

Diffusion Coefficient in Polymer Solutions

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Synopsis

Molecular diffusivity of a solute in a solvent may be determined by measuring the extent of dispersion of solute in solvent flowing in a straight circular tube under the conditions of laminar flow. This simple and rapid method for determination of molecular diffusivity in aqueous polymer solutions is discussed. Experimental results show a substantial reduction in the solute diffusivity with increase in polymer concentration.

INTRODUCTION

The technique of measurement and the prediction of diffusion coefficients in Newtonian fluids are fairly well known. Non-Newtonian fluids are often encountered in polymer processing industries, but the diffusivity data are not extensive and the methods of predictions are not well known. The different methods for the measurement of diffusion coefficient in non-Newtonian fluids have been discussed.¹⁻⁴ Most of these studies²⁻⁴ are essentially limited to sparingly soluble solutes which are solids at the experimental conditions. More recently Deo and Vasudeva⁵ have provided a simple and rapid method for the determination of diffusion coefficient in power-law fluids; the diffusion coefficient of benzoic acid in aqueous carboxy methyl cellulose solutions were determined by measuring the dispersion of solute in a straight capillary. The same method was used by Shah and Cox⁶ to determine the diffusion coefficient in non-Newtonian fluids by using the analysis of Fan and Hwang.⁷ The prior literature on diffusion in non-Newtonian fluids has been reviewed by Astarita and Mashelkar.⁸

The present work was therefore undertaken to determine experimentally the value of diffusion coefficient in non-Newtonian fluids using the flow method based on Fan and Hwang's analysis. With increase in CMC concentration, a substantial reduction in diffusion coefficient is observed. It is believed that such reduction has not been reported so far and may be of interest to those engaged in developing predictive correlations for molecular diffusion coefficient.

THEORY

Fan and Hwang⁷ derived an expression for the effective dispersion coefficient for unsteady-state laminar dispersion in power-law fluids flowing in a straight tube under nonreacting conditions. Their expression for dispersion coefficient can be written as

$$UL/D = [2(3n + 1)(5n + 1)/n^2]\tau \quad (1)$$

The conditions for the validity of eq. (1) have been reported as

$$\tau \gg 0.0682 [(3n + 1)/(n + 1)] \quad (2)$$

Cox et al.⁶ compared the numerical solutions of the convective diffusion equation with the dispersion model predictions and showed that Fan and Hwang's analysis is valid for large Ud_t/D provided $\tau > 0.7$. Anantha Krishnan et al.¹¹ pointed out that a distinction must be made between the area mean and the bulk mean concentrations. Ferrel and Himmelblau¹² showed that the two are essentially the same for Newtonian fluids when $\tau > 2$.

EXPERIMENTAL

The dispersion of Congo Red Dye in aqueous polymer solutions of carboxymethyl cellulose (CMC) was studied. The low-viscosity CMC supplied by BDH (UK) was used. The concentration of the polymer solutions was varied from 0% to 2%. The rheological data were obtained on a capillary viscometer at practically the same temperature at which dispersion studies were carried out.

For the measurement of the diffusion coefficient the tracer solution in a concentration of 0.3 g/l. was prepared in aqueous solution of CMC. The solvent (CMC) and the dye solution were then stored in two constant head reservoirs, respectively. The capillary tube of diameter of 0.135 cm and length of 10.05 m was connected to the three-way stopcock. The flow of the tracer through the tube was adjusted by adjusting the height of the reservoir. The three-way-stopcock was then manipulated to change the flowing fluid from the normally flowing solution of CMC to the tracer solution at the same flow rate. About 25 to 30 samples of the tracer solution were manually collected at the outlet during the time over which the tracer concentration changed from zero to the maximum value. Each sample was collected over a period of $< 0.02\bar{t}$ sec. The dye concentration in each sample was determined by measuring the optical density at a wavelength of 520 μm using an ELICO colorimeter. Linear relationship between the optical density and the dye concentration over the range of concentrations employed enabled the direct use of optical density for obtaining the step-response curves.

CALCULATION OF DIFFUSION COEFFICIENT

In the present study the dispersion model solution for doubly infinite boundary conditions was used since it is convenient to use and does not introduce any error for low values of dispersion number ($D/UL < 0.01$) encountered in the present work. The solution for doubly infinite boundary conditions can be written as

$$F = \frac{1}{2} \left\{ 1 - \operatorname{erf} \left[\frac{1 - \theta}{2} \left(\frac{Pe}{\theta} \right)^{1/2} \right] \right\} \quad (3)$$

where F = dimensionless tracer concentration at the outlet and Pe = Peclet number, UL/D . The nonlinear least-squares fit method¹³ was used to find the value of UL/D . Knowing the value of UL/D the value of the diffusion coefficient can be calculated from eq. (1).

