

Hydraulic Permeation of Liquids Through Swollen Polymeric Networks. I. Poly(vinyl Alcohol)-Water

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Synopsis

Poly(vinyl alcohol) membranes were prepared by crosslinking with terephthalaldehyde. Hydraulic permeation of water through this network structure was measured as a function of pressure for temperatures ranging from 18° to 35.8°C. The data were analyzed via a previously developed solution-diffusion theory for hydraulic permeation to give mutual diffusion coefficients. The activation energy for diffusion was found to be 6.5 kcal/mole which compared to the value of 4.3 kcal/mole for viscous flow of water indicates an influence of polymer-liquid interaction on the energetics of the diffusion process.

INTRODUCTION

In earlier papers¹⁻⁷ we developed and tested a solution-diffusion theory for the hydraulic permeation of liquids through swollen, homogeneous polymeric membranes that explicitly accounted for the liquid concentration gradient induced in the membrane by the applied pressure. This approach permits calculation of the mutual diffusion coefficient for the liquid-membrane system from experimental flux data. It was found that when the membrane is a highly swollen, hydrocarbon network and the liquid is a pure organic solvent that the mutual diffusion coefficient is largely determined by the solvent viscosity and that the diffusion mechanism for the most part appears to involve frictional resistances that can be described in hydrodynamic terms.^{1,2,4} It is the purpose of this series to apply the solution-diffusion theory mentioned above to hydraulic permeation in a wider range of systems than those employed earlier with the aim of developing a broader understanding of the mechanism of molecular diffusion and particularly to learn the extent of applicability of the hydrodynamic regime referred to above.

It is of particular interest to examine an aqueous system since inevitably there will be stronger solvent-polymer interaction than found in the relatively non-polar hydrocarbon systems reported on earlier. Over the years, there has been considerable interest in diffusion in the poly(vinyl alcohol)-water system at low water contents⁸⁻¹¹; however, recently an interest has developed in use of crosslinked poly(vinyl alcohol) highly swollen with water or hydrogels in bio-medical membrane applications.¹²⁻¹⁴ The latter seemed an attractive system to

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choose for our studies. It is the specific purpose of this paper to present some hydraulic permeation results and conclusions for this system.

MEMBRANE PREPARATION AND CHARACTERIZATION

Membranes were prepared by casting an aqueous poly(vinyl alcohol) solution on a glass plate, drying, followed by chemical crosslinking.¹⁵ The poly(vinyl alcohol) was Elvanol 71-30, a product of du Pont, which has a high molecular weight and a per cent hydrolysis of 99.0% to 99.8%. A 4% by weight solution was made in boiling distilled water. A predetermined amount of solution was poured onto a Plexiglas plate to produce a membrane 1.3 to 1.6 mils thick when dry. The dried films were stripped from the Plexiglas and crosslinked by immersion in a large quantity of a saturated aqueous solution of terephthalaldehyde, which also contained 20% Na₂SO₄ and 4.3% H₂SO₄, as described by Bashaw and Smith.¹⁶ After an appropriate period of time in the terephthalaldehyde solution, the membrane was washed in distilled water to remove uncrosslinked polymer and dissolved reagents from the crosslinking solution. The crosslinked membranes were allowed to come to swelling equilibrium with fresh water. Portions of the swollen film were thoroughly dried in order to obtain the dry thickness and to determine the equilibrium swelling needed in subsequent calculations.

The extent of crosslinking by this method depends on the time of immersion in the crosslinking solution. Figure 1 illustrates this by showing the volume fraction of polymer at equilibrium swelling in water, v_{r0} , as a function of time in the crosslinking solution. Only membranes crosslinked for 1 hr were used for subsequent hydraulic permeation experiments since these had the best mechanical properties to endure this test.

Since this method of crosslinking involves simultaneous diffusion and reaction of the terephthalaldehyde under circumstances when the polymer is only slightly swollen,¹⁶ the question of the spatial uniformity of the crosslink density

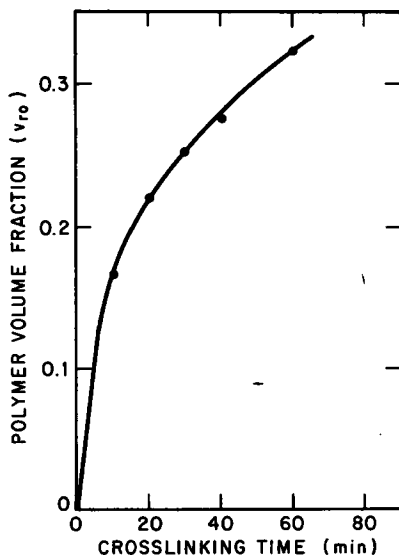


Fig. 1. Effect of crosslinking time on poly(vinyl alcohol)-water swelling equilibrium.

was raised and examined. The experimental approach consisted of comparing the swelling behavior of two films of different effective thicknesses after crosslinking for the same period of 20 min. This was done using a single 1.4-mil film. In one case, a single free film was immersed in the crosslinking solution so that both surfaces were available for diffusion. In a second case, two layers of film were wrapped around a glass test tube and sealed at the edges so that only the outer surface was exposed to the crosslinking solution. The thickness in the second case is effectively four times greater than in the first case, yet it was found that the difference in the equilibrium swelling in the two cases was only 0.01 volume fraction units. This demonstrates that crosslinking is not severely diffusion controlled and that the membranes are adequately uniform.

