Colloid Chemical Studies of Starching Materials. VI. Viscometric Studies of the Interaction between Polyvinyl Alcohol and Sodium Dodecyl Sulfate

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In a previous paper[1] of this series,[2] the intrinsic viscosity of polyvinyl alcohol in a sodium laurate solution was studied, and it was concluded that the effect of sodium laurate may be classified into three types, depending on the detergent concentration. Similar studies made in a sodium dodecyl sulfate (SDS) solution will be reported on here.

Experimental

Materials.—Two samples of polyvinyl alcohol, the same as in a previous paper, were used. They are Gohsenol NM-14 (the degree of polymerization is about 1400; the degree of saponification is 99.3%) and Gohsenol GM-14 (the degree of polymerization is about 1400; the degree of saponification is 87.6%), provided by the Nippon Gosei Kagaku Kogyo K. K. To dissolve the polymer, a weighed sample was added to cold distilled water and heated to 90°C within 15 min.; heating was continued at the same temperature for a further 30 min. As the detergent, sodium dodecyl sulfate, provided by the Nihon Yushi K. K., was recrystallized twice from distilled *n*-butanol and dried in vacuum at room temperature.

Apparatus.—The dilution viscometer used was the same as was described in the a previous paper. All measurements were made in a thermostat at 40°C. A series of viscometric measurements was undertaken in solutions of varying polymer concentrations but of a constant detergent concentration, and the viscosity values were expressed relative to that of the detergent solution, in order to obtain the intrinsic viscosity and related quantities of the polymer at that detergent concentration.

Results and Discussion

The Viscosity of the SDS Solution.—The viscosity of the aqueous SDS solution, used as

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[1] M. Nakagaki and H. Nishibayashi, This Bulletin, 31, 477 (1958).

[2] V of this series: M. Nakagaki and T. Nishii, ibid., 37, 60 (1964).

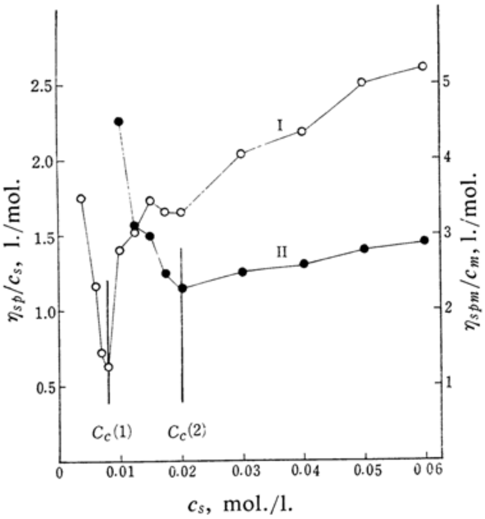

Fig. 1. Reduced viscosity of the SDS solution. Curve I: η_{sp}/c_s, Curve II: η_{spm}/c_m (on the right side ordinate)

the "solvent" in further experiments, was measured; the results are shown in Fig. 1. The relation between the reduced viscosity, η_{sp}/c_s, and the SDS concentration, c_s (mol./l.), as shown by curve I in Fig. 1, reaches a minimum at the SDS concentration of 0.008 mol./l. The minimum point is believed[3] to correspond to the critical micelle concentration, c_c, and agrees well with the values already reported by many authors.[4]

Therefore, the reduced viscosity for the micelle, η_{spm}/c_m, is shown by curve II in Fig. 1, where

$$\eta_{spm}/c_m=(\eta_s/\eta_c-1)/(c_s-c_c) \qquad (1)$$

Here η_s is the relative viscosity of SDS solution (relative to distilled water), and η_c is the relative viscosity at $c_c=0.008$ mol./l. A minimum point is found at 0.02 mol./l. This is believed to correspond to the "second" critical micelle concentration.[3,5] Thus, the following results were obtained:

$$\left.\begin{array}{l} c_c(\mathrm{I})=0.008 \text{ mol./l.} \\ c_c(\mathrm{II})=0.02 \text{ mol./l.} \end{array}\right\} \qquad (2)$$

