Diffusion and Solubility of Some Azo Dyes in Swollen Gelatin Matrices: The Effects of Dye Size, Matrix Swell, and Dye–Matrix Interactions

S. P. CHEN and H. W. OSTERHOUDT, *Research Laboratories, Eastman Kodak Company, Rochester, New York 14650*

Synopsis

The diffusion coefficient (D) and the solubility coefficient (K) of three sulfonated azo dyes were measured in swollen gelatin membranes at pH 12 by two techniques (time lag and desorption rate), with good agreement between the two. A strong correlation was established between log D and the reciprocal of the free volume of the matrix. Hence, as free volume of the matrix increased (due to increasing solvent imbibition), dye mobility increased. As dye size increased, however, mobility decreased. Dye affinity for gelatin, as measured in dilute solutions by dynamic dialysis, was small and could be related to the dye solubility in more concentrated gelatin matrices. Increasing ionic strength or decreasing alcohol content increased K without affecting the dye mobility. On the other hand, the presence of polymers with strong affinity for the dye anions, e.g., polyvinylpyrrolidone, immobilized a large fraction of the dye ions and greatly slowed the overall dye transport.

INTRODUCTION

The solubility and mobility of diffusants in solvent-swollen membranes and gels control the rates at which many practical processes occur. Thus the degree of separation attainable in gel chromatography and gel electrophoresis, the efficacy of membrane separations (by dialysis, ultrafiltration, or reverse osmosis), and the delivery rate of therapeutic drugs from patches placed on the skin can be profoundly influenced by diffusant solubility and mobility. This has been recognized by Kim et al.,[1] who examined the permeation of various solutes through poly(2-hydroxyethyl methacrylate) gels, and by Brown and Johnson,[2] who studied the diffusion of water-soluble compounds in polyacrylamide gels.

The behavior of various diffusants—perhaps the most important of which are dyes—in swollen gels is also critical to color image-transfer photography because such readily discerned characteristics as the appearance of the initial image and the sharpness of the final image can be traced in part to dye solubility and mobility. This has been recognized by other workers, including Liang and Tong,[3] who correlated dye diffusion with the degree of sorption to the polymer matrix, and by Beels and Claes,[4] who studied the influence of free volume on the diffusion of salts in water-swollen gels.

In this paper we examine the following topics: (a) How do the degree of swell of the matrix, the size of the diffusing dye ions, and the affinity between the dye and the polymer(s) control dye mobility? (b) Can dye–polymer affinity measurements made in dilute polymer solutions be correlated with affinity measurements made in swollen membranes, which are

Journal of Applied Polymer Science, Vol. 30, 2075–2094 (1985)
 CCC 0021-8995/85/052075-20$04.00

in fact concentrated polymer solutions? (c) What experimental procedures and techniques are appropriate for measuring mobility and affinity?

EXPERIMENTAL

Apparatus

The dialysis cells were modified versions of the type described by Little and Osterhoudt,[5] which provides adequate stirring of both compartments with a single magnetic stirring motor and a low ratio of cell volume to membrane area.

The method of monitoring the change in dye concentration in a compartment as time progressed varied with the kind of experiment. (1) A very rapid (essentially instantaneous) response time is required for the measurement of dye diffusion coefficients by either the time-lag or desorption-rate procedures. Hence, for these measurements we used a Brinkmann probe colorimeter (Model PC/1000), the probe of which was placed in a dialysis cell compartment. (2) For the dynamic dialysis experiments to measure with a transient technique the affinity of a dye for a dissolved polymer, we used a combination of a Milton-Roy Instrument Minipump (Model 196-93), which circulated solution from the dialysis cell to the detector and then back to the dialysis cell, and an ISCO Model 222 flow cell photometric detector, which monitored the time-dependent dye concentration in the lower compartment of the dialysis cell.

Methods and Computations

Time-Lag Measurements. A swollen gelatin film was mounted between the two compartments of the dialysis cell. Each compartment was filled with a stock solution, the lower compartment first. Then the assembled and filled cell was immersed in a water thermostat atop a submersible, water-driven magnetic stirring motor. The Brinkmann probe was inserted into the upper compartment, and a baseline with no dye present was taken. For a time-lag experiment, about 40 mL of concentrated dye solution (which was more than 3 times the volume of the lower compartment) was quickly flushed through the stirred lower compartment to achieve a dye concentration in it that closely approached that of the stock dye solution. The amount of dye (Q_t) that permeates the membrane as time (t) progresses after the addition of dye solution to the lower compartment is given[6] as

$$\frac{Q_t}{AhC_0K} = \frac{Dt}{h^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^\infty \frac{(-1)^n}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{h^2}\right) \tag{1}$$

in which A and h denote membrane area and thickness, C_0 is the concentration of the mobile dye in the compartment from which it diffuses, K is the ratio of the dye concentration in the membrane to the dye concentration in the solution, and D is the diffusion coefficient of the dye. Here it has been assumed that the dye concentration in the compartment to which dye diffuses is always very small compared to C_0. When a steady state is reached, eq. (1) becomes

$$\frac{Q_t}{A} = \frac{DKC_0}{h}\left(t - \frac{h^2}{6D}\right) \tag{2}$$

and this linear portion of the Q_t/A vs. t plot can be extrapolated to the t axis (see Fig. 1). At this intersection, $t = L$, and D can be determined from

$$D = h^2/6L \tag{3}$$

With D so determined, the value of K can be determined from the slope of the linear portion of the Q_t/A vs. t plot as

$$K = \left(\frac{h}{DC_0}\right)\frac{d(Q_t/A)}{dt} \tag{4}$$

Dye Desorption Rates from Gelatin Films. Disks of dry gelatin films ca. 0.005 cm thick and 3.45 cm in diameter were preconditioned (i.e., swelled) by immersing them in a gently stirred stock solution for at least 10 min at room temperature. The swollen dimensions and weights of the disks were measured, and, to a good approximation, the volume fraction of polymer (V_2) in the swollen film can be calculated as the ratio of the volume of the dry disk (corrected for the 10–13% moisture generally present) to the volume of the swollen disk. Thus, the corrected swelling ratio (S) and the volume fraction of polymer are related as $V_2 = S^{-1}$.

When a swollen specimen was to be dyed, it was transferred to a stirred dye solution of known concentration and volume (e.g., 10^4M and 50 or 100 mL) at constant temperature. The residence time in a dye bath was from 30 min to 2 h and, in every case, at least twice the time required to reach apparent equilibrium.

