Diffusion of glucose derivatives in aqueous solutions of hydroxypropyl cellulose

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(*Received* 18 *August* 1981)

The diffusion behaviour of glucose and three of its derivatives in aqueous solutions of hydroxypropyl cellulose was studied as a function of polymer concentration. A shearing type diffusion cell was used together with a schlieren optical system. The presence of polymer did not affect the diffusion of glucose. The derivatives, however, exhibited a linear decrease in diffusion coefficient with increasing polymer concentration. The results were discussed in terms of solvation and obstruction.

Keywords Diffusion; glucose; glucose derivatives; hydroxypropyl cellulose; obstruction; solvation

Introduction

The diffusion of small molecules in polymer systems has attracted the interest of several investigators[1–13] and a number of theories have been developed to account for the variation in diffusion coefficient of the diffusant on polymer concentration[8,14–16]. Here we report on the diffusion behaviour of glucose and three of its derivatives in aqueous solutions of hydroxypropyl cellulose. The measurements were carried out at a temperature of 25°C, at which water is a thermodynamically good solvent for the polymer[17]. The diffusants are of comparable size having different substituents which might be expected to influence the diffusion process.

Experimental

Materials and preparations. A commercial sample of HPC (hydroxypropyl cellulose, KLUCEL-G, Hercules Powder Company) with a weight-average molecular weight of approximately 300000 (according to the manufacturer) was used. The sample was purified by dialysis in cellophane tubing bags and recovered by freeze-drying, and finally dried in vacuum at 50°C. D(+)-glucose (G), D(+)-glucosamine hydrochloride (GA), *N*-acetyl-D-glucosamine (NAG) of PURISS grade and D-glucose-6-phosphate disodiumsalt (GP) of PURUM grade, were purchased from FLUKA AG and used without further purification.

HPC solutions were prepared by weighing and concentrations (mass/volume) were calculated from weight fractions and densities. The concentration of diffusant was 1% (w/w) in all measurements.

Diffusion measurements. Diffusion measurements were carried out in an apparatus built at this institute[18]. All measurements were carried out at 25.0°C and the temperature regulated to within ±0.01°C. The cell used for the formation of a sharp boundary was of the shearing type[19]. The broadening of the boundary was followed using a schlieren optical system and registered photographically.

When the concentration of HPC was the same on both sides of the boundary (ignoring the effect of diffusant on the polymer concentration in the solution below the boundary) a dip in the schlieren peak was observed as seen in *Figure 1*. We found that a small lowering of the HPC concentration in the solution above the boundary, containing no diffusant, was enough to remove the dip. See *Figure 1*. This lowering was larger than the concentration change due to the addition of diffusant to the solution below the boundary. The resultant gradient in polymer concentration was in all cases small and varied with the diffusant. It also increased with increasing polymer concentration. Since the diffusion coefficient of the polymer is considerably smaller than that of the diffusant it was assumed that the broadening of the schlieren peak reflects the diffusion of the migrating molecules only. If the two pictures in *Figure 1* are superimposed on each other, one can see that the overall shape of the curves is the same, supporting the validity of our compensation method.

The diffusion coefficients were evaluated as described by Nyström and Roots[10].

Results and Discussion

The dependence of diffusion coefficient on polymer concentration for G, GA, NAG and GP is shown in *Figure 2*. The lines drawn are least square fits and the maximum deviation is 2%. Intercepts are reported as D_0 values (D_0 is the diffusion coefficient in pure solvent) in

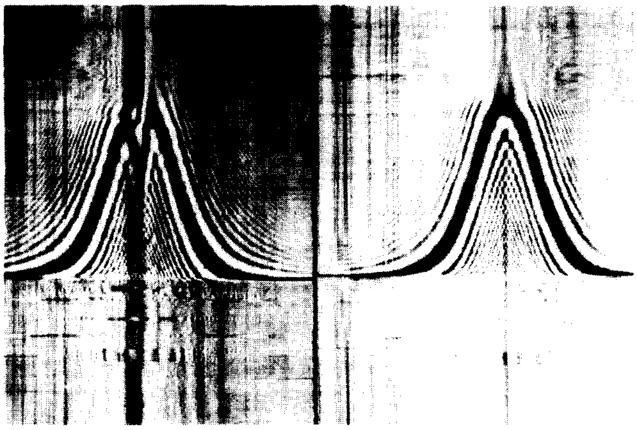

Figure 1 Diffusant GP in 2.0% (w/w) solutions of HPC. The polymer concentration gradient across the boundary necessary to remove the dip was 0.05% (w/w) in this case