A Method to Obtain Intrinsic Viscosity.—In order to obtain the intrinsic viscosity, $[\eta]$, the extrapolation to zero of the polymer concentration, c_p (g./100 ml.), was usually made on the basis either of Huggins' equation:

$$f_1=\eta_{sp}/c_p=[\eta]+k_1[\eta]^2c_p \qquad (3)$$

or Staudinger's equation:

$$f_2=\ln \eta_r/c_p=[\eta]-k_2[\eta]^2c_p \qquad (4)$$

It has already been pointed out by Heller[6] that the simultaneous use of f_1 and f_2, together with the mathematical consequence:

$$k_1+k_2=0.5 \qquad (5)$$

can appreciably reduce the arbitrariness in the extrapolation. This method has been used in one of our previous papers.[1]

The new method used in the present paper (in addition to the one described above), is based on the fact that the difference, Δf, between f_1 and f_2 should be proportional to the polymer concentration at a sufficiently low concentration range. The following equation, as readily derived from Eqs. 3, 4 and 5, can be used to estimate the value of $[\eta]$:

$$\Delta f=f_1-f_2=0.5[\eta]^2c_p \qquad (6)$$

An example for NM-14 in a 0.03 mol./l. SDS solution is shown in Fig. 2. As may be seen in Fig. 2, a linearity between Δf and c_p holds, and the tangent will give the value of $[\eta]$ according to Eq. 6. Figures similar to Fig. 2 were drawn for all the instances in this paper, and the values of $[\eta]$, k_1 and k_2 were determined to satisfy Eqs. 3, 4, 5 and 6 at the range of small c_p values.

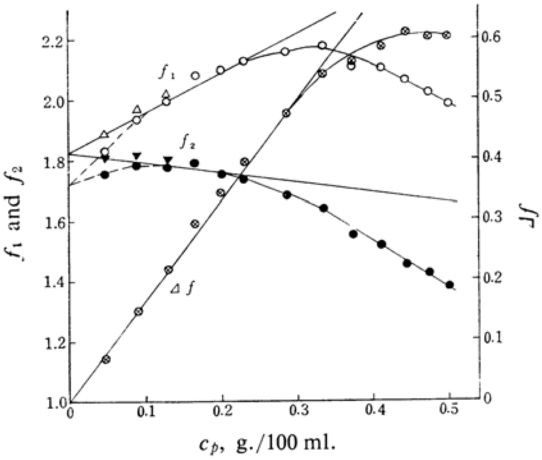

Fig. 2. An example of c_p dependencies of f_1, f_2 and Δf for NM-14 in 0.03 mol./l. SDS solution.
Corrected values for f_1(△) and f_2(▼)

Anomalies at Low Polymer Concentrations.—It is often found in experiments of this kind that the experimentally-obtained values show a kind of anomalous deviation from the linearity to be expected on the basis of Eqs. 3 or 4 at low polymer concentrations. This anomaly is, of course, partly due to the

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[3] N. Sata and K. Tyuzyo, ibid., **26**, 177 (1953).

[4] R. Goto and T. Sugano, "Surface Chemistry," (Vol. 7 in the "Zikken Kagaku Koza" series), Maruzen, Tokyo (1963), p. 167. The value of c_c varies between 0.003 and 0.010 mol./l.

[5] K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939).

[6] W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).

experimental error unavoidable because of the low value of the polymer concentration, but, more often, a systematic deviation from the linearity is observed. One of the expected reasons for this is the effect of the electric charge given to the polymer molecules by the combination of detergent anions, a charge which results in a positive deviation from the linearity; that is, the greater the experimental f-values, the smaller the polymer concentration, as has already been discussed in the previous paper.[1] Another reason should, however, be considered to explain the negative deviation from the linearity shown, for example, in Fig. 2 by broken curves.

The f_1 and f_2 values in the present paper have been calculated by using the viscosity values relative to the viscosity, η_s, of the "solvent," that is, the detergent solution not containing any polymer. If a part of the detergent is combined with the polymer, however, the actual value of the viscosity of the "solvent," $\eta_s{}^0$, should be the value at a concentration a little smaller than the analytical detergent concentration. Then, the values of f_1 and f_2 should be recalculated to $f_1{}^0$ and $f_2{}^0$. The results will probably show the linearity anticipated by Eqs. 3 and 4. The relations between f_1, f_2, $f_1{}^0$ and $f_2{}^0$ are given by the following:

$$\left.\begin{aligned} f_1 &= (\eta_s{}^0/\eta_s)f_1{}^0 - (1-\eta_s{}^0/\eta_s)/c_p \\ f_1{}^0 &= (\eta/\eta_s{}^0 - 1)/c_p \end{aligned}\right\} \qquad (7)$$