For a dye desorption experiment, a thoroughly dyed, swollen specimen was removed from the dye bath, quickly surface-dried with a tissue, and

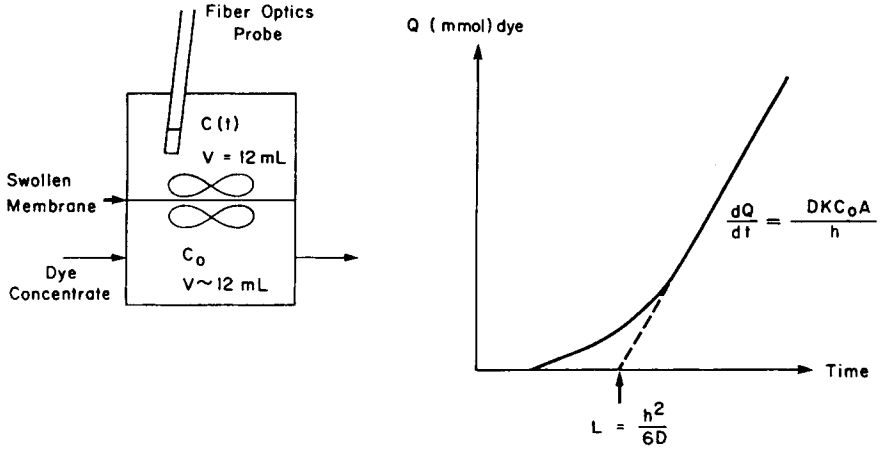

Fig. 1. Time-lag method used to measure the diffusion and solubility coefficients of dyes in swollen gelatin matrixes. L = time lag, K = solubility coefficient, A = membrane area, h = membrane thickness.

immersed in 50–200 mL of the stirred stock solution at constant temperature. The stirring was fast enough to keep the extracting solution well mixed but not so vigorous as to damage the swollen specimen. The dye concentration in the extracting solution was monitored with the Brinkmann probe colorimeter and was always much less than the dye concentration in the original dye bath (e.g., 10^{-6} vs. $10^{-4}M$).

Under these experimental conditions, eq. (5) can be used to determine D (cf. Ref. 6, p. 16):

$$\frac{M_t}{M_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{h^2}\right] \tag{5}$$

Here M_t is the amount of dye desorbed from the film at time t and M_0 is the amount sorbed before desorption began. A plot of M_t/M_0 vs. $t^{1/2}$ is generally linear up to $M_t/M_0 \leq 0.5$. At $M_t/M_0 = 0.5$, eq. (5) becomes

$$\left(\frac{t}{h^2}\right)_{M_t/M_0=0.5} = -\frac{1}{\pi^2 D} \ln\left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right] \tag{6}$$

and D can be computed from

$$D = \frac{0.04919}{(t/h)^2_{M_t/M_0=0.5}} \tag{7}$$

The solubility coefficient K can be calculated* from

$$K = M_0/C_0V \tag{8}$$

in which C_0 is the concentration of the original dye bath and V is the volume of the swollen membrane.

Dynamic Dialysis. Dynamic dialysis, as contrasted to equilibrium dialysis, allows rapid acquisition of dye–polymer affinity data. The procedure has been applied by others,[7-9] and, as they did, we compared the fluxes of dye through a membrane in both the presence and the absence of a dissolved polymer (here, gelatin) to which the dye might have affinity. To the extent that dye is sorbed to the polymer, there is less free dye in solution, the concentration gradient of dye across the membrane is lowered, and the dye flux is thereby decreased.

The membrane used in a dynamic dialysis experiment must be somewhat permeable to the dye but retain completely the substrate (polymer) to which the dye might be sorbed. We could use any of three membranes with reproducible results: (a) Gelman cellulose triacetate PEM (protein enrichment membrane) of nominal pore size 75 Å; (b) Nuclepore polycarbonate membranes with straight-through pores of 500 Å diameter; and (c) a crosslinked gelatin film prepared in the Kodak Research Laboratories.

* The K values defined in eqs. (4) and (8) correspond to mobile dyes dissolved in the membranes.

The sequence in a dynamic dialysis experiment was as follows: (a) The membrane was conditioned for ca. 30 min in the stock solution. (b) The membrane was mounted in the dialysis cell, the cell was completely assembled, and the proper amounts of stock solution were added to each compartment. (The compartment to which polymer was added is hereinafter referred to as the retentate compartment, and the compartment into which free dye diffused is called the diffusate compartment.) (c) The assembled and filled cell was placed atop a submersible magnetic stirring motor in a thermostated bath whose temperature was regulated at 25.0 $\pm$ 0.1°C. (d) The tubing connecting the diffusate compartment of the cell to the circulating system was filled with stock solution and connected (see Fig. 2), the Milton–Roy circulating pump was turned on, and a baseline was obtained with no dye present. (e) A concentrated (ca. $10^{-3}M$) dye solution was added to the retentate compartment, and its appearance in the diffusate compartment was monitored for ca. 30 min. (As discussed in Appendix A, dye was added at point A in Fig. 2.) (f) A 2-mL portion of either stock solution (in a control experiment) or polymer solution (in an affinity experiment) was added (point B in Fig. 2). (g) During and for ca. 30 min after the addition at (f), the rate of dye appearance in the diffusate compartment was monitored.

As specified in Appendix A, the amount of dye sorbed by the polymer is

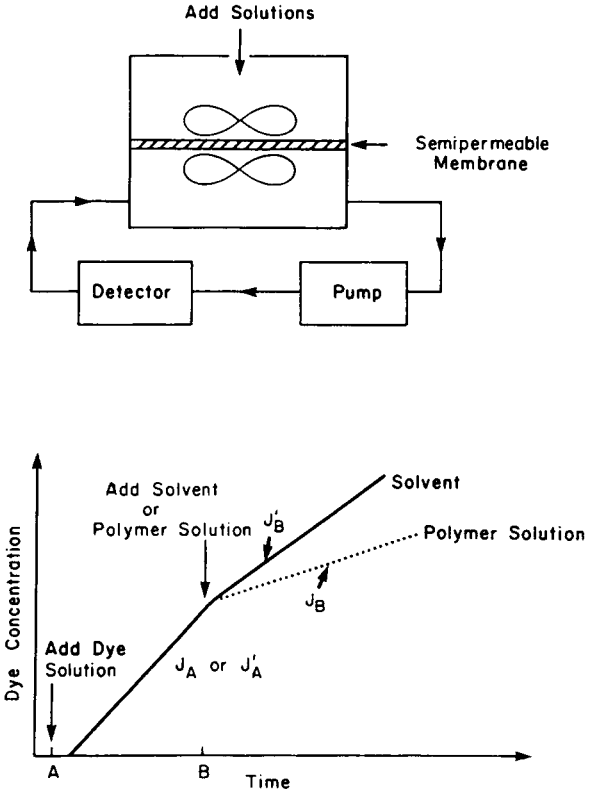

Fig. 2. Dynamic dialysis experiment used to measure dye–polymer affinity between dye anions and polymers in dilute solutions.

computed by comparing the dye fluxes just after point B in Figure 2 for the case with polymer in the retentate compartment to the (control) case without polymer present.

