University of Groningen

Non-newtonian flow of dilute polymer solutions

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1951

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
de Wind, G. (1951). *Non-newtonian flow of dilute polymer solutions*. Centen.

INTRODUCTION.

The influence of the rate of shear on the apparent viscosity of colloid solutions has been the subject of numerous researches in past and recent years.[1]) Most of these investigations are concerned with concentrated solutions, and in none of them a reliable method has been developed to extrapolate the effect of the shear rate to infinite dilution. The work which comes nearest to this aim is that of *Staudinger* and *Sorkin*[2]) who measured the apparent viscosity of dilute solutions of cellulose nitrate in butyl acetate at various shear rates. *Kuhn* and *Kuhn*[3]) have discussed this work in connection with theoretical considerations, and have come to the conclusion that the effect of the rate of shear on the viscosity is a property of the isolated molecule. To show this, the authors consider the intrinsic viscosity

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 c} \right)$$

as a function of the velocity gradient. Here η is the apparent viscosity of the solution, η_0 that of the solvent; c is the concentration of the polymer. According to *Kuhn* and *Kuhn* the intrinsic viscosity obtained decreases with increasing rate of shear. It is doubtful, however, whether the method of extrapolation has been quite reliable. *Staudinger* and *Sorkin* give no details about the viscometer used, nor do they mention how the correction for kinetic energy was applied and how large this correction was.

More recently *Lyons*[4]) investigated the viscous properties of cuprammonium solutions of cellulose. It was found that the influence of the velocity gradient on the viscosity did not persist at the limit of very high dilution. The experimental results are represented by the formula

$$\eta/\eta_0 = (1 + c/\lambda)^8 + (k - 8/\lambda)c,$$

[1]) See, for example, *A. Lude*, Rec. trav. chim. **68**, 1030 (1949).
[2]) *H. Staudinger* and *M. Sorkin*, Ber. **70**, 1993 (1937).
[3]) *W. Kuhn* and *H. Kuhn*, Helv. Chim. Acta **28**, 1572 (1945).
[4]) *W. J. Lyons*, J. Chem. Physics **13**, 43 (1945).

where λ depends on the rate of shear, but k does not. It follows from this equation that $[\eta] = k$ and thus is independent of the shear rate. It is somewhat hazardous, however, to draw a conclusion of this kind from a formula which is meant to apply to a large range of concentrations.

Conrad *) in recent work found $[\eta]$ to be dependent on the shear-rate. His method of extrapolating is essentially the same as that of *Staudinger* and *Sorkin*. After finishing our own work we have learned of data obtained by *Fuoss* **) who has made use of a method which is essentially the same as the one developed by us, except for the fact that he did not apply a statistical analysis to the data. *Fuoss* investigated solutions of polystyrene of molecular weight 6.7 10^5, and of some polyelectrolytes, and found the intrinsic viscosity to be effected by the shearing stress.

The theoretical aspects of the problem are as follows. It has been shown theoretically [5]) that the contribution of stiff rod-shaped or ellipsoidal particles to the viscosity decreases with increasing velocity gradient. The model generally accepted for polymer molecules in solution is not that of a stiff rod but rather that of the random coil. The influence of the shear rate on the viscosity contribution of these coiled molecules depends on the degree of flexibility of the coils. If the molecules are rigid, their viscous behaviour is similar to that of rods or ellipsoids. At the limit of complete flexibility, theoretical considerations of *Kuhn* and *Kuhn* [3]) and of *Hermans* [6]) have shown that there should be no effect of shear rate at all. These theories assume unhindered flow of the solvent through the polymer coil, but according to *Kuhn* and *Kuhn* this does not play an important role in the calculation.

It is the aim of the present investigation to develop a method for extrapolating the experimental results to infinite dilution so as to obtain the effect of the shear rate on the viscosity contribution of the isolated molecule. In all the measurements cellulose nitrate was the polymer and acetone the solvent.

*) C. M. *Conrad*, communication at the meeting of the American Chemical Society, Detroit, April 1950.

**) R. M. *Fuoss*, paper read at a symposium on polyelectrolytes at the Brooklyn Polytechnic Institute, April 1950.

[5]) R. *Simha*, J. Phys. Chem. **44**, 25 (1940); W. *Kuhn* and H. *Kuhn*, ref. 3; H. C. *Brinkman*, J. J. *Hermans*, L. J. *Oosterhoff*, J. Th. G. *Overbeek*, D. *Polder*, A. J. *Staverman* and E. H *Wiebenga*, Proc. Int. Rheol. Congress, Holland 1948, II 77.

[6]) J. J. *Hermans*, Kolloid Z. **106**, 28 (1944); Physica **10**, 777 (1943); Colloid Science II (Elsevier Amsterdam 1949), p. 113.

According to *Kuhn* and *Kuhn* the flexibility of the polymer molecules increases with their molecular weight. These authors claim, however, that cellulose nitrate molecules with a degree of polymerisation of about 600 in solvents with a viscosity of about 10^{-3} poise behave like perfectly rigid structures, showing a decrease of about 10 % in the intrinsic viscosity when the rate of shear is increased to 16000 sec^{-1}. For this reason our cellulose nitrate, which also had a degree of polymerisation of about 600, is a very suitable material to check previous experiments and theories.