and

$$\left.\begin{aligned} f_2 &= f_2{}^0 - [\ln(\eta_s/\eta_s{}^0)]/c_p \\ f_2{}^0 &= [\ln(\eta/\eta_s{}^0)]/c_p \end{aligned}\right\} \qquad (8)$$

where η is the relative viscosity of a solution containing a polymer as well as a detergent. If the amount of detergent combined with the polymer is so small that $\eta_s{}^0/\eta_s$ is very close to unity, $\ln(\eta_s/\eta_s{}^0)$ can be expanded in a power series of $(1-\eta_s{}^0/\eta_s)$ and the terms of the second and higher powers can be neglected. Then, Eq. 8 can be appoximated as:

$$f_2 = f_2{}^0 - (1-\eta_s{}^0/\eta_s)/c_p \qquad (8\text{a})$$

Equations 7 and 8a can explain how a negative deviation is observed when c_p is so small that the value is comparable to $(1-\eta_s{}^0/\eta_s)$, if $\eta_s{}^0 < \eta_s$ because of the deficiency of free detergent molecules as a result of the combination with the polymer. Equations 7 and 8a indicate, too, that Δf will not show any serious deviation from the linearity at the low polymer concentration because of the cancellation of the $(1-\eta_s{}^0/\eta_s)/c_p$ term in both equations (cf. Fig. 2).

$$\Delta f = f_1 - f_2 = (\eta_s{}^0/\eta_s)f_1{}^0 - f_2{}^0 \qquad (9)$$

In the example shown in Fig. 2, $\eta_s = 1.060$ was used. If the value $\eta_s{}^0 = 1.057$ is adopted and if the values of $f_1{}^0$ and $f_2{}^0$ are calculated, the corrected values (△ and ▼) are on the straight lines, as expected.

The Intrinsic Viscosity of PVA in an SDS Solution.—For the solutions of polyvinyl alcohol NM-14 and GM-14 in an SDS solution, the intrinsic viscosity, $[\eta]$, and the constants, k_1 and k_2, of Eqs. 3 and 4 are as shown in Figs. 3, 4 and 5 respectively, taking the SDS concentration on the abscissa. According to Eqs. 7 and 8a, the corrected intrinsic viscosity, $[\eta_0]$, should be:

$$(\eta_s/\eta_s{}^0)\,[\eta_1] \gtrsim [\eta_0] \fallingdotseq [\eta_2] \qquad (10)$$

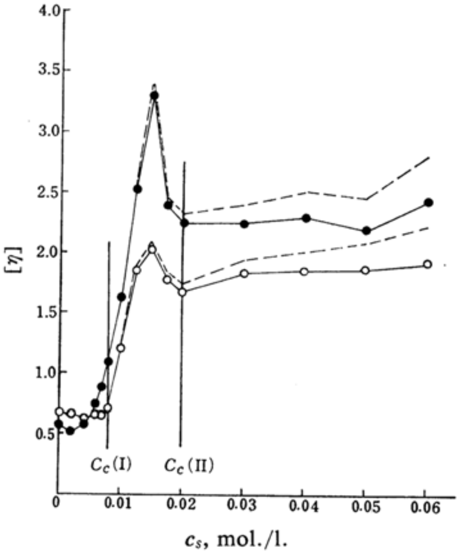

Fig. 3. Intrinsic viscosity of NM-14 (○) and GM-14 (●) in the SDS solution.

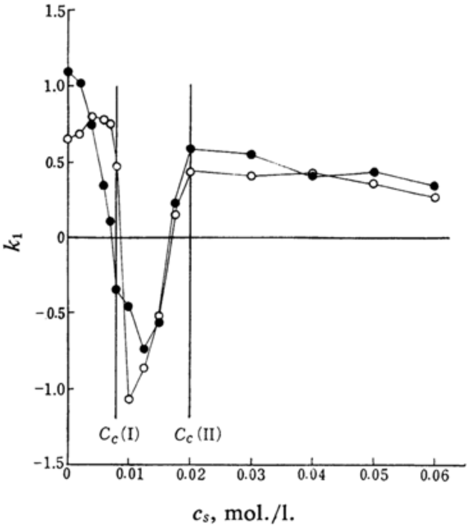

Fig. 4. Huggins' constant k_1 of NM-14 (○) and GM-14 (●) in the SDS solution.

