

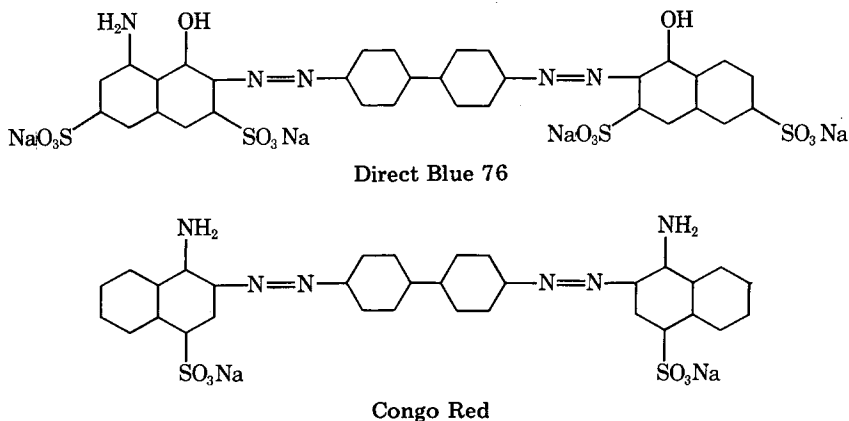
Taylor Diffusion in Polymer Solutions: Falsification by Slip Effects*

There has been a great deal of interest in experimental and theoretical work in diffusion in polymer solutions in view of its obvious pragmatic significance. In particular, a number of authors have focused their attention on diffusion of monomolecular solutes in polymer solutions. A review of the prior literature in this area has been provided by Astarita and Mashelkar.¹

A number of techniques are commonly used for measurement of diffusivity of monomolecular solutes in polymer solutions, which include flow techniques such as diffusion in flowing films^{2,3} and laminar jets⁴ or static techniques of different types.^{5,6}

In recent years, a simple and rapid method for the determination of diffusivity in polymer solutions using the so-called Taylor dispersion technique has been used by a number of authors.⁷⁻⁹ Singh and Nigam⁹ obtained results for the diffusion of Congo Red dye in aqueous solutions of carboxymethyl cellulose (CMC). These results are strikingly anomalous in the sense that there is a 1200% reduction in diffusivity when CMC concentration is changed from zero to 2%. We shall state as to why these results appear anomalous to us.

In the first instance, existing theories of diffusion in polymer solutions such as those by Li and Gainer,¹⁰ Osmer and Metzner,¹¹ Navari et al.,¹² and Kulkarni et al.¹³ show that for a system such as the one used by Singh and Nigam, the reduction in diffusivity is in no case larger than about 200%. Two doubts therefore arise concerning the measurements provided by Singh and Nigam. The first concerns the possibility that there may be a specific solute (Congo Red)-polymer (carboxymethyl cellulose) interaction in view of the ionic nature of the solute as well as the matrix through which the molecule diffuses. Fortunately, independent experimental studies by Farag et al.¹⁴ on diffusion of Direct Blue 76 dye in carboxymethyl cellulose solutions throws light on this issue. These authors show for this dye that in the same concentration range, there is actually an *increase* in the diffusion coefficient studied by Singh and Nigam. Farag et al. have attributed this effect to the solvation of polymer which occurs because of the large amount of water that is removed from the medium to solvate the sodium ion and the polar groups contained in the polymer molecule. It may be noted that the Congo Red dye used by Singh and Nigam and the Direct Blue 76 dye used by Farag et al. are structurally very similar, as can be seen by:



The interaction effects are therefore expected to be similar. However, it needs to be emphasized that the pH of the system does influence the degree of interaction between a specific dye and the polymer. In particular, for pH less than 5, Congo Red is expected to interact more strongly with CMC than Direct Blue 76, whereas at pH of 7 both dyes should act similarly. Unfortunately, neither Farag et al. nor Singh and Nigam reported the pH of their systems. However, it is unlikely that the 12-fold decrease in the diffusion coefficient as observed by Singh and Nigam can be attributed solely to this dye-polymer interaction.

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The foregoing implies that some additional factors invalidate the results of Singh and Nigam. There is a major difference between the technique used by Farag et al. and that used by Singh and Nigam. Farag et al. used a static technique, whereas Singh and Nigam used a flow technique. The question arises as to whether the use of the Taylor dispersion technique can cause errors in the measurement of diffusivity in polymer solutions. We later show that under the conditions typically encountered in Taylor dispersion measurements, there is a strong possibility of the so-called hydrodynamic slip effect. We present arguments to substantiate this viewpoint, and then provide an analysis which shows major errors that might arise when the Taylor dispersion techniques are used for diffusivity measurement in polymer solutions. Since this method is gaining popularity for this purpose, the analysis presented in this note would be of considerable general interest in stressing the caution to be exercised in the use of these techniques.

