Shear Viscosities of Cellulose Acetate-polymer

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Summary: The zero-shear viscosity of moderately concentrated solutions of cellulose acetate is studied in two different solvents namely; cyclohexanone and dioxane to investigate the effect of solvent on the polymer viscosity. For each solvent the ratio of the increment in the logarithemic zero-shear viscosity and logarithmic change of concentration (d ln η_0/d lnC) is calculated. To find out the effect of both temperature and concentration on the zero- shear viscosity of the polymer, solutions in dioxane are studied at various temperatures and it was concluded that the particle aggregation is affected when both the temperature and concentration are changed.

Introduction

Polymers can be characterized by various techniques like viscometry, osmometry, light scattering, I.R. dielectric relaxation studies, etc. The viscometric methods have been very frequently used due to their simplicity and high sensitivity to aggregation.

Calculation[1] for 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; (i) network theories focussing attention on entanglement junctions, and (ii) single-molecule theories focussing attention on single molecules but including intermolecular interactions. Williams, Wang and Zimm introduced a double model; one for a particular macromolecule and another for the 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 behaves as if suspended in a Newtonian fluid, and to resulting expression for viscosity is quite simple in form and qualitatively correct for the moderate concentrations.

For a simple[2] uni-directional 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.

$$\eta = \varepsilon/\gamma^2 \ldots\ldots\ldots(1)$$

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 does have its contributions to the energy but on a large time scale the contribution is almost zero.

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Generally the viscosity of polymer solutions is constant at low shear rate but above a certain critical value it falls rapidly. The low shear rate region is referred to as the first Newtonian region and the Bueche theory (Equation 1) applies. The viscosity of the polymer solutions and melts in this region is referred as the zero-shear viscosity.

L.A. Utracki[3] has studied the temperature dependence of the zero-shear viscosity and has related his work to the concentration dependence of the same, for polymer melts and solutions in organic and inorganic liquids.

The zero-shear viscosity[4] of a polymer is a complex function of several variables; such as molecular weight, polymer concentration, temperature, nature of solvent and molecular structure, etc.

S.H. Agarwal and Roger S. Porter have studied polyvinyl acetate in different solvents and have noted that the solvent effects are important in concentrated solutions.

V.P. Budtove[5] has given a theory for the viscosity of moderately concentrated solutions of polymeric substances, assuming a "local viscosity" effect and intermolecular hydrodynamic and thermodynamic interactions. The theory is based on clear physical assumption for the low concentration range and for high concentration range it becomes semi-empirical. However, it permits a description of a variety of relationships for the viscosity of concentrated polymer solutions and viscosity of solutions of mixtures of compatible and incompatible polymers.

The dependence[6] of viscosity on concentration is mainly because of 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. formation of extremely large supermoleculare structure.

Experimental

The polymer under investigation was a sample of cellulose acetate of Ravi Rayon Ltd; Kala Shah Kaku, Lahore (Pakistan) and the solvents

used were cyclohexanone and dioxane both being of analytical grade. The concentration of the solution (W/V) ranged between 2 to 6%.

The shear viscosity of all the samples were determined by HAAK Rotary viscometer (Roto-Visco-12, W.Germany) using the sensor system MV DIN as follows:

After[7] adjusting the zero and maximum indications the sensor system was filled with the sample. Keeping the temperature constant the scale reading(s) was recorded for the various speeds n (No of revolutions/minute), varying the range between 8,16,32,64,128,256 and 512. This process was repeated for different concentrations in each solvent and at different temperatures in one of the solvents.

The shear rate (γ expressed in S^{-1}); the shear stress (τ expressed in pascals) and viscosity (η expressed in mpa -s) were calculated by using the following formulae:

$$\gamma = M.n. \quad (2)$$
$$\tau = A.S. \quad (3)$$
$$\eta = \frac{G.S.}{(n)} \quad (4)$$

where M, A and G are constants depending on the system used. For this particular system the values are M = 1.29; A = 3.01 and G = 2333.

Results and Discussion

Cellulose acetate solutions in two solvents cyclohexanone and dioxane were studied at $35^{\circ}C$ temperatures. The zero-shear viscosity values for concenrations 2 to 6 g/dl are given in table 1, alongwith ln C and ln η_0 values for the two solvents.