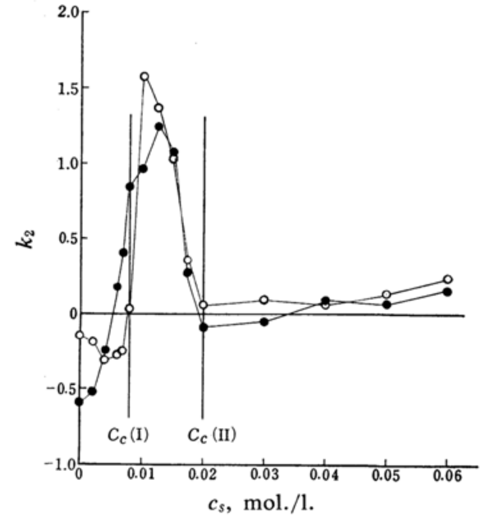

Fig. 5. Staudinger's constant k_2 of MN-14 (○) and GM-14 (●) in the SDS solution.

where $[\eta_1]$ and $[\eta_2]$ are the values of f_1 and f_2 respectively as extrapolated from the concentration range $c_p \gg (1-\eta_s{}^0/\eta_s)$ to the infinite dilution $c_p \rightarrow 0$. Since the correct value of $\eta_s{}^0$ should be larger than that of pure water, or $\eta_s > \eta_s{}^0 > 1$, the possible upper limit of $[\eta_0]$ is $\eta_s[\eta]$. The unrealizable upper limit, at which all the detergent is assumed to be combined with the polymer and nothing is left free in the solution, is shown in Fig. 3 by broken lines. The actual $[\eta_0]$ is expected to be much closer to $[\eta]$ than to $\eta_s[\eta]$; e.g., in the case of NM-14 in a 0.03 mol./l. SDS solution (cf. Fig. 2), $[\eta]=1.820$ and $\eta_s[\eta]=1.931$, while the value corresponding to the corrected values (△ and ▼) in Fig. 2 is $[\eta_0]=1.825$. Therefore, the errors, which might be caused by the decrease in the viscosity of the medium because of the combination of SDS with the polymer molecules, neither change the essential features of Fig. 3 nor affect the following discussion.

Figures 3, 4 and 5 show that the entire range of detergent concentration, c_s, is divided into three ranges by the first, c_c(I), and the second, c_c(II), critical micelle concentrations of the detergent. These three ranges for SDS exactly correspond to the three ranges described for sodium laurate in a previous paper,[1] although it was not noticed in that paper that the boundary concentration between the second and the third range is equal to the second critical micelle concentration.

The viscometric behavior of the polymer in these three ranges is as follows: (I) In SDS solutions at concentrations lower than c_c(I), $[\eta]$ is small, k_1 is positive and k_2 is negative. In this region, the effect of the detergent seems to be negligible, and the polymer behaves as if it were in water. (2) In SDS solutions of concentrations between c_c(I) and c_c(II), $[\eta]$ becomes large, k_1 becomes negative, and k_2 becomes large. The negative value of k_1, or a rapid increase in η_{sp}/c_p with a decreasing polymer concentration, is usually observed in aqueous solutions of polyelectrolytes. Polyvinyl alcohol molecules are, therefore, presumed to be combined with the SDS anions and to behave like polyelectrolytes. The maximum of $[\eta]$ is explained by the circumstances that the electric repulsion responsible for the expansion of the polymer molecules is partially shielded by the ion atmosphere of the counter ions (sodium ions) with the increase in the detergent concentration. (3) In SDS solutions at concentrations higher than c_c(II), $[\eta]$ is still large, although the value is a little smaller than the value at the maximum point. The value of k_1 is about 0.5, while the value of k_2 is nearly equal to zero. In this range, the viscometric behavior characteristic of the polyelectrolyte was not observed, probably because the electric charges of detergent anions combined with the polymer were almost completely shielded by the counter ions at this high detergent concentration. The high value of the intrinsic viscosity, indicating the high affinity to the medium or the extended configuration of the polymer molecules, may be due, as was already pointed out in the previous paper,[1] to the hydrophilic property of the polymer strengthened by the combination of detergent anions, to the intramolecular repulsion between electric charges resulting from the combination of detergent anions, to the expansion of the polymer molecules in order to secure the space necessary for the combined detergent molecules, or to the decrease in the flexibility of the polymer molecules because of the combination of detergent molecules.

