

Fig. 1

deduced. Some of these values are far less than would be expected from the theory outlined here. However, the experimental studies concerned give no information on the recombination coefficient. This is so great that the number-density of free electrons simply followed the changing equilibrium as the discharge cooled.

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A New Type of Phenomenon of Flow Birefringence in Macromolecular Solutions

DURING an investigation of solution states of methyl cellulose in aqueous systems, an unexpected new phenomenon was noted. The observed optical anisotropy as a function of the velocity gradient in the systems changed anomalously, as shown in Fig. 1 (solid lines). Reproducibility of the variations both of the degree of birefringence and the angle of

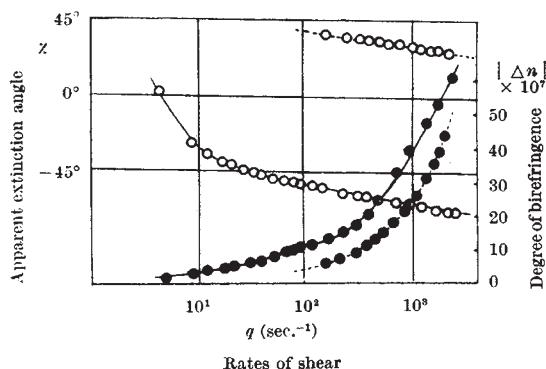


Fig. 1. Variations of the optical anisotropy and the degree of birefringence vs. the rates of shear: original methyl cellulose/water solution (dotted lines); aged methyl cellulose/water solution (solid lines).—○—, optical anisotropy (α); —●—, birefringence (Δn)

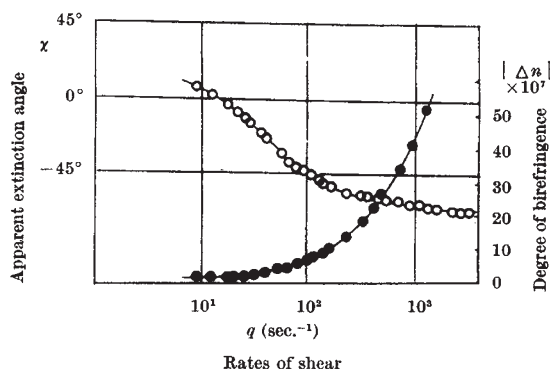


Fig. 2. Variations of the optical anisotropy and the degree of birefringence vs. the rates of shear in a methyl cellulose/methyl alcohol/water system

extinction versus the rates of shear were within experimental error.

Dilute aqueous solutions of 'Methocel' (Dow Chemical's powdered methyl cellulose: U.S.P. grade, MC-4,000 c.p., average molecular weight determined by viscometry about 140,000) were used in this investigation.

The dotted lines in Fig. 1 represent the normal flow birefringence obtained in the fresh solution, for comparison with the new phenomenon observed after the solution has been aged for two or more months at room temperature (about 30° C.).

A similar marked anomaly was noted in aged aqueous solutions even in fresh aqueous solution of methyl cellulose containing 50 volume per cent of methyl alcohol (see Fig. 2). With a mixed system of ethyl alcohol and water, an effect similar to that with methyl alcohol/water was noted.

It is difficult to find a theoretical explanation of the phenomenon. It seems to be connected with the fact that the solution states of aqueous methyl cellulose are not stable, in spite of the non-ionic nature of the polymer structure. The association of the chain molecules proceeds mainly due to dehydration of the molecules after the solution has been aged^{1,2}.

Further additional information has been obtained about this effect, using a solution which was mixed with considerable quantities of methyl alcohol in order to regulate the solvent power or the degree of dehydration of the polymer chains. The polymer concentration of the solutions was 1 per cent throughout the investigation, and no essential difference was found between the results obtained in the aged solutions and in the mixed systems. Both effects can probably be attributed to inter- and intramolecular hydrogen bonds between exposed hydroxyl groups of the polymer chains suffering dehydration during ageing, or artificially by the addition of a strong hydrophilic substance such as the alcohol.

The anomalous variations of the extinction angle with increasing rates of shear are still unexplained, and work is in progress to shed more light on the problem.

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