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The Effect of Glucose on the Permeability of Poly-(Vinylpyrrolidone) Films to Oxygen

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Summary

The permeability of glucose-containing poly-(vinylpyrrolidone)films to oxygen was studied. It was found that the permeability initially decreases with increasing glucose content reaching its minimum at about 16 wt.% of glucose, and then increases with further increase in glucose content. The amount of water in the films was also measured and the effect of glucose on oxygen permeation was related to the effect of water sorption on the same property.

Introduction

The effect of sugars on the behaviour of some biologically important systems has been considered previously (SUGGETT, 1975), and the presence of sugars has even been found beneficial in such applied systems as colour photography (JEFFREYS, 1959). This work examines the effect of D-(+)-glucose on the permeability of poly(vinylpyrrolidone) (PVP) films to oxygen.

Experimental

The permeation of oxygen through PVP films was measured using the recently developed spectrophotochemical method (PETRAK,1979). The films of PVP (K60, British Oxygen Chemicals Ltd.) containing various amounts of glucose were prepared by casting from the corresponding aqueous solutions. The films were dried first over $CaC\ell_2$ at room temperature and then equilibrated at 58% relative humidity (using a saturated NaBr aqueous solution). The amount of water in the films equilibrated at 58% relative humidity and room temperature for 2 days was measured by thermogravimetry using a Stanton Redcroft TG 750 thermobalance equipped with a derivative unit. The softening points of the films were measured using

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a Stanton Redcroft thermo-mechanical analyzer TMA 691.

Results and Discussion

Our spectro-photochemical method allows us to evaluate, in a single experiment, both the diffusion coefficient, D, and the permeation coefficient, P, for oxygen in polymer films at a given relative humidity; the amount of oxygen, C_1, initially present in the polymer films can also be estimated (PETRAK and PITTS, 1980). The value of C_1 is related to the solubility of oxygen in the polymer under the experimental conditions. The experimental values of D,P, and C_1 are given in Table 1.

TABLE 1

The values* of diffusion, permeation and the solubility coefficients for oxygen in glucose containing PVP films

Sample no.	glucose wt.%	$P(cm^2 s^{-1})$ x10^{10}	C_1(mole dm^{-3}) x10^3	$D(cm^2\ s^{-1})$ x10^9	ℓ** μm
0	0.0	13.2	2.7	3.4	120
1	1.1	11.0	3.1	2.5	110
2	2.0	10.8	3.0	2.6	107
3	3.1	9.5	2.7	2.6	115
4	7.4	8.6	2.6	2.3	180
5	13.4	7.0	2.9	2.1	128
6	14.5	6.1	2.6	2.5	142
7	28.8	6.7	2.5	2.6	196
8	29.7	9.5	2.5	3.9	155

* an average of at least four determinations

** ℓ is the film thickness

The effect of glucose on the permeation coefficient of oxygen through PVP films is shown graphically in Fig. 1. The thickness of the PVP films used for the permeability measurements varied between 100-200 μm. The experimental values of oxygen transport parameters have not been corrected for the possible effect of film thickness on the equilibrium water content in the films (cf. PETRAK and PITTS, 1980). We think, however, that this effect is negligible here.

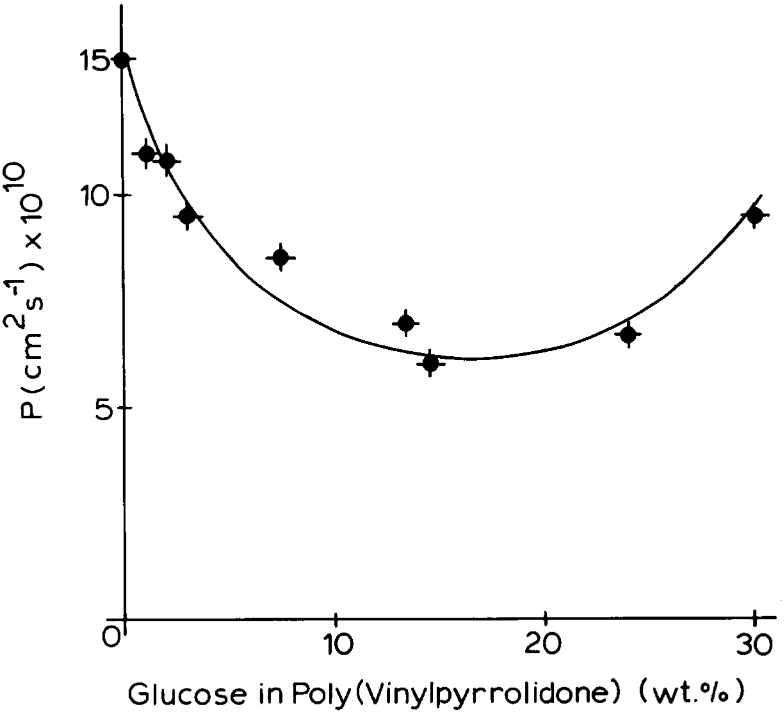

Figure 1. Permeation of oxygen through PVP/glucose films. The effect of glucose on the permeation coefficient P.