The dynamic dialysis procedure, despite its convenience and speed, has certain potential drawbacks. One of these is dye binding to the membrane, and we observed significant sorption of dye 1 (cf. the following section) to the Gelman PEM membrane. We could, fortunately, reduce this problem to an inconvenience, which did not affect our affinity data, by repeating the control experiments until a constant dye flux was obtained from experiment to experiment. This ensured that the membrane was saturated with dye before an affinity experiment. The Gelman membrane could then be used for a long time.

Materials

The stock solutions were made from deionized water and reagent grade KBr, KOH, NaBr, NaOH, and isopropyl alcohol.

The gelatin films to be used as membranes were machine-coated from solutions of lime-processed ossein gelatin and crosslinked to various degrees with formaldehyde.

Some gelatin films were coated with various amounts of polyvinylpyrrolidone to give a PVP content in the dried films of ≤ 25 wt %. The PVP was type NP-K90 from GAF Corp.

For the measurements of dye sorption to gelatin in dilute solution, a deionized, lime-processed ossein gelatin was used. Hence, for the comparison of affinity in dilute solution to the solubilization in swollen film, the same kind of gelatin was used.

Three dyes (structures shown in Fig. 3) were synthesized in the Kodak Research Laboratories. Each dye was dissolved in the stock solution appropriate for the experiment.

RESULTS AND DISCUSSION

Effects of Swell and Diffusant Size

The pronounced effect of swell on dye transport is graphically shown in Figure 4 for dye 1. Here, for three of the four membranes, the dry gelatin

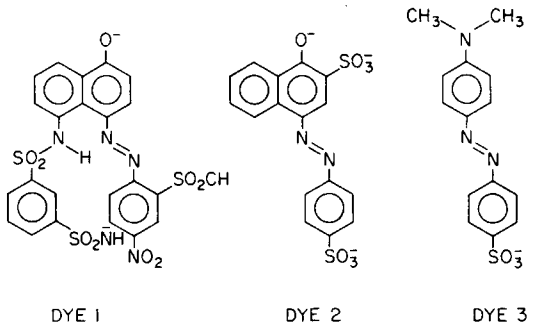

Fig. 3. Structures of dyes studied, given as anions that exist at pH 12.

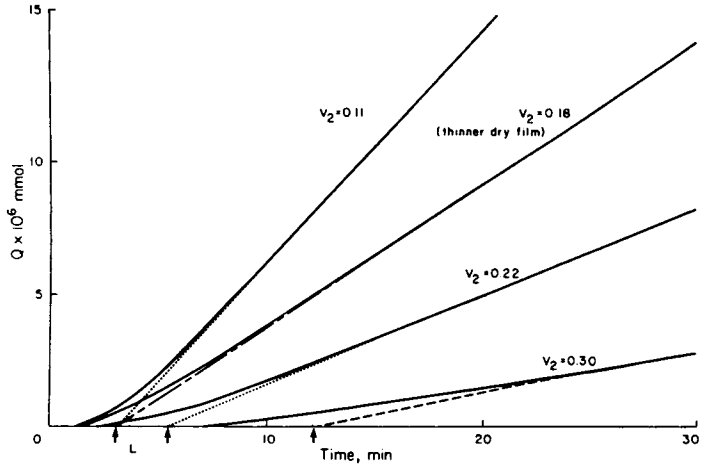

Fig. 4. Time-lag plot of diffusion of dye 1 ($0.9 \times 10^{-4}M$) through four gelatin films of different gelatin volume fraction (V_2) at pH 12, $0.19M$ KBr.

thicknesses were similar, whereas the swell ratio, which is the reciprocal of the polymer volume fraction V_2, varied from 3.3 to 9.1. The amount of dye that permeated after 20 min differed by nearly an order of magnitude for the two membranes having the least and greatest degrees of swell. The dotted lines in the graph are the extrapolations of the steady states of dye permeation. The intercepts on the time axis yield the time lags, from which the diffusion coefficients were calculated (Table I).

The swollen thickness used in the calculation of the diffusion coefficients and V_2 was measured with a Federal gauge and the Green–Levenson swellometer[10] and should be good to within 10% for all the membranes. We estimate 10% reproducibility in knowing the time lag or the "half-time." Hence, the overall uncertainty for D is 30%, and the uncertainty in the solubility coefficient is estimated to be comparable to that in D.

TABLE I
Effect of Dye 1/Gelatin Interaction on Dye Solubility and Transport in Gelatin Films at pH 12, 25°C (Dye Concn = $10^{-4}M$)

Gelatin film	[KBr] (M)	[i-PrOH] (vol %)	$\alpha_g' \times 10^2$ (mL/mg gel)	K		$D \times 10^7$ (cm²/s)		V_2
				Desorption rate	Time lag	Desorption rate	Time lag	
A	0.145	25	0.65	1.9	4.2	2.47	3.03	0.134
	0.193	0	2.66	3.2	5.6	4.02	3.86	0.111
	1.50	0	2.95	4.0	7.2	3.30	5.46	0.102
B	0.145	25	0.65	1.6	3.2	1.45	1.69	0.193
	0.193	0	2.66	5.1	5.5	1.17	1.63	0.180
	1.50	0	2.95	5.3	8.8	1.14	1.72	0.190
C	0.145	25	0.65	1.1	3.7	1.12	0.58	0.225
	0.193	0	2.66	4.5	5.7	1.03	0.97	0.220
	1.50	0	2.95	4.7	10.6	0.91	1.10	0.224
D	0.145	25	0.65	1.3	1.7	0.59	0.31	0.314
	0.193	0	2.66	4.4	9.4	0.59	0.31	0.296
	1.50	0	2.95	6.2	11.8	0.37	0.33	0.310

Table I also gives diffusion coefficients for dye 1 from desorption-rate experiments. The agreement between the diffusion coefficients measured by the two techniques is reasonably good. Because the two procedures and the equations associated with each are so different, the agreement between the two sets of data makes us confident of the validity of these diffusion coefficients.