The second critical micelle concentration, c_c(II), is said to be the concentration above which the I-band of X-ray diffraction is observed. It is presumed that this means that the solution is saturated with the usual micelle and that the excess of the detergent forms a large lamellar micelle or a kind of crystallite at concentrations higher than c_c(II). In this range of detergent concentrations, on the other hand, the variations in $[\eta]$, k_1, and k_2 with the concentration, c_s, is not large. This is probably due to the saturation of the solution with the usual micelle.

A Comparison between SDS and SL.—The shape of the curve, $[\eta]$ vs. c_s, for the SDS solution is very similar to that for the sodium laurate (SL) solution reported on in the previous paper,[1] except that the concentration ranges of the detergents used are different.

The difference is obviously due to the difference in the critical micelle concentration, c_c(I), the values being 0.025 N for SL and 0.008 N for SDS. Therefore, it is supposed that all the experimental plots would come onto one curve if the scales of the ordinate and abscissa were changed properly, and that the reduced abscissa would be c_s/c_c. As for the ordinate, it is noticeable that the value of $[\eta]$ shows a tendency to approach a limiting value $[\eta_\infty]$ when c_s becomes large. The values of $[\eta_\infty]$ are assumed to be as cited in Table I, and the reduced curve is drawn as in Fig. 6, in which the data for SL reported in the previous paper are plotted, as well as the data for SDS.

From Table I, it may be seen that the $[\eta_\infty]$ value for GM-14 is about 1.28 times larger than that for NM-14 in either detergent solution, and that $[\eta_\infty]$ in SDS is about 1.08 times larger than in SL for either polymer. In other words, GM, with an imperfectly-saponified polymer, expands more readily when subjected to a combination of detergents than NM, with a completely saponified polymer, and SDS, with a higher lipophilicity can expand the polymers more than SL, with a lower lipophilicity. This would suggest that the polymer-detergent interaction is due to the contact of the hydrophobic parts of the molecules, if it is presupposed that the greater expansion of the polymer is caused by the larger amount of detergent combined.

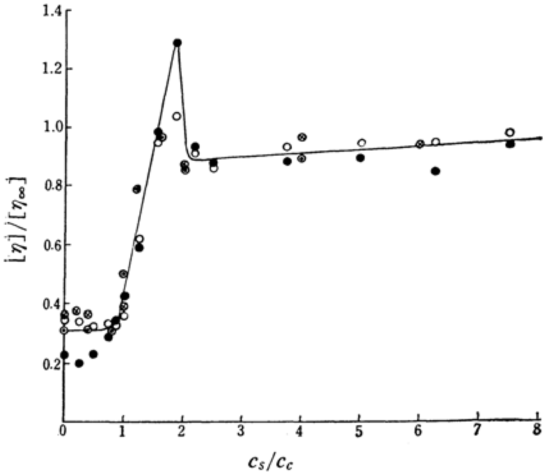

Fig. 6. Reduced curve of intrinsic viscosity vs. detergent concentration.
NM(○) and GM(●) in SDS, and NM(⊗) and GM(⊙) in SL

TABLE I. ASSUMED VALUES OF $[\eta_\infty]$

	NM	GM	GM/NM	Aver.
SDS	1.95	2.56	1.31	1.28±0.03
SL	1.86	2.32	1.25	
SDS/SL	1.05	1.10		1.08±0.03

Summary

The intrinsic viscosity and related constants have been measured for polyvinyl alcohol NM-14 and GM-14 in a sodium dodecyl sulfate solution. At a detergent concentration lower than the first critical micelle concentration (0.008 N), the viscometric property of the polymer is close to that in distilled water. At an intermediate detergent concentration between the first and the second critical micelle concentration (0.02 N), the viscometric property of the polymer is like that of polyelectrolyte, probably because of the electric charges given by detergent anions combined with the polymer. At a detergent concentration higher than the second critical micelle concentration, the intrinsic viscosity of the polymer is high and the polymer combined with the detergent is more extended than in distilled water. The interaction between the polymer and the detergent is very likely due to the contact of hydrophobic parts of the molecules.

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