The zero-shear viscosity (η_0) versus concentration is plotted inFig. 1. It is evident from the curves that the zero-shear viscosity increases regularly with increasing concentrations. However, the increase in dioxane is more pronounced.This behaviour can be attributed to the different extents of entanglements and different particle-particle aggregates[6] i.e formation of unique supermolecular structures. There is only one oxygen atom in the molecule of cyclohexanon where as in dioxane there
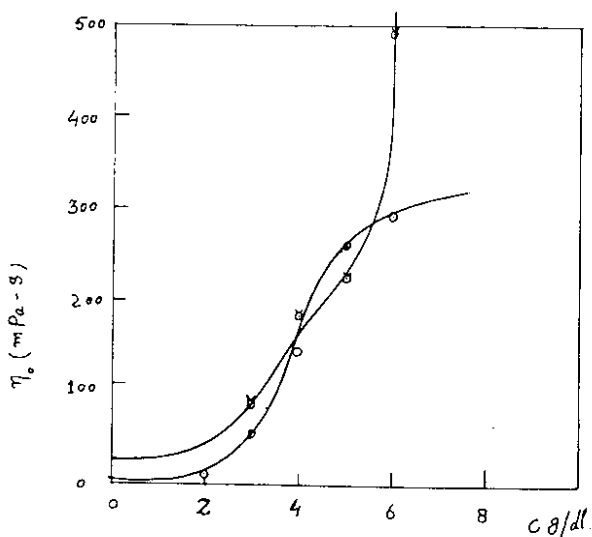
Fig. 1: Plot of η^O (mpa-s) vs concentration (g/dl) for cellulose acetate in two solvents; $\odot$ Cyclohexanone, $\eth$ dioxane, at 35°C.
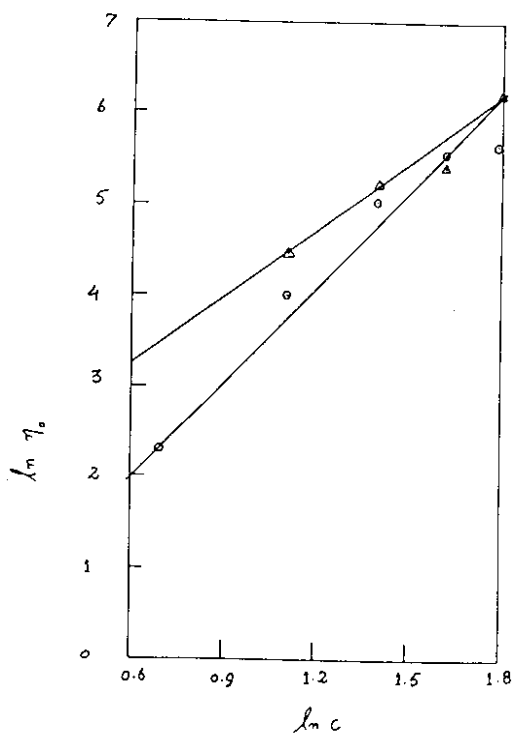

Fig. 2: 2 Plot of ln η^O vs lnC for solutions of cellulose acetate, at 35°C in two solvents; $\odot$ cyclohexanone,$\triangle$dioxane.

This is further supported by a plot of ln η_0 VS ln C (Fig. 2). From this plot the values of (d ln η_0/d ln C) for the two solvents are worked out. For the solution in dioxane this value is 2.46 and in cyclohexanone it is 3.49. These values are in good agreement with the results of the work of G.C. Berry et al[9] who have found for various polymers the value of (d ln η_0/d ln C) to be in the vicinity of 2.8

The solutions of cellulose acetate in dioxane were studied at various temperatures (25-65°C). The values of zero-shear viscosity (η_0) for different concentrations in dioxane, at different temperatures are given in Table 2.
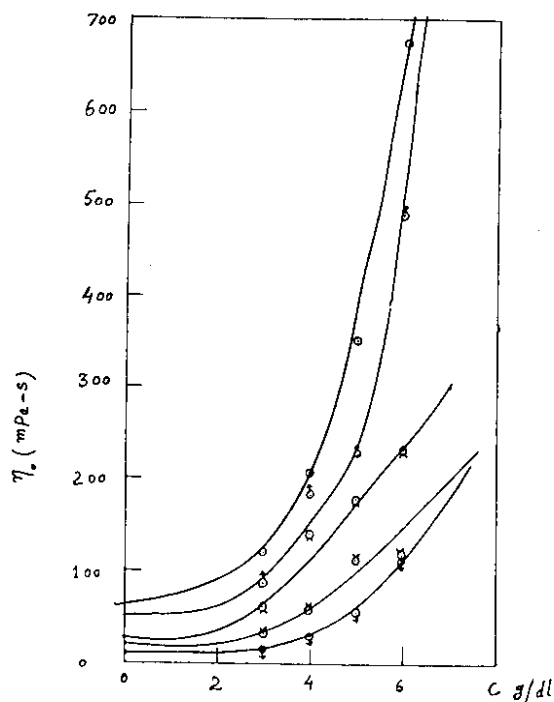

Fig. 3: η_0 (mpa-s) vs concentration C(g/dL) for cellulose acetate solutions at different temperatures t°C; $\odot$ 25°C, $\eth$ 35°C, φ45°C, $\eth$ 55°C, φ 65°C; in dioxane.