According to the free-volume theory of diffusion formulated by Fujita[11] and Yasuda et al.,[12,13] an increase in swell will increase the free volume of the membrane and hence the diffusion rate. When the contribution to free volume is dominated by the solvent present, log D should be linearly correlated with $1/V_1$, where V_1 is the volume fraction of the solvent in the swollen membrane. The slope of such a correlation should be related to the "characteristic volume required to accommodate the diffusing permeant molecules."[12,13] The diffusion coefficients given in Table I are plotted in Figure 5, and indeed a straight line fits the data well. Diffusion coefficients of the other two dyes are given in Table II and are plotted in Figure 6. The three plots are linear and can be extrapolated to reasonable values for diffusion coefficients of the dyes in aqueous solutions at $V_1 = 1.0$ (solvent only, no polymer). As the dye size increased, the slope became more negative. This, too, was expected inasmuch as a large ion would be expected to require a larger cavity in the swollen network before it can move. Such cavities are not viewed as being fixed in space, but rather as being formed and

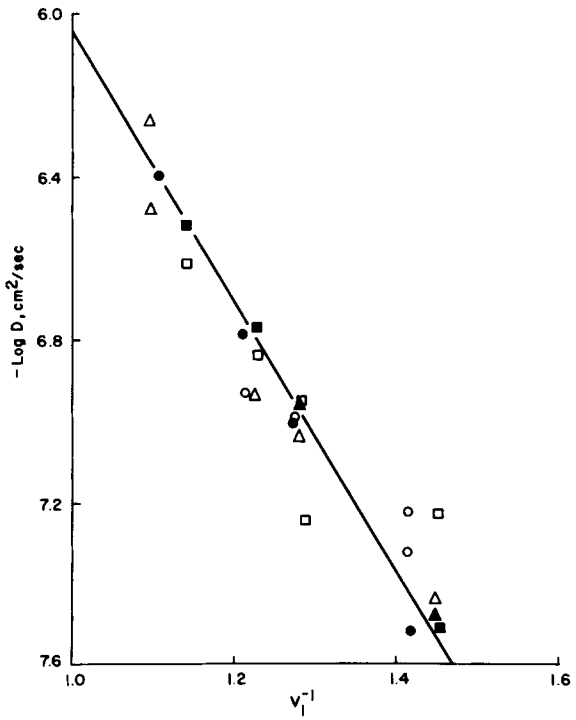

Fig. 5. Free-volume correlation of diffusion coefficients of dye 1 in gelatin films at pH 12 and 0.19M KBr (○, ●), 1.5M KBr (△, ▲), and 0.15M KBr, 25 vol% isopropyl alcohol (□, ■); (○, △, □) desorption rate; (●, ▲, ■) time lag.

TABLE II
Effect of Dye Structure and Gelatin Matrix on Dye Solubility and Transport at pH 12, 0.19*M* KBr, and 25°C (Dye Concn = $10^{-4}M$)

Gelatin film	Dye	$\alpha_g' \times 10^2$ [a] (mL/mg gel)	K Desorption rate	K Time lag	$D \times 10^7$ (cm²/s) Desorption rate	$D \times 10^7$ (cm²/s) Time lag	V_2
A	3	1.34	1.9	3.2	8.59	11.9	0.107
B			2.3	4.4	4.10	5.39	0.180
C			2.6	4.6	3.24	3.97	0.210
D			3.0	3.8	1.50	1.77	0.304
A	2	2.05	2.8	4.1	4.38	6.24	0.114
B			4.9	5.2	1.95	2.40	0.199
C			4.4	4.2	1.63	1.66	0.231
D			5.6	5.2	0.85	0.73	0.295
A	1	2.57	3.2	5.6	4.02	3.86	0.111
B			5.1	5.5	1.17	1.63	0.180
C			4.5	5.7	1.03	0.97	0.220
D			4.4	9.4	0.59	0.31	0.296

[a] These α_g' values were obtained with a Nuclepore membrane and gelatin solutions prepared by identical procedures.

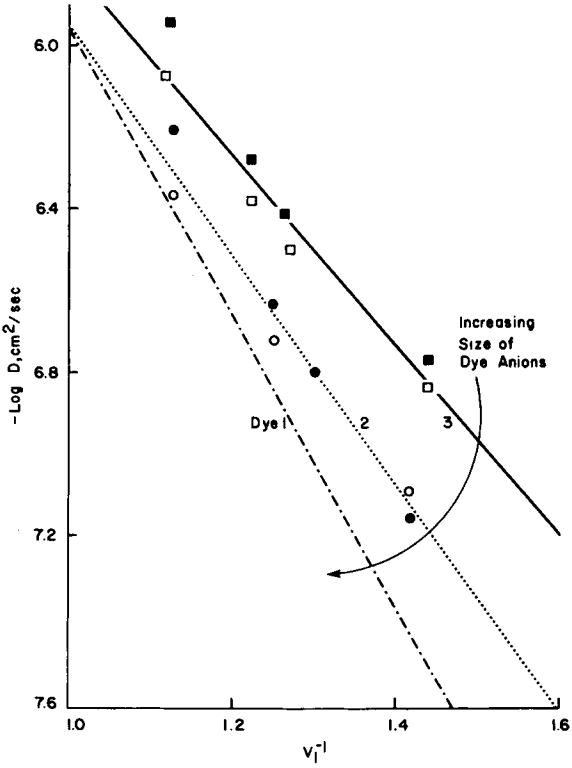

Fig. 6. Free-volume correlation of diffusion coefficients of dye 1, dye 2, and dye 3 (methyl orange): (○, □) desorption rate; (●, ■) time lag.

TABLE III
Dye 1/Gelatin Interactions; Effects of Ionic Strength, Dye, and Gelatin Concentrations at pH 12, 25°C

Item	[KBr] (M)	[Gel] (%)	$W \times 10^6$ (mmol dye/mg gel)	$C_f \times 10^4$ (M)	$\alpha_g' \times 10^2$ (mL/mg gel)	Membrane
1	0.19	1.0	1.18	0.39	3.1	CTA
2	0.19	1.0	1.29	0.39	3.3	CTA
3	0.19	1.0	1.23	0.39	3.1	CTA
4	0.19	1.0	3.10	0.81	3.8	CTA
5	0.19	1.0	3.32	1.18	2.8	CTA
6	0.19	1.0	12.3	3.79	3.2	CTA
7	0.19	0.5	2.40	1.41	1.7	CTA
8	0.19	1.0	2.56	1.27	2.0	CTA
9	0.19	2.0	2.26	1.08	2.1	CTA
10	0.19	1.5	2.32	1.18	2.0	CTA
11	1.50	1.0	2.96	1.23	2.4	CTA
12	1.50	1.0	3.18	1.24	2.6	Gelatin $S = 2.8$
13	0.19	2.0	0.85	0.33	2.6	Nuclepore
14	0.19	2.0	1.67	0.67	2.5	Nuclepore
15	0.19	2.0	3.40	1.32	2.6	Nuclepore
16	0.19	2.0	5.18	1.96	2.6	Nuclepore
17	0.19	2.0	6.42	2.72	2.4	Nuclepore
18	0.19	2.0	8.33	3.33	2.5	Nuclepore
19	0.19	2.0	9.70	4.06	2.4	Nuclepore
20	0.19	2.0	11.1	4.77	2.3	Nuclepore
21	0.19	2.0	13.1	5.38	2.4	Nuclepore

destroyed continuously because of the segmental motion of the matrix polymer.

