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Flow Properties of Moderately Concentrated Solutions of Cellulose Acetate Polymer

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NOTE

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INTRODUCTION

Calculations [1] of rheological properties of polymeric solutions have usually been restricted to very dilute or to very concentrated solutions. In either case, one starts with a model for the microstructure. Between these two conceptual extremes lies the broad class of moderately concentrated solutions. To cover this region theoretically, two approaches have been used; 1) network theories focusing attention on entanglement junctions, and 2) single-molecule theories focusing attention on single molecules but including intermolecular interactions. Williams, Wang, and Zimm introduced a double model; one for a particular macromolecule and another for solutions containing like molecules in which the chosen macromolecule is suspended. This approach has turned out to be quite successful because spheres immersed in a suspension of like spheres behave as if suspended in a Newtonian fluid, and the resulting expression for viscosity is quite simple in form and qualitatively correct for moderate concentrations.

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For a simple [2] unidirectional flow field in a liquid, the viscosity is written as the ratio of energy dissipation (ϵ) per unit volume and the square of the shear rate (γ), i.e.,

$$\eta = \epsilon/\gamma^2 \tag{1}$$

This equation is used to obtain an expression for the viscosity of polymer solutions and melts. On a small time scale, there exists Brownian motion, which makes its contributions to the energy, but on a large time scale the contribution is almost zero. The viscosity of polymer solutions and melts in the low-shear-rate limit is referred to as "zero-shear viscosity." In practice, this can be obtained by extrapolating the viscosity-shear rate curves to zero shear rate. Utracki [3] has studied the temperature dependence of zero-shear viscosity and has related his work to the concentration dependence of this viscosity for polymer melts and solutions in organic and inorganic liquids.

The dependence [4] of viscosity on concentration is largely due to the dependence of the ratio of viscosities at zero and infinite shear rates on the concentration of solutions. The factor attributable to this dependence may be the space immobilization of the solvent and irregular particle-particle aggregates, i.e., the formation of an extremely large supermolecular structure.

EXPERIMENTAL

The polymer was a sample of cellulose acetate of Ravi Rayon Ltd., Kala Shah Kaku, Lahore (Pakistan), and the solvents were cyclohexanone and dioxane, both of analytical grade. The concentration of the solution (w/v) ranged between 2 to 6%.

The shear viscosity of all the samples was determined with a Haake Rotary viscometer (Roto-Visco-12, West Germany) using the sensor system MV DIN. The shear rate (γ expressed in s^{-1}), the shear stress (τ expressed in Pa), and the viscosity (η expressed in mPa·s) were calculated from the instrument readings. The zero-shear viscosities were obtained by linear extrapolation.

RESULTS AND DISCUSSION

Cellulose acetate solutions in cyclohexanone and dioxane were studied at 35°C. It is evident from the results in Table 1 that the zero-shear viscosity (η_0) increases regularly with increasing concentration. However, the increase in dioxane is more pronounced,

TABLE 1

No.	Concentration, C g/dL	ln C	Cyclohexanone η_0, mPa·s	Cyclohexanone ln η_0	Dioxane η_0, mPa·s	Dioxane ln η_0
1	2.00	0.693	10	2.30	-	-
2	3.00	1.099	55	4.01	88	4.47
3	4.00	1.388	154	5.04	182	5.21
4	5.00	1.609	258	5.55	227	5.43
5	6.00	1.792	288	5.66	490	6.19