RESULTS AND DISCUSSION

The molecular diffusion coefficient of Congo Red Dye in water and four different concentrations (0.1%, 0.5%, 1%, and 2%,) of CMC solutions were studied by measuring the extent of dispersion in a straight tube. For each solution two to three different measurements were carried out at different flow rates. All the experiments were carried out where the dispersion model was valid. The criterion for the validity of the dispersion model and the values of the dispersion number encountered in the present study have been reported before.¹⁴ The experimentally determined values along with the rheological data are reported in Table I.

The results indicate that the value of the diffusion coefficient decreases with increase in CMC concentration. In case of 2% CMC solution a 12-fold reduction in the value of the diffusion coefficient was observed as compared to water. In the case of water, a diffusion coefficient (for Congo Red Dye in water) of 5.5×10^{-6} cm²/sec was reported by Trivedi and Vasudeva¹⁵ in comparison to our value of 4.4×10^{-6} cm²/sec. Hansford et al.³ have obtained a diffusion coefficient of benzoic acid for different concentrations of CMC solutions by measuring the mass transfer from a rotating disk. They found only a marginal reduction whereas the present results show a substantial reduction in the diffusion coefficient. The probable reason for the substantial reduction in the solute diffusivity may be that the polymer-solvent intermolecular forces are expected to be different from the solvent-solvent intermolecular forces. It may be noted that in the present study very low flow rates were employed and therefore the wall-shear rate values are much lower (4–18 sec⁻¹) so that the reported values can be assumed to be those approaching zero-shear rate value.

It is interesting to mention that by using flow techniques for the measurement of the diffusion coefficient in polymer solutions several authors^{4,16–18} have reported an increase in the solute diffusivity as the polymer concentration increases. Predictive models^{19–21} based on an extension of Eyring's liquid-state model have been developed for the prediction of diffusivity of small solutes in polymeric solutions. None of these models confirms the increase in solute dif-

TABLE I
Diffusion Coefficient of Congo Red Dye in CMC Solutions

CMC, wt-%	<i>n</i>	<i>K_{n-2}</i> , g/sec cm	Wall-shear rate, 1/sec	<i>D_m</i> × 10 ⁶ , cm ² /sec	Mean value, <i>D_m</i> × 10 ⁶ , cm ² /sec	<i>D_m</i> water/ <i>D_m</i> CMC sol.
0.0	1.0	0.0075	15.3	4.3	4.4	
			8.1	4.5		
0.1	0.995	0.012	18.5	3.82	3.8	1.2
			9.15	3.78		
0.5	0.93	0.061	18.8	1.35	1.60	2.8
			9.65	1.64		
			6.75	1.77		
1.0	0.875	0.37	10.12	1.44	1.20	3.7
			7.6	0.99		
			5.03	1.21		
2.0	0.83	1.8	10.10	0.376	0.37	12.0
			7.30	0.354		
			5.76	0.380		

fusivity as the polymer concentration increases. Li and Gainer¹⁷ reported the data of Astarita, Osmer, and Metzner which showed increased liquid diffusivity with increased CMC concentration. Later, Osmer²² has shown that by applying the necessary correction to these microinterferometric data, the liquid diffusivity actually decreased with increase in CMC concentration. Osmer has also reported that he was unsuccessful in duplicating the data of the one system in which Li and Gainer found an increase in diffusivity with increased polymer concentration, indicating that this increase may have been due primarily to experimental error. Astarita⁴ found that there was an increase in the value of the diffusion coefficient of benzoic acid for a 2% CMC solution. Deo and Vasudeva⁵ have recently pointed out that this increase in the value may be because of a possible error in the measurement of solubility data. In fact, Naveri et al.²⁰ have shown convincingly that the only system in which an increasing polymer concentration can result in increasing diffusivities are those with a zero or positive energy of activation difference. No system reported at this time appears to satisfy this condition. Therefore the possibility of an increase in the solute diffusivity as the polymer concentration increases is not unequivocally substantiated so far.

The authors believe that the diffusion coefficient values reported in Table I are substantially correct, although they have no explanation to offer for the fact that they are unexpectedly low.

CONCLUSIONS

The molecular diffusion coefficients of Congo Red Dye in aqueous CMC solutions are reported over a wide range of CMC concentration. The diffusion coefficient was found to be a strong function of CMC concentration. An about 12-fold reduction in the diffusion coefficient value was observed with 2% CMC solution.

Notation

a	radius of the capillary tube (cm)
d_t	diameter of the capillary tube (cm)
D	effective diffusion coefficient (cm ² /sec)
D_m	molecular diffusion coefficient (cm ² /sec)
F	dimensionless concentration of the tracer at the outlet
L	length of the capillary tube (cm)
n	flow index
t	time (sec)
\bar{t}	mean holding time (sec)
U	average linear velocity of the fluid (cm/sec)
	Dimensionless Groups
θ	t/\bar{t}
Pe	Peclet number (UL/D)
τ	characteristic time $(\bar{t}D_m)/a^2$, i.e., ratio of characteristic time for the convective transport to that for radial diffusion

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