

LETTER TO THE EDITORS

The Interaction of Sodium Dodecyl Sulfate with Vinyl Polymers in Aqueous Solutions

The interaction of "hydrogen bonding addends" with vinyl polymers in aqueous solutions has been studied previously by means of viscometry.¹ In the present work this study has been extended to the action of sodium dodecyl sulfate (SDS), a very strong denaturing agent of proteins.² The polymers investigated are polyacrylic acid (PAA), polymethacrylic acid (PMA), polyacrylamide (PAAM), polymethacrylamide (PMAM) and polyvinyl alcohol (PVA). They were all polymerized from their respective monomers with hydrogen peroxide and purified by dialysis, except PVA which is a commercial preparation (Moviol 70-96). The measurements were carried out at 30.0°C. in Ostwald-Fenske viscometers in which the time of flow of water was about 300 sec. The dependence of the reduced specific viscosity on polymer concentration (at several SDS concentrations) was determined, the reference solvent being the pure SDS solution of the respective concentration. In the case of PMA and PAA hydrochloric acid was added to suppress self-ionization of the polyacids.

In Figures 1-3 the results are summarized for PAA, PMA, and PVA. The common effect of SDS on all three polymers is the large increase of the reduced specific viscosity. However, the detailed dependence of the reduced specific viscosity on concentration is particular for each polymer. In the case of PAA all the lines η_{sp}/c vs. c at different SDS concentrations are practically horizontal and by extrapolation to zero (polymer concentration we obtain an intrinsic viscosity for the PAA-SDS complex. The increase in intrinsic viscosity is roughly proportional to the concentration of SDS. (In making this extrapolation we imply the existence of a complex which depends only on the total SDS concentration and which does not depend on the ratio polymer:detergent.)

A distinctly different behavior is shown by PMA in 0.1% SDS in that the reduced specific viscosity decreases sharply with increasing polymer concentration and approaches that of SDS-free solutions while at low polymer concentrations it comes close to that of 0.4% SDS. A likely explanation for this phenomenon is that in this region the complex depends not only on the total SDS concentration but also on the ratio polymer:SDS. We have therefore refrained from extrapolating to zero (polymer) concentration as the meaning of the "intrinsic viscosity" is doubtful. At higher SDS concentrations the line η_{sp}/c vs. c is normal. It was also observed that the addition of SDS to PMA solutions prevents the precipitation of the polymer on heating.³

In PVA solutions containing 0.4% SDS the concentration dependence is the same as in PMA at 0.1%. (In 0.1% SDS the viscosities of PVA were found to be identical with those in pure water.) Isemura and Imanishi⁴ have found that at SDS concentrations higher than those investigated here the line η_{sp}/c vs. c is horizontal and that the intrinsic viscosity decreases with increasing SDS concentration. This is in agreement with their observation that the electrophoretic mobility of PVA increases sharply on addition of SDS and decreases after passing through a maximum. The effect of SDS on the viscosity of aqueous solutions of polyvinylpyrrolidone has been investigated⁵ and found to be similar to that on PMA and PVA.

The viscosities of PAAM and PMAM in 0.4 and 2.0% SDS were measured over a polymer concentration range of 0.3-1.0% and found to be identical with those in pure water (within experimental error). We conclude from the viscosity measurements that SDS does not interact with the polyamides. (The intrinsic viscosity of the PAAM used was 34 and that of PMAM 11.)

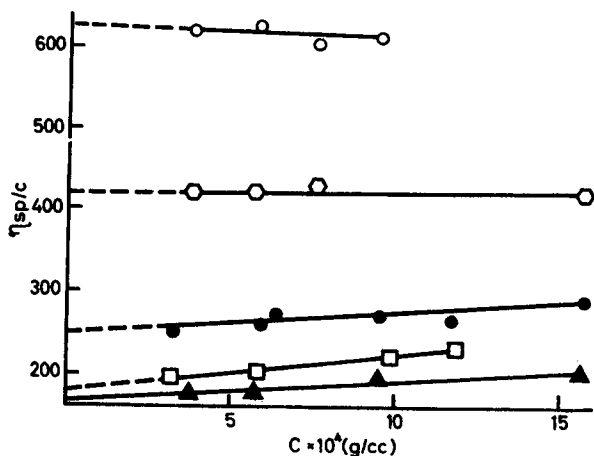


Fig. 1. The reduced specific viscosity of polyacrylic acid in aqueous solutions of sodium dodecyl sulfate. (\blacktriangle) Pure water; (\square) 0.1% SDS; (\bullet) 0.4% SDS; (\square) 1.0% SDS; (\circ) 2.0% SDS. (All solutions contain 0.2N HCl.)