SLIP EFFECT IN CAPILLARY FLOWS

Taylor dispersion experiments involve a transient study of tracer distribution in polymer solutions flowing through long and narrow capillaries. Evidence is mounting in recent years which shows that when polymer solutions flow through such long and narrow capillaries, macromolecular migration away from the capillary surface occurs causing a significant reduction in polymer concentration in the immediate vicinity of the capillary wall.¹⁵⁻¹⁷ In any flow process in which the stress or the strain rate level varies with the position of the fluid, the macromolecular orientation and extension and consequently the free energy also varies with the position. In order that the free energy become independent of position at steady state, compensating concentration gradients are introduced. The net result is the migration of macromolecules from the regions of high shear (wall region) to that of low shear (tube center).

Although numerous experimental observations have appeared in the literature demonstrating the presence of such an effect, it is only recently that at least some semiquantitative theoretical calculations have been presented to estimate the extent of such slip effect in polymer solutions. We shall use the arguments presented by Metzner et al.¹⁶ to estimate the extent of the slip effect.

The result of macromolecular migration is a physical buildup of a solvent layer around the capillary wall through which the rest of the polymer solution slips. This apparently gives rise to a slip velocity v_s at the surface. Metzner et al. show that the magnitude of this slip velocity in relation to the mean velocity can be approximately calculated as

$$\frac{v_s}{V_R} = \left(64 \left(\frac{\mu_a}{\mu_s} \right)^2 \frac{L}{D} \frac{D_P}{V_R D} \right)^{1/3} \quad (1)$$

where μ_a is the apparent viscosity of the bulk polymer solution, μ_s is the solvent viscosity, L is the length of the capillary, D is the diameter of the capillary, and D_P is the diffusivity of the polymer molecule in the polymer solutions. Using the data provided by Singh and Nigam, we calculated v_s/V_R , and it appears that slip velocities of the same order as the bulk average velocity could easily be present. Although the theory of Metzner et al.¹⁶ is only semiquantitative, it does show that major slip effects are to be expected in the experiments performed by Singh and Nigam. It might also be noted from eq. (1) that slip effects become accentuated with a decrease in capillary diameter and an increase in length. Singh and Nigam have used an L/D ratio approaching 7500; this is excessively high. For the quasi-steady-state approximations in the Taylor dispersion theory to be valid, we have to satisfy the following condition in the case of a power law fluid⁹:

$$\frac{LD_P}{4V_R D^2} > 0.5 \quad (2)$$

It is immediately seen that requirements of eq. (2) are quite contradictory to the requirements of equation (1). In other words, to ensure that the Taylor dispersion theory is valid, one would prefer to have large capillary lengths and small capillary diameters, whereas these are precisely the conditions which promote the slip effect, see eq. (1). It thus appears that in the Taylor dispersion measurements which are generally carried out, slip effects cannot be avoided.

In the following we attempt to present a theory which corrects the Taylor dispersion theory for the presence of the slip effect.

TAYLOR DISPERSION IN THE PRESENCE OF SLIP EFFECT

It is well known (see, for example, Nunge and Gill¹⁸) that the Taylor dispersion coefficient is a strong function of the velocity profile within the tube. In the case of power law fluids (consistency index K and power law index n), simple hydrodynamic analysis performed by replacing the no-slip condition [$v = 0$] by the slip condition [$v = v_s$] at the wall gives

$$v = v_s + \frac{nR}{n+1} \left(\frac{\Delta P R}{2KL} \right)^{1/n} \left[1 - \left(\frac{r}{R} \right)^{1+1/n} \right] \quad (3)$$

where R is the capillary radius and ΔP is the pressure drop. Taylor dispersion analysis can be readily performed with this modified velocity profile. An expression for the Taylor dispersion coefficient D_{eff} is then obtained:

$$D_{\text{eff}} = \frac{R^2(V_R - v_s)^2}{D_P} \frac{n^2}{2(3n+1)(5n+1)} \quad (4)$$

which can be reorganized to deduce the molecular diffusivity as

$$\frac{(D_P)_{\text{observed}}}{(D_P)_{\text{actual}}} = \left(\frac{V_R - v_s}{V_R} \right)^2 \quad (5)$$

It is at once evident that the presence of slip effect (finite v_s) leads to a falsification of the results in that an apparent reduction in the molecular diffusivity is observed. In the case of the data presented by Singh and Nigam, the presence of 50–80% slip would imply apparent diffusivities which are 4–25 times lower than the true diffusivity. It therefore appears that the strong reduction effects observed by Singh and Nigam⁹ are a result of major slip effects which occur in narrow and long capillaries.

CONCLUSIONS

The Taylor dispersion technique for measurement of small solute diffusivities in macromolecular solutions can lead to erroneous results due to the presence of a possible slip effect. We have demonstrated that the apparently anomalous effects observed by Singh and Nigam could be ascribed to the slip phenomenon.

NOMENCLATURE

D	capillary diameter
D_{eff}	Taylor diffusivity
D_P	polymer diffusivity
K	consistency index
L	capillary length
n	power law index
ΔP	pressure drop
r	radial distance
R	capillary radius
v	axial velocity
v_s	slip velocity
V_R	average velocity
μ_a	viscosity of polymer solution
μ_s	solvent viscosity

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