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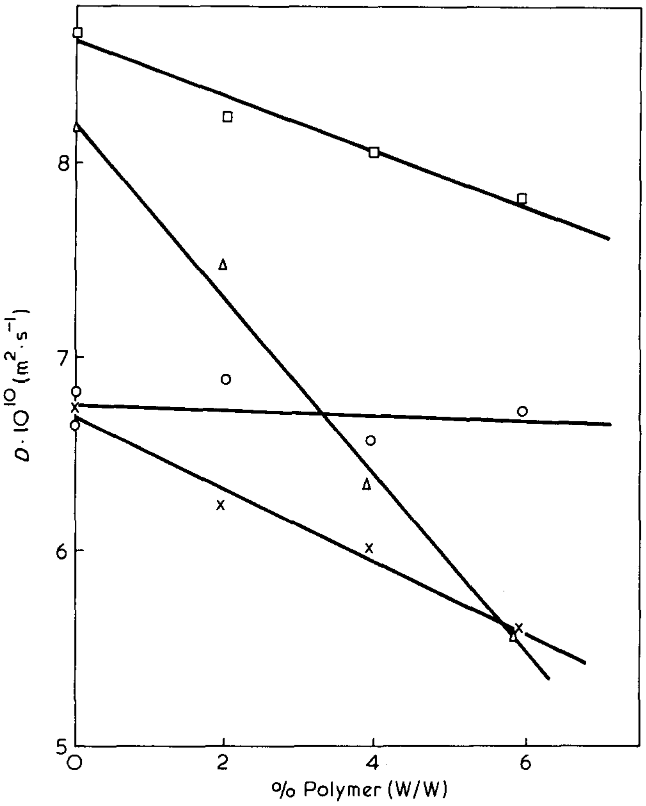

Figure 2 Diffusion coefficient vs. HPC concentration (○) G, (□) GA, (X) NAG, (△) GP

Table 1 D_0 values and k values

Diffusant	$D_0 \cdot 10^{10}$ ($m^2 \cdot s^{-1}$)	$k \cdot 10^3$ ($m^3 \cdot kg^{-1}$)
G	6.75	0.5
NAG	6.69	2.7
GP	8.22	5.6
GA	8.62	1.6

Table 1. As can be seen, the diffusion coefficient of the two uncharged diffusants are the same within experimental error. The higher values for the ionic species is due to the accelerating effect of the smaller counterions[20].

In *Figure 3* is reported the ratio D/D_0 vs. polymer concentration. The concentration dependence can be described by an equation of the type

$$D/D_0 = 1 - kc \qquad (1)$$

where c is the concentration of the polymer. Values of the constant k, applying to our measurements are found in *Table 1*.

In the case of NAG, our result can be compared with those of Iijima *et al.*[9] who studied the diffusion of NAG in solutions of the polymers sodium polystyrene sulphonate (NAPSS) and poly(methacrylic acid) (PMA). Their data could be described by equation (1) with $k = 2.5\ 10^{-3}$ m^3 kg^{-1} in NAPSS solutions and $k = 2.6\ 10^{-3}$ m^3 kg^{-1} in the case of PMA. This is in good agreement with our value $k = 2.7\ 10^{-3}$ m^3 kg^{-1} for NAG. They concluded that there was no specific interaction between diffusant and polymer. This is confirmed by the agreement with our result for NAG. One may therefore assume that the decrease in D/D_0 is merely due to obstruction effects.

A number of theories based on obstruction effects have been developed to account for the decrease in D/D_0 with increasing polymer concentration[14-16].

Wang[14] arrived at the expressions (2) and (3), describing the diffusion of small molecules in polymer solutions up to fairly high concentrations of polymer

$$D/D_0 = 1 - \alpha(v_2 + H/\rho_1)c_2 \qquad (2)$$

$$D/D_0 = \left\{1 - \alpha\left[\frac{v_2 + H/\rho_1}{v_2 + (1 - w_2)/\rho_1 w_2}\right]\right\}\left[1 - \frac{w_2}{1 - w_2}\right]H \qquad (3)$$

where α is a geometrical factor dependent on the shape of the obstructing particles whose value is 3/2 for spheres and 5/3 for rods, v_2 = partial specific volume of polymer, ρ_1 = density of solvent, c_2 = concentration of polymer, w_2 = mass fraction of polymer and H = mass of solvent bound per unit mass of polymer.

Expression (2) applies when the diffusant is unable to penetrate the solvation layer and equation (3) is valid if penetration can occur.

Application of equations (2) and (3) to the diffusion of NAG in HPC solutions yields the values $H = 1.4$ for the non-penetrating case and $H = 0.9$ for the penetrating case. This corresponds to 27 and 16 water molecules bound per monomer unit, respectively, indicating that expression (3) is more adequate than expression (2).

