JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 3247–3253 (1976)

Diffusion in Aqueous Polymer Solutions

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Synopsis

The diffusion of Direct Blue 76 dye in aqueous dilute polymer solutions was studied using the capillary method. The polymer systems studied included dilute solution of carboxymethyl cellulose, poly(ethylene oxide), and polyacrylamide. It was found that the diffusion coefficient of Direct Blue 76 in carboxymethyl cellulose is higher than that in pure water, while in polyacrylamide and poly(ethylene oxide) solutions the value is lower than that in pure water. The diffusion coefficient of Direct Blue was found to decrease with increasing polymer concentration in case of poly(ethylene oxide) and polyacrylamide, while in case of carboxymethyl cellulose the diffusion coefficient increases with polymer concentration. The effect of temperature on the diffusion coefficient of Direct Blue 76 in the three polymers was found to obey the Arrhenius equation. The activation energy for diffusion of Direct Blue 76 in water, poly(ethylene oxide), polyacrylamide, and carboxymethyl cellulose was found to be 4.38, 7.7, 5.44, and 5 kcal, respectively, for polymer concentration of 0.25 g/l.

INTRODUCTION

Diffusion of low molecular weight solutes in polymer solutions has received great attention owing to its importance in polymer technology. Emphasis has been placed on the diffusion of solutes of simple chemical structure such as gases and low molecular weight organic compounds.[1–16]

In the present work, the diffusion of a relatively high molecular weight solute with a bulky structure, namely, Direct Blue 76, was studied. Such a study would be of importance in the kinetics of mixing polymer solutions with solutions of low molecular weight compounds. The application of water-soluble polymers in different fields such as cosmetics, food technology, and coatings involves mixing with low molecular weight compounds.

EXPERIMENTAL

Measurement of the diffusion coefficient was carried out by the capillary method. The basis of the method is discussed elsewhere.[17] The technique was used by Wang[18–23] to study the diffusion of low molecular weight solutes in proteins.

A set of five capillaries each of length 3 cm and radius 0.5 mm, open at the top and closed at the bottom, were filled with the dye–water solution (1 g/l.) using a syringe. The filled capillaries were centrifuged to remove air bubbles, topped

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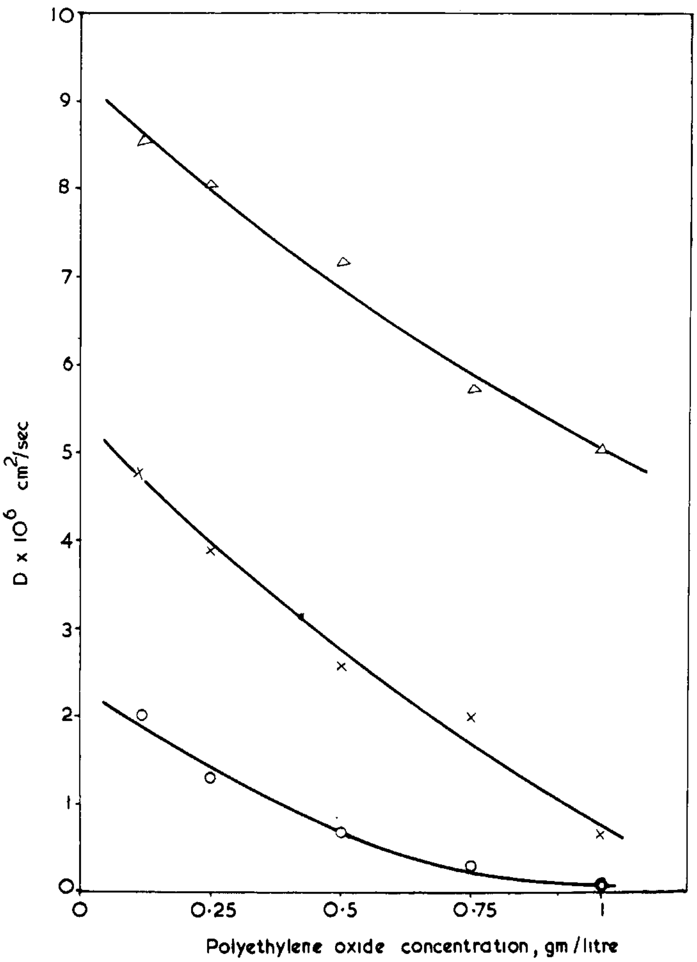