The data analysis to follow here requires thermodynamic information which can be adequately obtained from, say, the Flory-Huggins equation for swollen networks^{1,2,4} if estimates of the crosslink density, ν_e/V_0 , and the interaction parameter, χ_1 , are available. Equilibrium swelling data can be used to obtain one if the other is known, but it cannot give both. Bashaw and Smith,¹⁶ however, give force-elongation data on a similarly produced poly(vinyl alcohol) network that had an equilibrium ν_{r0} of 0.30 from which a crosslink density can be calculated.¹⁷ The membrane used in the permeation experiments here had $\nu_{r0} = 0.348$. Adjustment of the Bashaw and Smith data for this difference in swelling yields an estimate of 4.8×10^{-4} mole/cm³ for ν_e/V_0 for our system. Substitution of these values of ν_{r0} and ν_e/V_0 into the Flory-Huggins equation¹⁵ yields $\chi_1 = 0.62$, which compares with the value of 0.67 given by Kawai¹⁸ at $\nu_{r0} = 0.35$ and with 0.52 determined by extrapolating the data of Sakurada et al.¹⁹ to this concentration. These estimates of the needed parameters are adequate for present purposes, as parametric analysis of the current data has shown.¹⁵

EXPERIMENTAL HYDRAULIC PERMEATION RESULTS

Membranes crosslinked for 60 min as described above were selected for hydraulic permeation measurements. The membrane was washed and allowed to come to swelling equilibrium in distilled water. An equilibrium volume fraction of polymer, ν_{r0} , of 0.348 was determined for this membrane. The swollen membrane was installed in the apparatus described previously,² and the flux of water was measured as a function of the applied upstream pressure which never exceeded 150 psi owing to the fragile nature of the membrane. Measurements were made at four temperatures, with the results shown in Figure 2.

It is of interest to note that the flux- Δp data exhibit a slight curvature. Previous plots of this type show more curvature mainly because the measurements were carried to higher pressure levels in those cases.

ANALYSIS OF FLUX DATA USING SOLUTION-DIFFUSION THEORY

According to the solution-diffusion theory developed earlier,¹⁻⁷ the pressure differential ($p_0 - p_i$) induces a liquid volume fraction differential ($\nu_{10} - \nu_{1i}$) inside the membrane which leads to the flux $n_1 \hat{V}_1$ according to the following adaptation of Fick's law:

$$n_1 \hat{V}_1 = - \frac{D}{1 - \nu_1} \frac{d\nu_1}{dx} = \frac{D}{l_d \nu_{r0}^{2/3}} (\nu_{10} - \nu_{1i}). \quad (1)$$

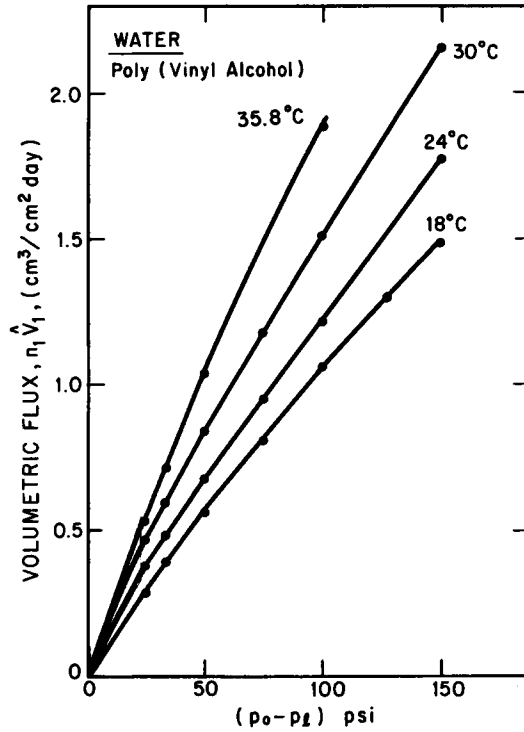


Fig. 2. Hydraulic permeation data for poly(vinyl alcohol)-water system.