Effects of Ionic Strength and Alcohol Content

Affinity of Dye for Gelatin. Table III gives dye–gelatin affinity data for dye 1 and gelatin at pH 12, two levels of ionic strength (0.19 and 1.5M KBr), and various dye and gelatin concentrations. Experiments in the first 11 lines were done with the Gelman PEM asymmetric cellulose triacetate (CTA) membrane, but the data in line 12 were obtained with a hardened (i.e., crosslinked) gelatin membrane and the rest with a Nuclepore membrane. Examination of these data reveals that the affinity of dye 1 to gelatin at pH 12 in 0.19M KBr apparently varied over the range $1.7 \times 10^{-2} \leq \alpha_g' \leq 3.8 \times 10^{-2}$, depending on the experimental conditions. Here $\alpha_g' = W/C_f$, where W is the millimoles of dye sorbed per milligram of polymer at a free-dye concentration of C_f(mol/L). The variations in the data seem greater with the CTA membrane because of substantial adsorption of the dye on the membrane. However, the average value of α_g' for data from this membrane (2.7×10^{-2} mL/mg gel) compared favorably with that from the Nuclepore membrane (2.5×10^{-2} mL/mg gel). Furthermore, α_g' obtained with the swollen gelatin membrane at a swell ratio of 2.8 is close to that of the CTA membrane under similar experimental conditions. This is reassuring because it indicates that sorption of the dye to the CTA and gelatin membranes and diffusion of a fraction of the gelatin molecules through the

pores of Nuclepore membrane (pore diameter = 500 Å) did not hinder the acquisition of reasonable affinity data with any of these membranes.

Data obtained with the Nuclepore membrane are plotted in Figure 7. W is linearly related to C_f over the C_f range used (3×10^{-5}–$5.4 \times 10^{-4}M$). The slope of the plot yields an average α_g' of 2.42×10^{-2} mL/mg gel. The observed linearity suggests that this portion of the sorption isotherm is well removed from saturation of the polymer by the dye.

The influence of alcohol on the interaction between gelatin and dye is shown in Table IV and Figure 8. Even though a CTA membrane was used in the studies, precautions were taken to ensure good reproducibility. From the plot, note that α_g' for gelatin and dye 1 decreases with increasing isopropyl alcohol content (with concomitant decreases in ionic strength), and α_g' for the solvent containing 25 vol % alcohol is less than one-fourth the value with no isopropyl alcohol.

For further comparisons, values of $\alpha_g' \times 10^2$ of 0.65, 2.66, and 2.95 in Table IV were chosen as representative of three solvent systems of pH 12 (0.15M KBr and 25 vol % i-PrOH, 0.19M KBr, and 1.5M KBr). With the same gelatin membrane swelled in these three systems, diffusion and permeability data were taken; these will be discussed next.

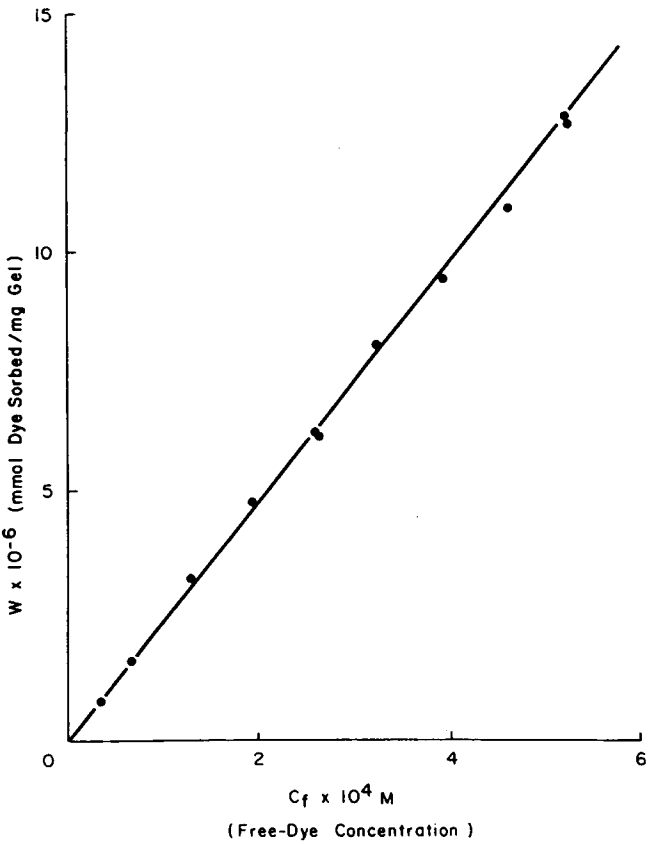

Fig. 7. Effect of free-dye concentration on amount of dye sorbed for dye 1 on gelatin at pH 12, 0.19M KBr; slope = $\alpha_g' = 2.4 \times 10^{-2}$ mL/mg gel.

TABLE IV
Dye 1/Gelatin Interactions; Effect of Isopropyl Alcohol Content in its Mixture With pH 12, 0.19*M* KBr Aqueous Solutions[a]

[*i*-PrOH] (%)	μ[b]	$W \times 10^6$ (mmol dye/mg gel)	$C_f \times 10^4$ (*M*)	$\alpha_g' \times 10^2$ (mL/mg gel)
50	0.10	0.59	1.44	0.41
25	0.15	0.92	1.41	0.65
10	0.18	2.22	1.28	1.74
0	0.20	3.15	1.19	2.66
0	1.51	3.42	1.16	2.95

[a] Gelman CTA membrane was used in these experiments.
[b] Total ionic strength derived from KBr and KOH in the aqueous solution.

Dye Transport in Swollen Gelatin Membrane. Figure 9 shows the traces from time-lag experiments with dye 1 at pH 12 through the same gelatin film (Sample B) with different salt concentrations and alcohol content. Note that (a) the swollen thicknesses of the gelatin film in the three solvents did not differ by more than 5%, and (b) the values of α_g' shown in the figure were obtained in dilute gelatin solutions (1%) in the same solvents. The higher the α_g', the greater the dye–gelatin affinity. If this affinity immobilized the dye in the swollen gelatin matrix, we would have seen prolonged time lags.[14] We found, however, that the time lag did not change much with changing α_g', and the diffusion coefficients (Table I) were similar. On the other hand, the slopes, which are proportional to the permeability coefficients, steadily increased as α_g' increased. The solubility coefficients computed from the ratio of the permeability and diffusion coefficients are included in Tables I and II.

Since the solubility coefficients are all greater than unity, there is a favorable partitioning of the dye from solution into the swollen gelatin network, despite the fact that the dyes were anionic and the gelatin bore a net negative charge at pH 12. This partitioning was influenced by the

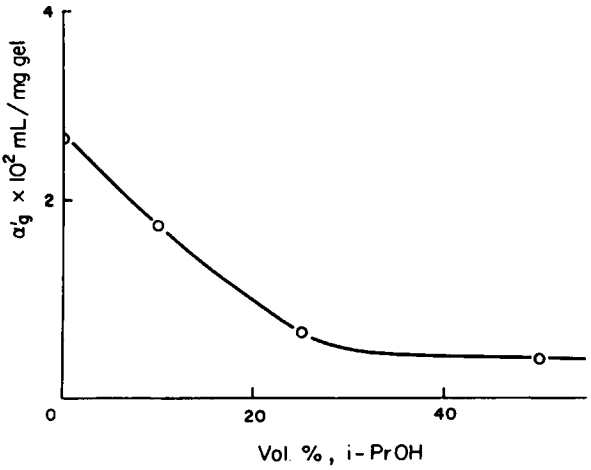

Fig. 8. Dependence of dye–gelatin affinity for dye 1 on vol % of isopropyl alcohol in its mixture with the aqueous solution of pH 12, 0.19*M* KBr.