Fig. 1. Effect of poly(ethylene oxide) concentration on the diffusion coefficient of Direct Blue 76: (O) 25°C; (X) 35°C; (Δ) 55°C.

up with fresh solution, and mounted in a holder. The holder with the capillaries was immersed in 500 cc polymer solution which had been equilibrated in a constant-temperature bath.

Diffusion was allowed to proceed for the requisite period. The holder and tubes were removed from the polymer solution, and the solution in the capillary tubes was analyzed using a Beckman spectrophotometer.

Under these conditions, the solution of the one-dimensional diffusion equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

can be represented with enough accuracy by[17]

$$\frac{DT}{h^2} = \frac{4}{\pi^2} \ln \left[\left(\frac{8}{\pi^2} \right) \frac{C_0}{C_{av}} \right]$$

where C_{av} is the average concentration of the dye within the capillary tubes at the end of the run; C_0 is the initial concentration of the dye within the capillary

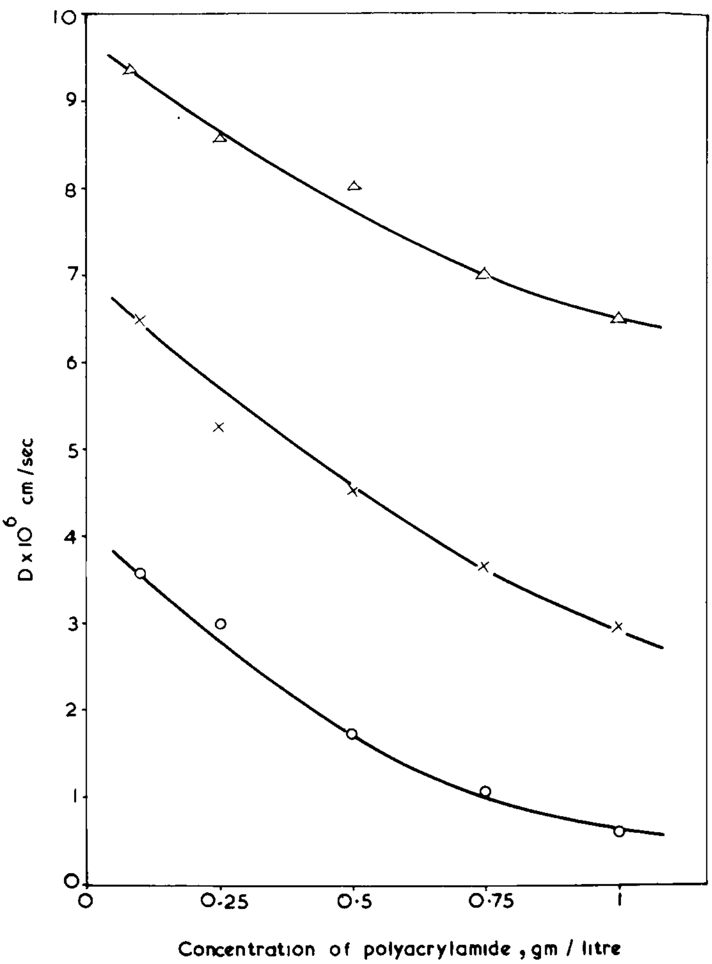


Fig. 2. Effect of polyacrylamide concentration on the diffusion coefficient of Direct Blue 76: (O) 25°C; (X) 35°C; (Δ) 55°C.

tubes; D is the diffusion coefficient of the dye, cm^2/sec; h is the height of the capillary tube, cm; and t is the time of the run, sec.

