

(1) In a soap solution at the concentration lower than its critical micelle concentration, polyvinyl alcohol behaves as it does in water. It is therefore concluded that the effect of soap is negligible at this low concentration. Here, $[\eta]$ is small, k_1 nearly equal to 0.5 and k_2 is nearly equal to zero. This is the usual behavior of polyvinyl alcohol in water, or more generally, of nonionic polymer in a rather poor solvent.

(2) In a soap solution near the critical micelle concentration $[\eta]$ is large, k_1 is negative and k_2 is larger than 0.5. The negative value of k_1, or a rapid increase of η_{sp}/c with decreasing polymer concentration, is usually observed on aqueous solutions of polyelectrolytes. In this range of soap concentration, therefore, polyvinyl alcohol molecules are supposed to be combined with soap molecules, and to behave like polyelectrolyte molecules because of the electrical charges due to the soap ions. The combination of polyvinyl alcohol and soap occurs near the critical micelle concentration of the soap, but the formation of micelle does not seem to be very important to this combination, because at the critical micelle concentration (0.025 N) the intrinsic viscosity of Gohsenol NM is still low while that of Gohsenol GM is already large. This may suggest that the combination of soap with polyvinyl alcohol is due to the aggregation of the hydrophobic part of the soap molecule with the hydrophobic part of the polymer molecule. This will explain the fact that the combination occurs near the critical micelle concentration, because the micelle formation of soap is also due to the aggregation of hydrophobic part of soap molecules. This will, further, explain that Gohsenol GM combines with soap at lower soap concentration than Gohsenol NM does, because GM retains about 10% of acetyl groups so that it is more hydrophobic than NM, the latter being saponified completely.

(3) In a soap solution of high concentration, $[\eta]$ is large and both k_1 and k_2 are positive. This is the usual behavior of nonionic polymer in a good solvent. This will mean that the electric charges of soap molecules combined with the polymer are shielded completely by the ion atmosphere of the counter ion (sodium ion) at this high soap concentration, so that the polymer behaves like a nonionic polymer. The high value of the intrinsic viscosity may be due to the following several reasons. a) The carboxyl group of soap combined with the polymer adds hydrophilic property. A polymer molecule is usually the more extended, the higher the affinity of the polymer to solvent. b) As far as the intermolecular interaction of polymer molecules are concerned, it has been assumed that the electric charge of soap combined with the polymer is completely shielded by counter ions. However, the shielding is probably not perfect inside the molecule. The electric repulsion between segments in a polymer molecule will extend the polymer. c) The soap

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[6] R. H. Ewart, *Advances in Colloid Sci.*, **2**, 211 (1946).

[7] F. Eirich and J. Riseman, *J. Polymer Sci.*, **4**, 417 (1949).

[8] D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951)

[9] L. H. Cragg, *Chem. & Ind.*, **1952**, 623.

molecules combined with the polymer will occupy its own volume. This will make the polymer molecule expanded. d) By the combination with soap molecules, polymer molecules become stiff and lose flexibility to some extent. This will also result the extension of the polymer molecules. The extension of polymer molecules by these reasons will increase the intrinsic viscosity.

Summary

The concentration dependence of the viscosity of polyvinyl alcohol in solutions of constant soap concentration is studied. At the soap concentration lower than its critical micelle concentration, the effect of soap on the viscosity of polyvinyl alcohol is very little. At the soap concentration near the critical micelle concentration, soap molecules are combined with the polymer, the latter behaving like a polyelectrolyte. At high soap concentration, the polymer behaves like a non-ionic polymer in a very good solvent.

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