The data on the amount of water in the PVP films, as determined by the thermogravimetric analysis, are given in Fig.2. The samples 0-4 showed a single, broad peak on the DTG curves, the samples 5-8, however, gave two peaks - a sharp peak overlapping with a broad one. This means that water is desorbed in two different modes. Let us refer to the slowly desorbing water as "bound", and the faster desorbing water as "free" (SCHEUPLEIN and MORGAN, 1967).

As might be expected, the presence of glucose modifies the melt behaviour of PVP films. The experimental data are given in Table 2.

TABLE 2

Softening points of glucose-containing PVP films

Sample no.	glucose content /wt.%/	softening point, ^{o}C(a)	
		at 58% rel. humidity	dehydrated film(b)
0	0	59	154
4	5	45	140
5	10	29	137
6	15	20	123
7	25	4	108
8	30	0	-

(a) The literature values for Ganex V-904 (PVP) are: $T_g = 60^{o}C$, softening point = $157^{o}C$ (The Sadtler Standard Spectra, Polymers and related Products, Sadtler Research Laboratories, 1967).

(b) The samples were first heated to $110^{o}C$ and then cooled over $CaCl_2$ before the measurements.

It can be seen from the above data that both the diffusion coefficient and, particularly, the permeation coefficient for oxygen in PVP vary with the increase in the amount of glucose in the film. The permeability of the PVP films first decreases reaching a minimum at about 16 wt.% glucose content before it increases again. The oxygen solubility C_1 remains almost unchanged. The total amount of water in PVP films increases only slightly with increasing glucose content (cf. Fig.2). The DTG measurements suggest that the way water is bound in the polymer films varies depending on the amount of glucose present. As the amount of "bound" water decreases the amount of "free" water increases (cf. Fig.2). The hydration properties of glucose must play a part here. Our unpublished results obtained with other compounds such as urea and guanidine show that the observed effect of glucose is not a general phenomenon. It has been reported (KABAYAMA et al., 1958a; KABAYAMA and PATTERSON, 1958b) that one of the glucose isomers, β-D-glucose, can replace almost exactly "a chain