The accuracy of the technique was checked using $1M$ potassium chloride; the determined diffusion coefficient of the solution in water was in agreement with the value reported in the literature using other techniques. Three types of polymers were used: carboxymethyl cellulose sodium salt (C.M.C), a product of Hercules Company; poly(ethylene oxide) (Polyox), a product of Union Carbide; and polyacrylamide (Separan), a product of the Dow Chemical Company.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the effect of polyacrylamide, poly(ethylene oxide), and carboxymethyl cellulose concentration on the diffusion coefficient of Direct Blue 76. The diffusion coefficient of Direct Blue 76 decreases with polymer concentration in case of polyacrylamide and poly(ethylene oxide) solutions, while it increases with polymer concentration in case of carboxymethyl cellulose. This

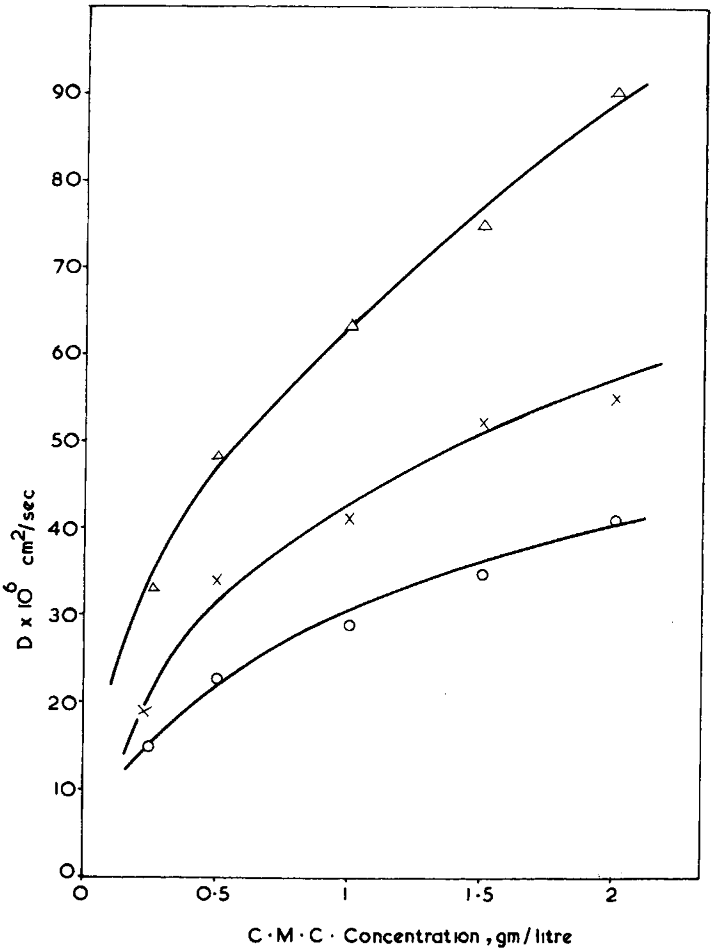
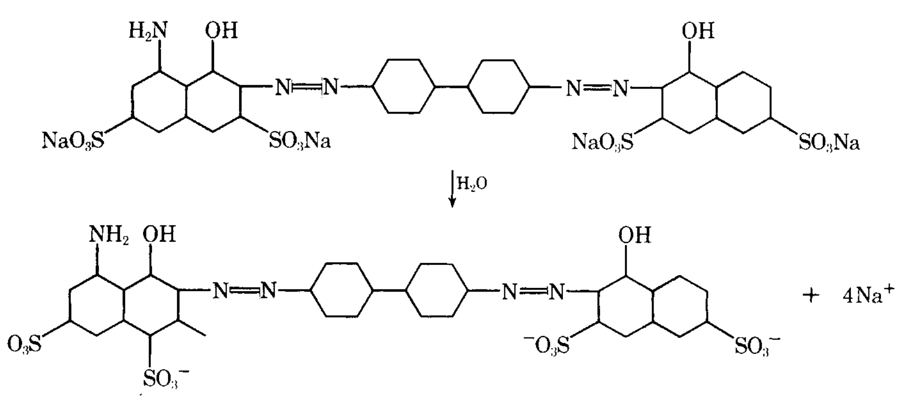