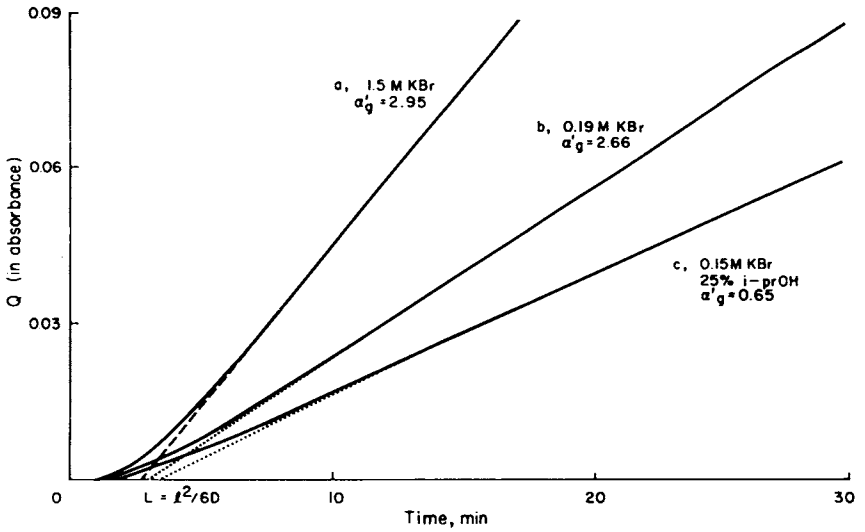

Fig. 9. Time-lag traces of dye 1 through gelatin film B at pH 12 in three solvent systems. To obtain Q in millimoles of dye permeated, multiply by (a) 1.56×10^{-4}, (b) 1.62×10^{-4}, (c) 1.13×10^{-4}.

solvent. With decreasing isopropyl alcohol content and concomitant increases in ionic strength, there was greater affinity between the dye and the gelatin. This could have been due to less Donnan repulsion between the dye and gelatin as ionic strength increased or to more noncoulombic attraction between the two at lower isopropyl alcohol levels (or both). Whatever the origins of these trends, it is clear that the partitioning between the phases, at least one of which contains polymer, can vary as much as four times with changes only in the composition of the solvent.

The dye solubility coefficient (K) can also be varied by changing the size of the dye anions. As shown in Table II and Figure 3, when the size of the dye anion steadily decreases, K also decreases. This trend is observed for both the desorption-rate and the time-lag experiments, when the same gelatin sample is compared. All the measurements were made with the solvent system, pH 12 at 0.2M ionic strength. Here again dye sorption into a swollen gelatin matrix decreased in the same order as dye–gelatin affinities measured in dilute gelatin solutions in the same solvent for the dyes concerned. Measured α'_g values are linearly related to the molecular weights of the dye anions. (Molecular weights are 603, 433, and 304 for dyes 1, 2, and 3, respectively.) As shown in Figure 3, the three dyes have different valencies at pH 12: monovalency (dye 3), divalency (dye 1), and trivalency (dye 2). This suggests that at pH 12, 0.2M ionic strength, the Donnan repulsion was small compared with the noncoulombic affinity between the dyes and the gelatin chains.

Correlation of Partition Coefficients With Affinity

Coefficients. Here it was necessary to correct for the fact that the solubility coefficient in the swollen film ought to be influenced by the volume fraction of polymer in the swollen film. To do so, we plotted the data as

$(K - 1 + V_2)$ vs. $\alpha_g' V_2$, a relationship derived in Appendix B. Values of K from the time-lag experiments were used in the plot in Figure 10. Here we observed a clear trend of greater sorption into the membranes (as measured by K) with greater affinity between polymer and the dye (as measured by α_g'). It would be risky, however, to try to predict K precisely from α_g'. This should not be surprising inasmuch as α_g' was measured with $V_2 \leq 0.02$, whereas K was measured with $V_2 > 0.1$. Nevertheless, the degree of correlation obtained and the agreement between the observed and predicted slopes in Figure 10 (1.30×10^{-3} and 1.35×10^{-3}, respectively, the latter of which is governed by the density of dry gelatin, 1.35 g/cm^3) are satisfying. We therefore conclude that it is possible to predict at least approximately the degree of sorption of a solute from solution to swollen polymer (membrane) phase from affinity measurements made with both the permeant and the polymer in dilute solution.

Effect of Immobilizing Polymers on Transport

We expected that polyvinylpyrrolidone (PVP), in addition to having a strong affinity for dye 1 ($\alpha_g' = 6.4$), would also slow the initial transport of this dye in a swollen membrane. With well-(formaldehyde) crosslinked films of comparable dry and swollen thicknesses, we found that as little as 2 wt % PVP in the membrane greatly extended the time lag (L) and accordingly decreased the apparent diffusion coefficient (Fig. 11). Figure 12 shows that L increased linearly with PVP content. Thus we conclude that, for dye 1

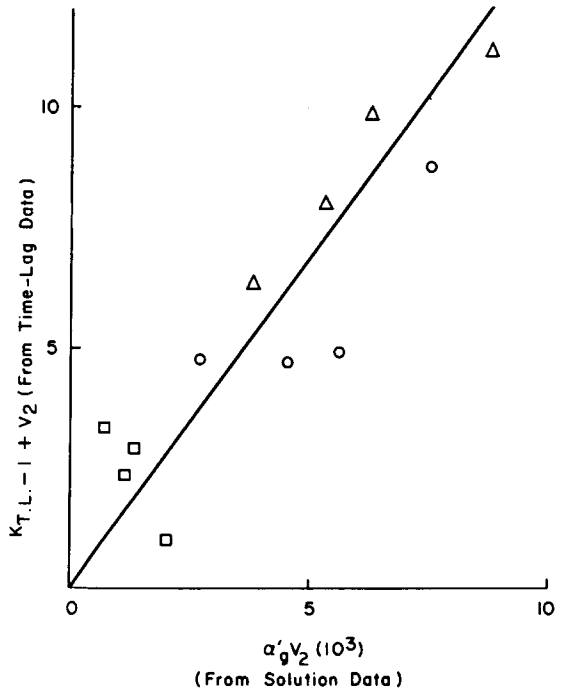

Fig. 10. Correlation of dye solubility coefficients in gelatin films with dye–gelatin interaction coefficients in gelatin solutions at pH 12: (○) 0.19M KBr; (△) 1.5M KBr; (□) 0.15M KBr, 25% isopropyl alcohol.