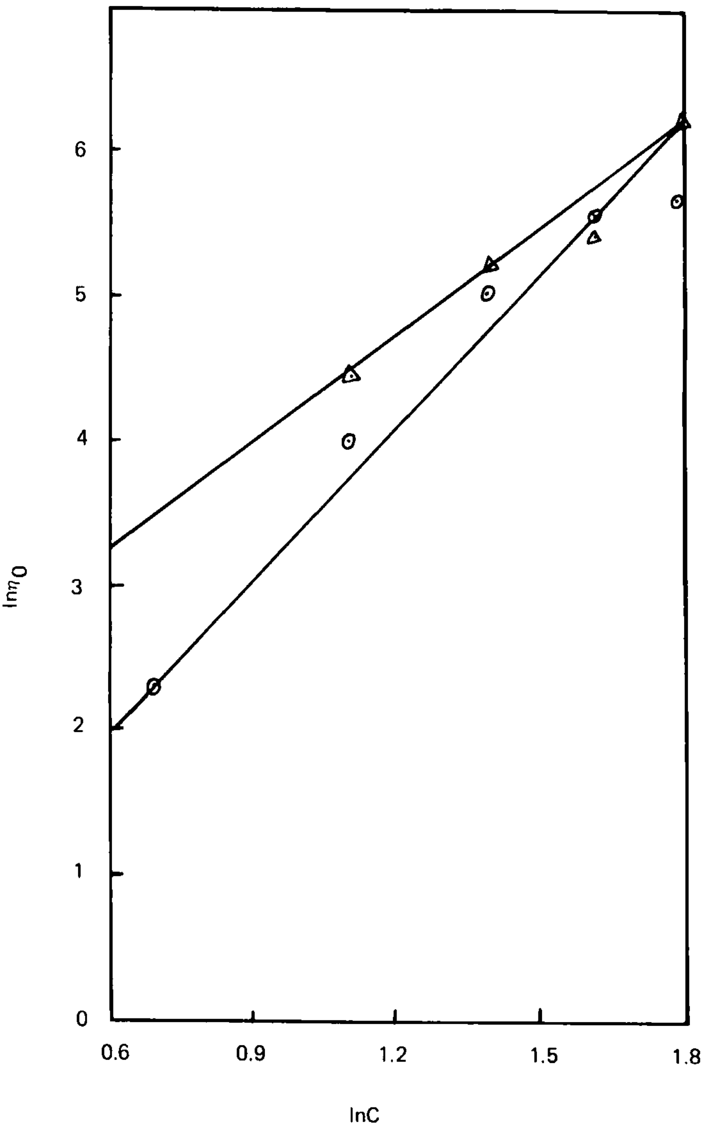

FIG. 1. Logarithmic plot of zero-shear viscosity (η_0) vs concentration (C) for solutions of cellulose acetate in two solvents, (○) cyclohexanone and (△) dioxane, at 35°C.

possibly due to the different extent of entanglements and different particle-particle aggregates [4], i.e., formation of unique supermolecular structures. There is only one oxygen atom in the cyclohexanone molecule but two in dioxane. Thus more hydrogen bonds [5] are expected between cellulose acetate and dioxane than between cellulose acetate and cyclohexanone, giving rise to larger molecules in dioxane than in cyclohexanone.

This is further supported by Fig. 1. The slopes $\partial \ln \eta_0/\partial \ln C$ for

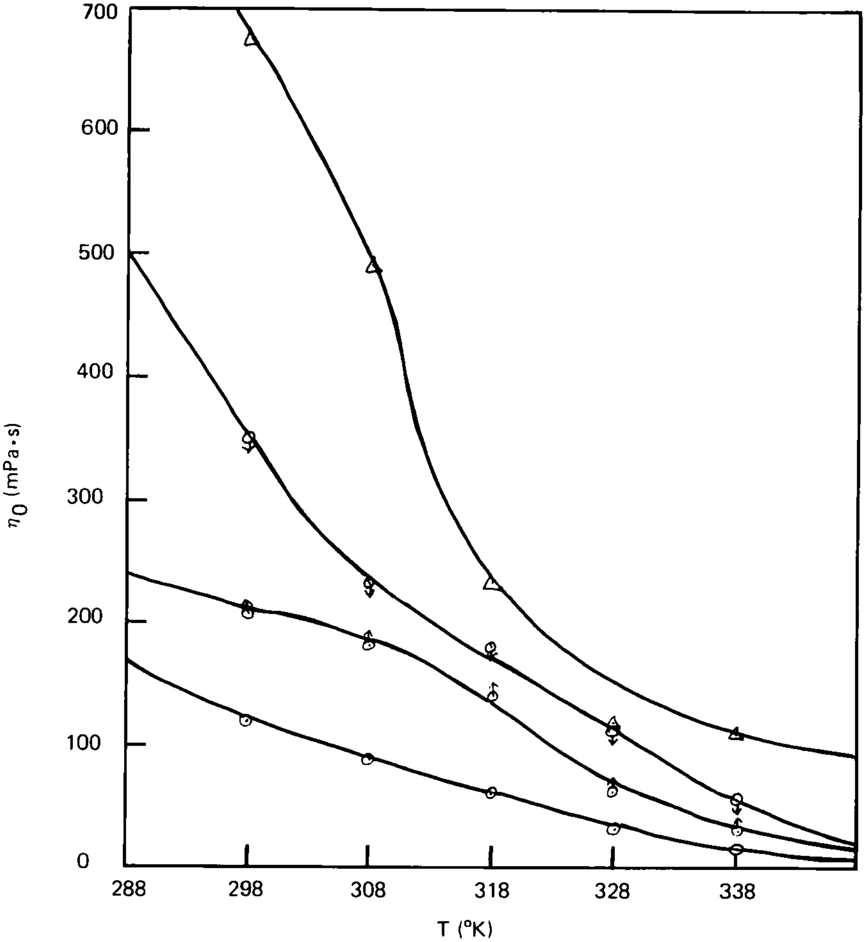

FIG. 2. Temperature dependence of zero-shear viscosity for solutions of cellulose acetate in dioxane: (○) 3 g/dL, (♂) 4 g/dL, (♀) 5 g/dL, and (△) 6 g/dL.

the two solvents are 2.46 for dioxane and 3.49 for cyclohexanone. These values are in good agreement with the results of the work of Berry, Metzger, and Chu [6], who found the value of $\partial \ln \eta_0 / \partial \ln C$ for various polymers to be in the vicinity of 2.8.

Solutions of cellulose acetate in dioxane were studied at various temperatures 25-65°C (Fig. 2). We found that the effect of concentration on the viscosity in dioxane at lower temperatures is more pronounced than at higher temperatures. This may be attributed, as suggested by Sharma [4], to two factors, namely, the decrease of solvent viscosity with rising temperature and the diminishing aggregations among the macromolecules and with the solvent. On the other hand, the effect of temperature at higher concentrations is more pronounced and is very low for dilute solutions (Fig. 2), and this result supports the above agrument.

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