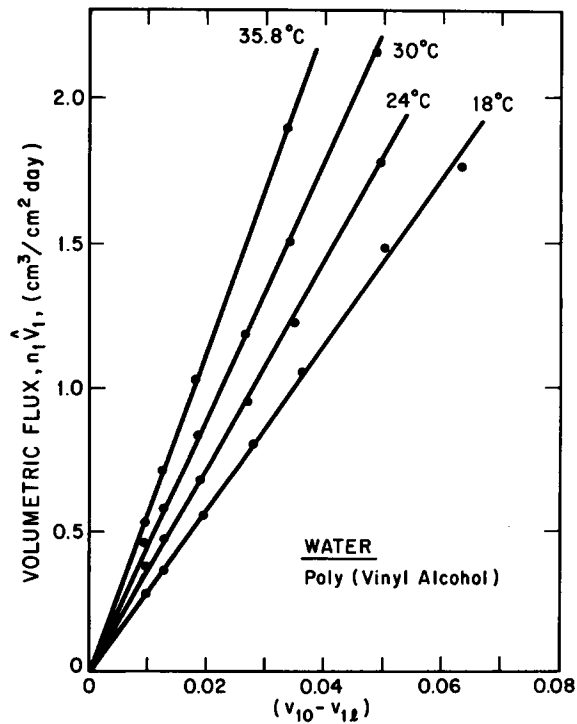


Fig. 3. Water flux as a function of water volume fraction difference across membrane. Flux data same as in Fig. 2, ($v_{10} - v_{11}$) calculated from ($p_0 - p_1$) as described in text.

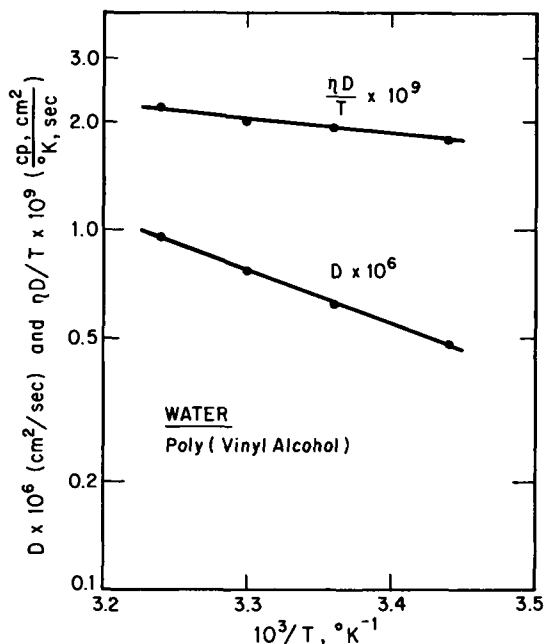


Fig. 4. Temperature dependence of transport parameters for the poly(vinyl alcohol)-water system. The symbol η refers to the viscosity of pure water at temperature T .

In this equation, D is the mutual diffusion coefficient (assumed independent of liquid concentration) and l_d is the dry thickness of the membrane. As described previously,¹⁻⁷ $(v_{10} - v_{1i})$ can be calculated as a function of $(p_0 - p_i)$, using thermodynamic equations and the parameters χ_1 and v_e/V_0 mentioned above. The equilibrium swelling $v_{r,0} = 1 - v_{10}$ was found not to depend on temperature to a detectable degree over the range of conditions used here.

Figure 3 shows the flux data from Figure 2 replotted versus the calculated volume fraction difference $(v_{10} - v_{1i})$. The plots are quite linear justifying the assumption of a constant D . Values of the diffusion coefficient were determined from the slopes of these lines using eq. (1). A typical Arrhenius plot of these values is shown in the lower part of Figure 4. The straight line gives a constant activation energy of 6.5 kcal/mole.

CONCLUSIONS

The above results indicate the utility of the solution-diffusion model in analyzing data for the present system. It is of interest now to examine in detail the temperature dependence of the so-determined diffusion coefficient. The activation energy of 6.5 kcal/mole agrees generally with the value of 5.9 kcal/mole determined by Peter and Mittelstadt²⁰ using a different technique, and both are larger than the activation energy for the viscosity of water which is 4.3 kcal/mole. This suggests that in this system the frictional processes controlling diffusion are not the same as those governing viscous flow of pure water.

A more sensitive method of examining the relation between the diffusion coefficient and liquid viscosity and how both depend on temperature is to look at the combination of terms $\eta D/T$, where η is the viscosity of pure water. As pointed out earlier,^{1,4} in all diffusional processes where the friction coefficients

for diffusion are governed by hydrodynamics, e.g., a form of Stoke's law applies, the group $\eta D/T$ will be independent of temperature. Earlier data for toluene in a crosslinked rubber network gave a constant value for this group, leading to the conclusion that a hydrodynamic regime of diffusion was operative. This means that interaction between the polymer and liquid is unimportant in the energetics of the transport process. Data for cyclohexane in the same polymer were more scattered, and no definitive conclusion could be reached regarding the residual temperature dependence of $\eta D/T$ in that case.

In the upper part of Figure 4, $\eta D/T$ is plotted versus $1/T$, and it is rather conclusive that there is a small residual temperature dependence for this quantity. This means that the majority of the temperature dependence of D may derive from the temperature dependence of η for water, but it also points to a certain influence of polymer-solvent interaction on the energetics of transport. This should not be too surprising in view of the strong hydrogen bonding forces possible between poly(vinyl alcohol) and water. In general, it might be said that hydrodynamics may govern the general trend of diffusion in concentrated polymer solutions or swollen membranes but cannot account for all of the fine details in very polar systems.

This research was sponsored by a grant from the National Science Foundation for which the authors are grateful.

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Received June 11, 1974

Revised November 8, 1974