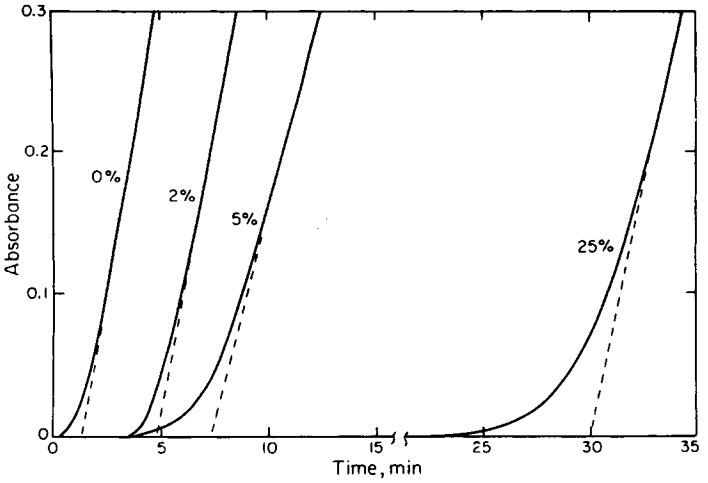

Fig. 11. Time-lag traces of four gelatin films containing different amounts of polyvinylpyrrolidone for dye 1 ($5 \times 10^{-4}M$) at pH 12, 0.19M KBr.

to traverse a membrane containing PVP, the dye must first saturate all the binding sites present before there is dye free to migrate through the matrix.

According to the immobilization model of Cooper,[14] which uses the Langmuir adsorption isotherm, L is related to the reciprocal of the diffusant concentration on the upstream side. As shown in Figure 13, reduction in dye concentration progressively increased the time lag. Indeed, the correlation was linear, as shown in Figure 14 for two membranes containing 2% and 5% of PVP. The slopes in this plot are a function of the adsorption

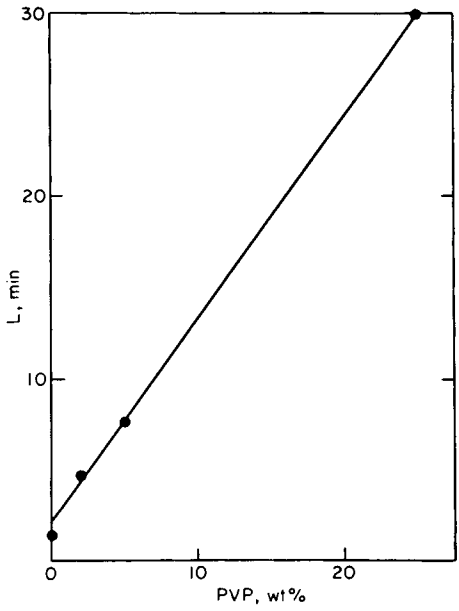

Fig. 12. Dependence of the time lag L of dye 1 ($5 \times 10^{-4}M$) on the wt % of polyvinylpyrrolidone in swollen gelatin films at pH 12, 0.19M KBr.

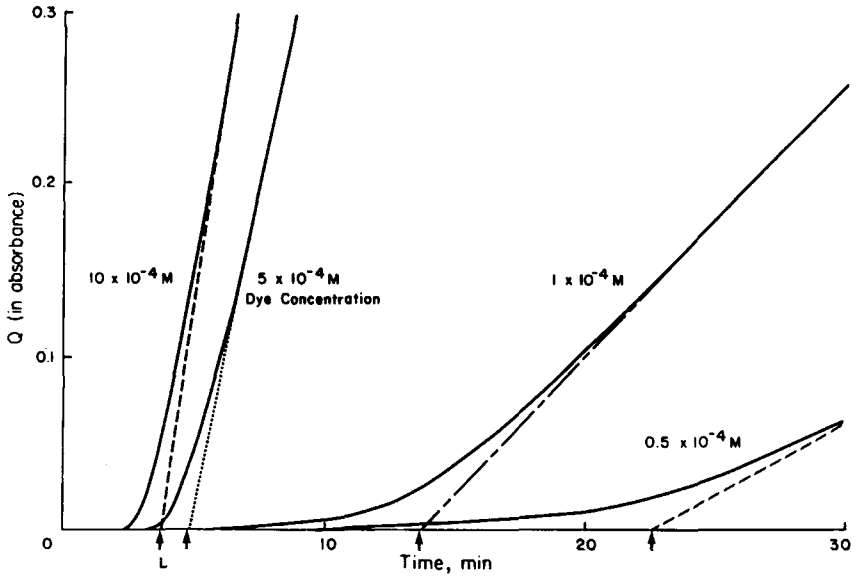

Fig. 13. Time-lag traces of the gelatin film containing 2 wt % polyvinylpyrrolidone for dye 1 at different concentrations (pH 12, 0.19*M* KBr).

coefficients in the Langmuir isotherm as well as the concentration of the adsorption sites, and the intercepts are related to the intrinsic mobilities in the matrix in the absence of any immobilizing sites and to the thickness of the film.

The concentration dependence of L for the gelatin film D is also shown in Figure 14. Note that the polymer coverage in this film is more than twice that of the film containing PVP. Within the experimental uncertainties we could draw an almost horizontal line through the data (○), indicative of little or no immobilization in the swollen gelatin film.

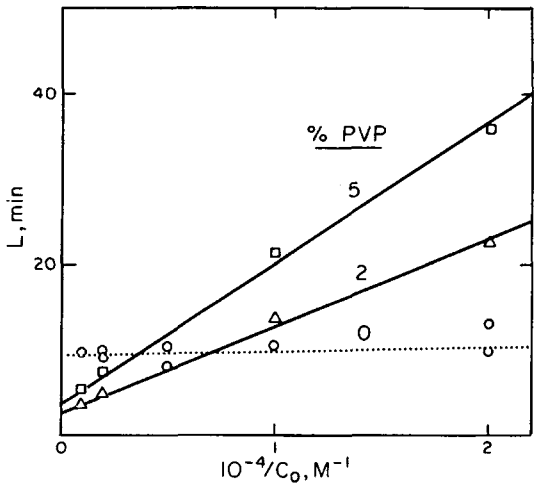

Fig. 14. Correlation of time lag L with dye concentration C_0 for dye 1 at pH 12, 0.19*M* KBr in gelatin films containing different amounts of polyvinylpyrrolidone; (○) 0 wt % (film D); (△) 2 wt %; (□) 5 wt %.

CONCLUSIONS

1. The time-lag and desorption-rate methods were used to measure the mobility and the solubility of dyes in swollen gelatin matrices. A good correlation was achieved among free volume in the matrix, dye ion size, and mobility as measured by the diffusion coefficients.