Fig. 3. Effect of C.M.C. concentration on the diffusion coefficient of Direct Blue 76: (O) 25°C; (X) 35°C; (Δ) 55°C.

result can be interpreted in terms of the structure of both the dye and the polymer. Direct Blue 76 is an anionic dye; it contains in its structure the solubilizing group —SO_3Na; in solution, it ionizes to sodium ion and negatively charged dye ion:



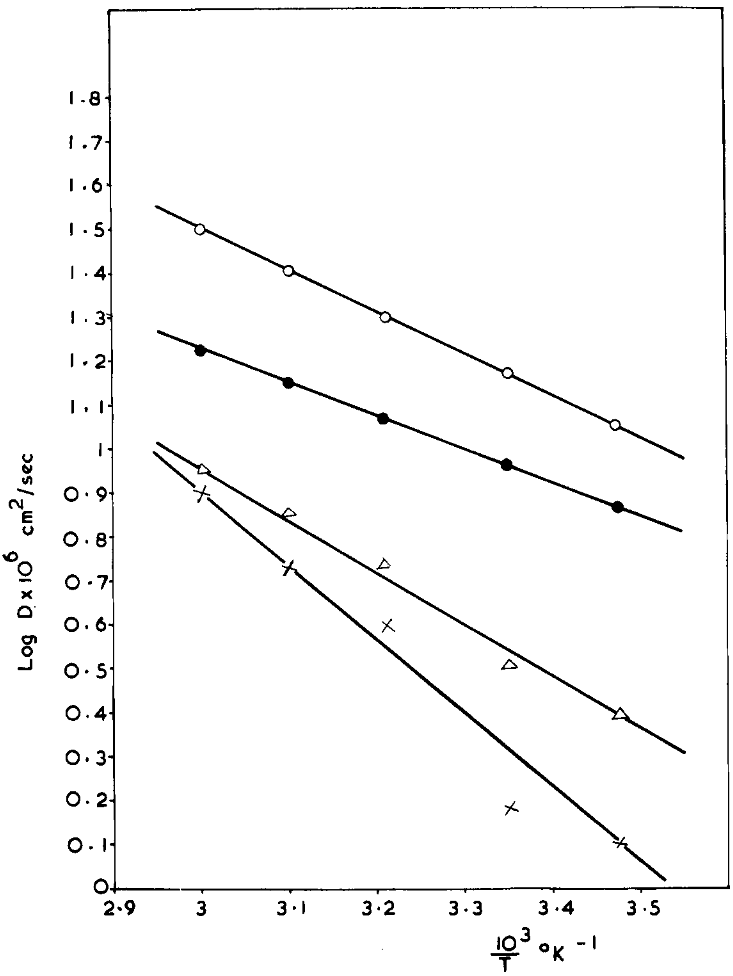
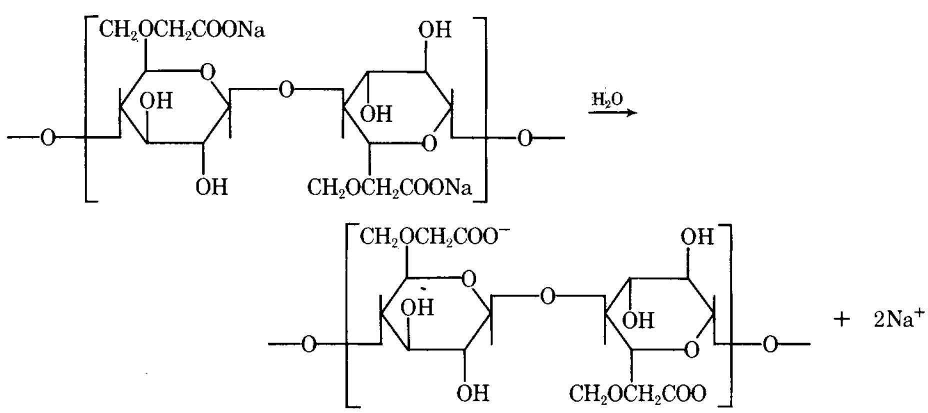