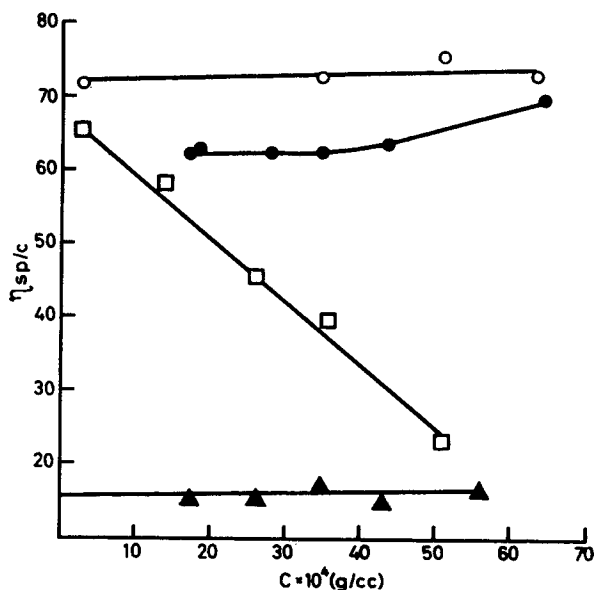


Fig. 2. The reduced specific viscosity of polymethacrylic acid in aqueous solutions of sodium dodecyl sulfate. (\blacktriangle) Pure water; (\square) 0.1% SDS; (\bullet) 0.4% SDS; (\circ) 2.0% SDS. (All solutions contain 0.2N HCl.)

Neurath and Putnam⁶ have found that the addition of SDS to serum albumin solutions caused a marked increase of the reduced specific viscosity. "Whereas in dilute solutions the viscosity increment is usually independent of protein concentration . . . in relative low detergent concentration (1% or less) η_{sp}/c decreases with increasing protein concentration and tends to approach the value observed for the native protein." The similarity between the effect on serum albumin and on the synthetic polymers

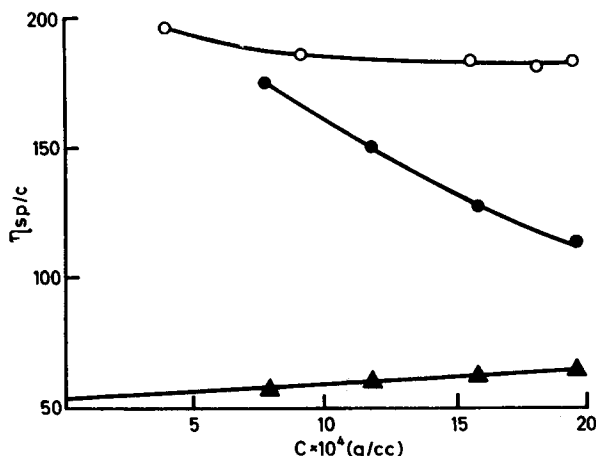


Fig. 3. The reduced specific viscosity of polyvinyl alcohol in aqueous solutions of sodium dodecyl sulfate. (▲) Pure water; (●) 0.4% SDS; (○) 2.0% SDS.

investigated by us is striking. In the case of PMA we have, besides the viscometric behavior, the similarity of prevention of heat coagulation.⁷ We have reason to assume that the interaction of SDS with protein is the same as with the synthetic polymers. If so, the present investigation can contribute to the understanding of the nature of the interaction.

It was assumed² that the interaction involves cationic sites on the protein chain. The behavior of PAA, PMA, PVA, and polyvinylpyrrolidone suggests that this need not be the case, but that the interaction may involve neutral polar groups such as aspartic acid (at low pH) as well as serine and proline. The interaction is not directly with the polymer backbone but does involve specific polar groups as there is no interaction with the polyamides. The fact that there is no interaction with PMAm, a particular poorly dissolved polymer,³ contradicts the assumption⁴ that the interaction is best with hydrophobic polymers.

References

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Received March 13, 1962