2. The extent of interaction between dye 1 and gelatin at pH 12 was measured in dilute aqueous solution by dynamic dialysis. The magnitude of the interaction, α_g' as defined by the ratio of the amount of dye sorbed [W (mmol dye/mg gel)] to the free dye concentration [C_f (mmol/mL)], is equal to 2.7×10^{-2} at pH 12, 0.2M KBr. The affinity coefficient of dye 1 to gelatin is therefore rather modest and, in fact, one of the smallest among the water-soluble polymers we studied. With gelatin, W was linearly related to C_f in the range of free dye concentration (C_f from 3×10^{-5} to $8.4 \times 10^{-4}M$). α_g' was increased by simultaneous increases in ionic strength and reduction of the alcohol content in the stock solution. With the three dye anions studied, α_g' was approximately proportional to the molecular weight of the dye anions at pH 12, 0.2M KBr, even though the valency of the dyes varied from 1 to 3.

3. A strong correlation between the solubility coefficient K (obtained from the time-lag measurements with swollen, crosslinked polymer films) and α_g' (measured in dilute polymer solutions) was achieved. As K increased there was scarcely any decrease in the dye mobility in the swollen matrix, and the overall transport was commensurately increased because of the greater affinity (α_g').

4. Polyvinylpyrrolidone (PVP) in a gelatin matrix at concentrations down to 2 wt % seriously slowed the initial transport of the dye anions. The time lags were proportional to the amount of PVP present and could also be linearly related to the reciprocal of the dye concentration in the feed solution.

We are grateful to Mrs. J. P. Butler and Mrs. J. A. Edin for assistance in experimental work. We are also indebted to Drs. K. Liang, R. L. Reeves, N. F. Irani, P. Bagchi, and other colleagues for fruitful discussions and suggestions and for supplying materials.

APPENDIX A: COMPUTATION OF EXTENT OF DYE–POLYMER AFFINITY FROM DYNAMIC-DIALYSIS DATA

The concentration of dye in the diffusate compartment during a typical dynamic-dialysis experiment is shown in Figure 2. As mentioned in the text, the amount of dye sorbed to dissolved polymer can be computed from the slopes just after point B. The equations for doing this are derived below.

Dye flux (J) through the membrane is given by Fick's first law of diffusion

$$J = -D\frac{dc}{dx} \tag{9}$$

in which D is the diffusion coefficient of dye in the membrane and dc/dx is the concentration gradient. Referring to Figure 2, at the beginning of a control experiment (point A), dye was added to the upper (retentate) compartment of the dialysis cell. Let J_A' be the dye flux measured between points A and B, and let M_T be the total amount of dye added at the start of the experiment. Then, for steady-state diffusion

$$J_A' = \frac{DM_T}{hV_0} \tag{10}$$

in which h is the membrane thickness and V_0 is the volume of solution in the retentate compartment (8 mL). At point B in the control experiment, the dye solution in the retentate compartment was diluted by adding a small volume (ΔV, typically 2 mL) of stock solution. This caused a lower flux (J_B'), which is given as

$$J_B' = \frac{D(M_T - M_d)}{h(V_0 + \Delta V)} \tag{11}$$

Here M_d is the amount of dye that has diffused through the membrane between times A and B, over the time span used, $M_d << M_T$. The ratio of the two fluxes in the control experiment is

$$\frac{J_B'}{J_A'} = \frac{(M_T - M_d)V_0}{M_T(V_0 + \Delta V)} \tag{12}$$

At the beginning of an experiment in which polymer is to be added, the initial step is the same as before and the initial flux (J_A) is given by eq. (10). Hence $J_A' = J_A'$. Then at point B a volume ΔV of polymer solution is added, and an amount of dye (M_a) is sorbed to the polymer. The flux (J_B) then becomes

$$J_B = \frac{D(M_T - M_d - M_a)}{h(V_0 + \Delta V)} \tag{13}$$

and the ratio of fluxes becomes

$$\frac{J_B}{J_A} = \frac{(M_T - M_d - M_a)V_0}{M_T(V_0 + \Delta V)} \tag{14}$$

From eqs. (14) and (12)

$$\frac{J_B}{J_B'} = \frac{(M_T - M_d - M_a)}{(M_T - M_d)} \tag{15}$$

and defining

$$\epsilon = 1 - (J_B/J_B') \tag{16}$$

we have

$$\epsilon = M_a/(M_T - M_d) \tag{17}$$

Since $M_d << M_T$

$$\epsilon = M_a/M_T \tag{18}$$

and from eq. (16) we can compute the fraction of dye that is sorbed.

APPENDIX B: DERIVATION OF THE RELATIONSHIP BETWEEN THE AMOUNTS OF DYE SORBED IN DILUTE SOLUTION AND IN SWOLLEN MEMBRANE

One of our goals was to compare dye affinity in a dilute polymer solution with dye sorption into a swollen membrane of the same polymer. If the affinity in one case can be directly correlated with the sorption in the other, only the easier dilute-solution (i.e., dynamic dialysis) measurements are necessary to determine dye–polymer affinity. Thus it is appropriate to derive a relationship between the two cases. To do so, we assumed that the affinity between dye and polymer in the swollen membrane is the same as in dilute solution.

Per milliliter, the total dye (C_T) in a swollen film is the sum of the dyes in the free or interstitial volume (C_F) and the dye sorbed by the polymer (C_P):

$$C_T = C_F + C_P \tag{19}$$

C_F is given as

$$C_F = \frac{(1 - V_2)C_f}{10^3} \tag{20}$$

in which V_2 is the volume fraction of polymer present in the swollen film and C_f is the dye concentration (mol/L) in the external solution.

The dye sorbed to the polymer is given as

$$C_P = W\rho V_2 \tag{21}$$

in which W is moles of dye bound per gram of polymer, and ρ is the density of polymer. Since

$$W = \alpha_g' C_f \tag{22}$$

we can write

$$C_P = \alpha_g' C_f \rho V_2 \tag{23}$$

Here α_g' is an affinity parameter obtained from the slope of a plot of W vs. C_f from dynamic-dialysis data. Hence,

$$C_T = \frac{(1 - V_2)C_f}{10^3} + \alpha_g' \rho V_2 C_f \tag{24}$$

The solubility coefficient (K) is defined as the ratio of the concentration of dye inside the membrane to that outside the membrane. This ratio, if units of mol/L are used, is

$$K = \frac{10^3 C_T}{C_f} = (1 - V_2) + 10^3 \alpha_g' \rho V_2 \tag{25}$$

Rearranging yields

$$K - 1 + V_2 = 10^3 \rho V_2 \alpha_g' \tag{26}$$

This therefore is the basis for the plot shown in Figure 10, which is linear as predicted.

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Received May 23, 1984
Accepted September 17, 1984