Fig. 4. Plot of log D vs. 1/T for the diffusion of Direct Blue in different polymers: (O) 0.25 g/l. C.M.C.; (●) pure water; (Δ) 0.25 g/l. Separan; (X) 0.25 g/l. Polyox.

On the other hand, carboxymethyl cellulose is a polyelectrolyte which ionizes in solution to give sodium ions and a negatively charged polymer chain:



Carboxymethyl cellulose molecules exist in dilute solutions as stretched chains owing to the repulsion of the negatively charged segments present in the polymer molecule.[25] This stretched configuration offers less resistance to the diffusing solute than the more bulky coiled configuration, according to the Wang theory.[19] As a polyelectrolyte, carboxymethyl cellulose exerts two effects on the diffusing dye molecule. The first effect is that interionic attraction takes place between the polymer molecules and the diffusing dye molecules; the result of this effect is that activity of the diffusing dye (the effective concentration) will decrease and accordingly the chemical potential and the diffusion coefficient will decrease. The second effect is that carboxymethyl cellulose is a highly solvated polymer, i.e., a large amount of water is removed from the medium to solvate the sodium ions and the polar groups contained in the polymer molecule.[26] The removal of this enormous amount of water from the medium decreases the amount of water available as a solvent, and accordingly the apparent concentration of the dye will increase with consequent increase in the chemical potential of the dye and its diffusion coefficient. It seems that the second effect is predominating in the present case, and this explains the increase in the diffusion coefficient of the dye with increase of carboxymethyl cellulose concentration.

The fact that the diffusion coefficient of the solute increases with increasing carboxymethyl cellulose concentration was found also by Astarita et al.[27] who studied the diffusion of some nonionic solutes, e.g., allyl alcohol, ethanol, and glycerol, in carboxymethyl cellulose solutions. Hansford et al.[7] studied the diffusion of benzoic acid in carboxymethyl cellulose solutions. They reported a decrease in the diffusion coefficient of benzoic acid in carboxymethyl cellulose solutions. This is probably because Hansford et al. used relatively concentrated non-Newtonian solutions where the enhancing effect of polymer solvation is overshadowed by the drastic increase in viscosity and the interionic attraction effects between the sodium salt of carboxymethyl cellulose and benzoic acid.

Polyacrylamide and poly(ethylene oxide) differ in structure from carboxymethyl cellulose in that they are nonionic polymers, and this has its impact on the properties of their solutions, particularly, molecular configuration and solvation. Polymer molecules are likely to exist in the coiled form in dilute solutions unless stretched by a high shear.[24] The degree of solvation of polyacrylamide and poly(ethylene oxide) is far less than that of carboxymethyl cellulose because both polymers contain fewer polar groups than carboxymethyl cellulose per molecule. The coiled molecules of polyacrylamide and poly(ethylene oxide) highly obstruct the diffusion of the dye molecule;[19] this effect, coupled with the increased viscosity of the medium, leads to a decrease in the diffusion coefficient of the dye. It seems that the role played by solvation in case of polyacrylamide and poly(ethylene oxide) in increasing the diffusion coefficient of the dye is not significant, and the net result is a decrease in the diffusion coefficient of the dye.

Figure 4 shows the effect of temperature on the diffusion coefficient of the dye in different polymers. The data fit the Arhenius equation

$$D = D^0 e^{-E/RT}$$

The activation energies for diffusion in water, poly(ethylene oxide), polyacrylamide, and carboxymethyl cellulose are 4.38, 7.7, 5.44, and 5 kcal, respectively, for a polymer concentration of 0.25 g/l.

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Received October 1, 1975
Revised January 9, 1976