For glucose there is virtually no dependence of the diffusion coefficient on polymer concentration as seen in *Figure 3*. A similar result was obtained by Nyström and Roots[10] for the diffusion of sucrose in HPC solutions. Kitchen[6] studied the diffusion of glucose in dextran solutions and observed a decrease in D/D_0 with increasing dextran concentration. Another study was made by Brown *et al.*[7] who examined the diffusion of glucose in HEC gels and observed a decrease in diffusion coefficient with increasing HEC concentration. It can therefore be inferred that the diffusion behaviour of glucose is dependent on the nature of the polymer matrix. One common feature among the polymer systems in which glucose is retarded is the formation of a more rigid network, due to branching in the case of dextran and crosslinks in the gel, than in HPC solutions where one can expect a looser network.

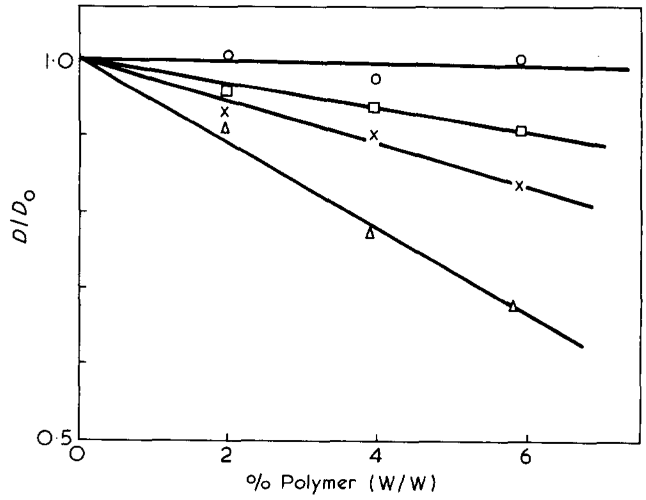

Figure 3 The ratio D/D_0 vs. HPC concentration. (○) G, (□) GA, (X) NAG, (△) GP

In the case of GA and GP additional complications are introduced due to their ionic nature. As is seen in *Figure 3* the positively charged GA is less retarded than NAG while the divalent anion GP shows the strongest concentration dependence. This might partly be attributed to different hydration of the solutes, since the number of potential sites for hydrogen bonding is larger in GP than in GA, thus resulting in differences in the effective volume of the diffusing species. It is clear that the diffusion of small molecules in polymer systems is a complex phenomenon dependent on the nature of both diffusant and polymer matrix.

Acknowledgements

We thank R. Bergman for technical advice in performing the measurements.

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The irreversibility of dimensional changes in epoxy adhesives undergoing uptake and expulsion of water

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(*Received* 28 *September* 1981; *revised* 17 *November* 1981)

An optical interference method, developed to measure swelling inhomogeneities during water uptake by epoxy-based adhesive films[1], has now been used to study the extent of dimensional recovery during subsequent removal of the water responsible for swelling. A microscope cover slip is employed as marker to evaluate displacements normal to a resin film that is sandwiched between it and a rigid substrate. By placing an optical flat close to the free surface of the cover slip, a cavity is created within which optical interference can occur between light incident upon and light reflected from the specimen. Normal displacements in the resin cause similar displacements in the cover slip, i.e. the geometry of the cavity is altered, and this produces changes in the pattern of interference fringes. It is found that repeated exposure of the specimen to both wet and dry environments (distilled water at 62°C and dry air at 62°C) leads to reversible changes in the displacement field normal to the adhesive film when the exposure is relatively modest ($\sim$1 day at 62°C), but that prolonged exposure ($>$2 days at 62°C) produces irreversible changes.

Keywords Adhesives; water-uptake; swelling; irreversibility; interferometry; Moiré-images

Introduction

Indirect experiments suggest that the accommodation of water by epoxy resins and the consequences of this accommodation are reversible. Thus, the increase in weight during water uptake can be more or less reversed by drying. So too can the associated change in glass transition temperature[2]. The information sought by the experiments reported here relates to the dimensional stability of resins during the uptake and expulsion of diffused water and is, therefore, more fundamental to an understanding of the apparent reversibility of accommodation of water.

Experimental

Method. Adhesive joints consisting of a 19 mm diameter, 0.15 mm thick microscope cover slip, are bonded with an adhesive film to a rigid substrate. These are mounted inside a controlled humidity chamber so that the free surface of the cover slip is in close proximity to an optical flat. The gap between cover slip and optical flat is made small enough to cause interference between incident and reflected light, and changes in the pattern of interference are photographed during the swelling and shrinking of the adhesive film that accompany water uptake and expulsion respectively.

In order to obtain the normal displacement field, photographs of the interference pattern taken during a run are superimposed on to a 'base line' photograph of the same interference pattern, but taken at the start of the run, so as to generate a system of Moiré fringes which bear a 1:1 correlation to the cover slip deformation.

Full details of the experimental method have been published by Sargent and Ashbee[1].

Results

Figure 1(a) is a sequence of Moiré images obtained for a specimen manufactured from American Cyanamid FM

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