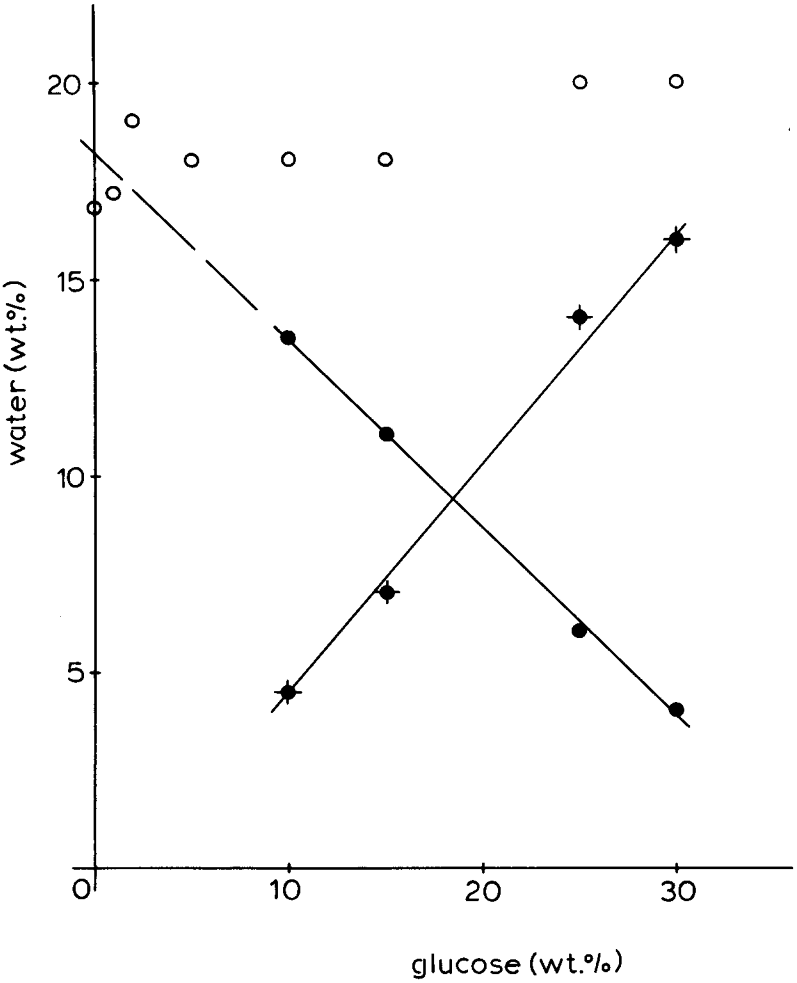

Figure 2. The amount of water in PVP films: o-total; ●-"bound"; +-"free".

conformation of water molecules" in a tridymite ice lattice with the dimensions expanded to ambient temperature. Thus, glucose-water hydrogen bonds are believed to replace the water-water hydrogen bonds (SUGGETT, 1975). The effect of glucose on permeability can thus be related to the effect of sorption of water on the same property. In the presence of glucose, the permeation of oxygen through PVP films decreases on water sorption reaching a

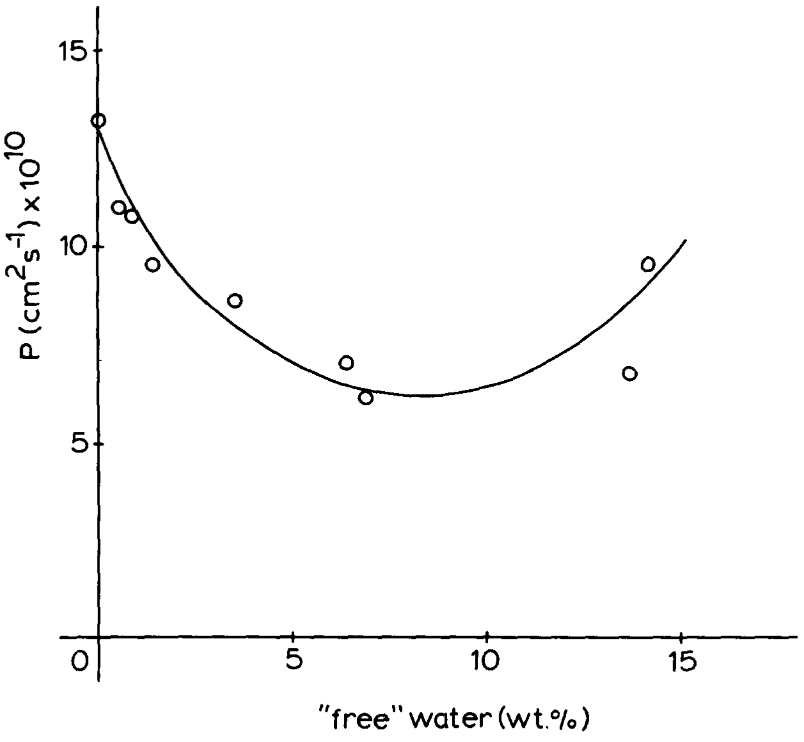

Figure 3. Permeation of oxygen through PVP/glucose films. The effect of water sorption on the permeation coefficient P.

a minimum at about 10 wt.% of water, and increases again with further increase in the water content (Fig. 3). This is in a qualitative agreement with the findings of KAMIYA and TAKAHASHI (1979) who studied the effect of water sorption hysteresis on hydrogen transport in a regenerated cellulose.

It may not be entirely fortuitous that the minimum on the permeation coefficient v. glucose content curve (Fig. 1) coincides with the intercept of the "free" and "bound" water content lines (Fig. 2). Also, the permeability of the glucose-containing films approaches the permeability of films free of glucose when the amount of "free" water approaches the total amount of water present in the film (cf. Fig. 1). These observations when related to some earlier studies of diffusion (KAMIYA and TAKAHASHI, 1977) may not be fully interpreted as resulting from glucose restricting the segmental motions of the polymer chains before the increased water uptake causes swelling and an increase in the mobility of the polymer matrix. A full explanation may have to include the reduction in the free volume of the polymer matrix as caused by the voids being filled by glucose. We feel that the extent to which different types of the diffusional transport (i.e., viscous, elastic, viscoelastic) play part in the overall process (VRENTAS and DUDA, 1978) may vary as the amount of glucose in PVP changes. However, any detailed mechanistic interpretation of our data would not be appropriate without the knowledge of the local-states variables for the PVP-glucose-water mixture.

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