These results are plotted in Fig. 3. It is observed that the effect of concentration on the viscosity at lower temperature is more pronounced where as at higher temperatures the effect of concentration is small. This may be attributed, as suggested by R.S. Sherma [6] to two factors, namely; the decrease of solvent viscosity and the diminishing of aggregations between the macromolecules among themselves and also with the solvent. On the

are two oxygen-atoms present. Thus more hydrogen bonds are expected between cellulose acetate and dioxane than in case of cyclohexanone. Hence the supermolecules formed in diioxane are bigger than in cyclohexanone and the values are thus different.

Table 1:

No	C(g/dl)	In C	In Cyclohexanone		In dioxine	
			η_0(mpa-S)	In η_0	η_0(mpa-S)	In η_0
1	2	0.6932	10.0	2.3026	-	-
2	3	1.0986	55.20	4.0110	87.60	4.4728
3	4	1.3883	154.00	5.0370	182.20	5.2051
4	5	1.6094	257.60	5.5515	227.00	5.4250
5	6	1.7918	287.60	5.6616	489.80	6.1940

Table 2:

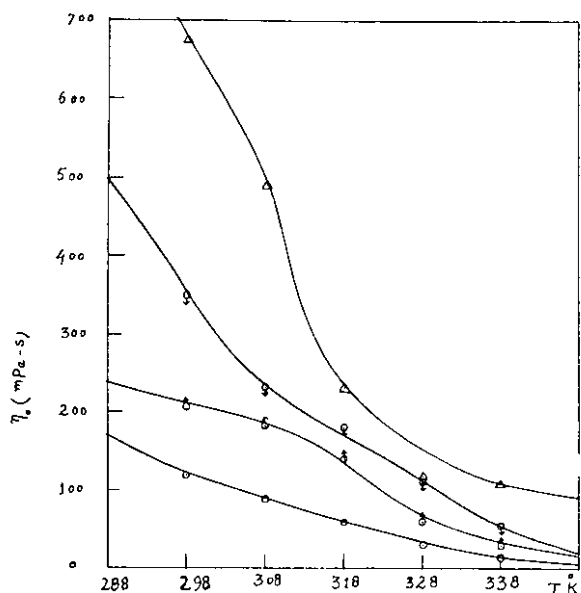| No	$T^O K$	η_0(mpa-S) for concentrations C (g/dl)			
		3	4	5	6
1	298	119.80	207.60	350.00	674.40
2	308	87.60	182.00	227.00	489.80
3	318	59.40	141.20	176.50	29.20
4	528	29.80	58.00	111.00	116.00
5	338	14.20	26.80	55.00	111.20

Fig. 4: η_0 (mpa-s) vs absolute temperature ($T^O K$) for solutions of cellulose acetate in dioxane: $\ominus$ 3 g/dL solution, $\varnothing$ 4 g/dL solution $\ominus$ 5 g/dL solution, $\triangle$ 6 g/dL solution.

other hand the effect of temperature at higher concentrations is more pronounced and is very low for the dilute solutions (Fig. 4) and this result supports the above argument.

References

1. P. Brun, *J. Rheo.*, **24** *(3), 263 (1980).*
2. Anil Kumar and Santosh K. Gupta, Fundamentals of Polymer Science and Engineering printed 1978, Tata McGraw-Hill Publishers Ltd. (New Delhi) pp. 336-470.

3. L.A. Utracki and R. Simha; *J. Rheo.,* **25** *(3), 329 (1981).*

4. S.H. Agarwal and Roger S. Porter; *J. Rheo.,* **25** *(2), 171 (1981).*

5. V.P. Budtove; *Eur. Polym. J.,* **17,** *191 (1981).*

6. R.S. Sharma; *Rheol.Acta,* **18,** *549 (1979).*

7. Instructions Mannual for Haake Rotary Viscometer (Roto- Visco-12, W. Germany).

8. Peter R. Dvornic; *Macromolecules,* **17,** *1348 (1984).*

9. G.C. Berry, P. Metzger and S.G. Ghu, proceedings of China-U.S. bilateral symposium on Polymer Chemistry and Physics, held October, 1979 (Beijing-China) published 1981.