JOURNAL OF APPLIED POLYMER SCIENCE VOL. 18, PP. 831-842 (1974)

The Interactions of Ionic Dye Permeants with Poly(vinyl Alcohol) Membranes

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Synopsis

The well-known interaction between Congo Red and poly(vinyl alcohol), PVA, was studied by equilibrium dialysis. The diffusion of Congo Red into PVA membranes was much more rapid in 0.1*N* NaCl solution than in water. The dye appeared to be practically immobilized by the membranes in both solvents. A short survey of the dialytic behavior of various classes of ionic dyes through PVA membranes with water as solvent was undertaken. Anionic dyes permeated the membranes only very slowly, whereas cationic dyes permeated the membranes relatively rapidly and dyed them considerably. The existence of negative charges on the PVA membranes was demonstrated by performing dialysis experiments with the anionic dye Orange II and the cationic dye Acridine Orange in water and in excess electrolyte (1*N* NaCl).

INTRODUCTION

The gelation of poly(vinyl alcohol) solutions by Congo Red is a well-known phenomenon believed to be due to nonionic forces. It is thought that the amino groups of the dye form hydrogen bonds with the hydroxyl groups of the polymer.[1] We were interested in determining the effectiveness of a nonionic interaction such as this toward immobilizing a dye permeant within a membrane. Previous dialysis experiments in our laboratory with gelatin membranes of moderate charge densities led us to conclude that electrostatic attraction alone between the membranes and dye permeants of opposite charge was not sufficient to immobilize the dyes effectively within the membranes.[2]

It is our purpose here, however, simply to describe the various aspects of the interactions of ionic dye permeants with PVA membranes rather than to present a comprehensive study of dye immobilization.

Ordinarily poly(vinyl alcohol) (PVA) is considered to be an uncharged polymer.[3,4] The presence of one or two carboxyl endgroups per molecule, however, has been demonstrated in PVA of foreign manufacture.[5,6] Schurz and Schlor[7] called PVA a polyelectrolyte. The PVA membranes behaved in these dialysis experiments as if they were composed of polyanions. This behavior is demonstrated by performing dialysis experiments with the anionic dye Orange II and the cationic dye Acridine Orange in water and in excess electrolyte (1*N* NaCl). Negative behavior of cellulose films

and fibers in contact with aqueous solutions is well known; it is considered due to the dissociation of carboxyl groups. This can yield a charge density of from 0.005M to 0.05m in a swollen cellulosic film.[8,9] It is possible that carboxyl groups are a source of the charge on the PVA membranes. If we assume two carboxyls per molecule and a molecular weight of 10^5, a reasonable estimate of the carboxyl density in our PVA membranes is 0.01M.

EXPERIMENTAL

Materials

The dyes used in this study are listed in Table I along with their structures and numbers given in Colour Index.[10] All of the dyes (with four exceptions) were certified Eastman organic chemicals (Eastman Kodak Co.) ranging from 91% to 99% dye content (except Light Green SF, 85%, and Indigo Carmine, 80%) and were used without further purification. The four exceptions were Acridine Orange (Eastman organic chemicals, reagent grade, 98%); tartrazine (Eastman organic chemicals, practical grade); Solantine Pink 4BL (Allied Chemical Co.), and Sky Blue 6BX (E. I. du Pont de Nemours and Co., Inc.).

The PVA used in this study was medium-viscosity Elvanol 71.30 (E. I. du Pont de Nemours and Co., Inc.) containing 0.5 to 1.8 wt-% residual poly(vinyl acetate).[11] PVA films were made by coating on Du Pont Mylar film base an 8% (w/v) water solution of the Elvanol at room temperature at a wet thickness of 0.01 cm. Film samples were annealed 20 min at ca. 130°C in closed weighing bottles, then easily lifted from the Mylar base.

Membranes were prepared by immersing the annealed film samples in the appropriate solvent overnight with one exception. When 1N NaCl solution was the solvent, the film samples were first swollen in water and then transferred to the salt solution, where they remained overnight. In this manner, the polymer volume fraction v_2 of the swollen film samples was controlled to 0.38 ± 0.02. (A PVA film sample put directly into 1N NaCl solution did not swell nearly as much as it would have in water; v_2 was approx 0.49.) The volume fraction v_2 was obtained from dry and wet lateral dimensions measured by a scale, dry thickness was measured by a hand micrometer, and wet thickness was measured by a Federal thickness gauge with the sample sandwiched between two pieces of Mylar film base. The swollen samples were then cut again by a steel die to a diameter of 3.43 cm and mounted in the membrane holder of the dialysis cell. The swollen thickness was (9.2 ± 0.3) × 10^{-3} cm.

Apparatus and Procedure

The dialysis apparatus and procedure were those described by Little and Osterhoudt.[12] The swollen membrane was mounted in a poly(methyl methacrylate) holder (i.e., Plexiglas or Lucite), which exposed a membrane

area of 3.34 cm². Top and bottom cell pieces, also of PMMA, were fixed to the holder making compartments of 7.12 ml in volume. The circulatory system, including stainless steel tubing, a controlled-volume minipump (Milton Roy Co.), and a monitoring flow cell, added 5.06 ml in volume to each compartment. Some experiments were performed with unequal volumes in top and bottom (25.46 ml and 10.54 ml, respectively). Magnetic stirrers were placed in the cell compartments during assembly, and the stirrers were located approx 0.3 cm from the membrane. The cell was assembled while it was immersed in the solvent of the experiment and both compartments became filled with the solvent. The cell was mounted in a water bath at 25.0°C and rested on a submerged magnetic stirring motor. The motor was driven by a tap-water stream; it turned the stirrers in both compartments.

Monitoring systems from Instrument Specialties Co. were employed for both retentate (Model 224) and diffusate (Model 222) compartments. The spectral absorption of the circulating dye solution in each compartment was monitored at a selected wavelength, and continuous line traces were recorded of the change in absorption with time as dye concentration changed in either cell compartment. The wavelength 450 nm was used for red and orange dyes, and 600 nm was used for blue and purple dyes and Light Green SF. For flow diagram and cell design schematics see Little and Osterhoudt.[12]

As a preliminary to each experiment, the responses of the two monitoring units were compared. A baseline was established with solvent circulating through both monitoring systems from a vial. Dye was added to the vial at the proposed initial concentration of the experiment. The ratio of the response to the dye solution of the diffusate unit to that of the retentate was usually near 0.960. The response of the retentate in the subsequent experiment was reduced by this factor in the calculations. The preliminary vial experiment also indicated the extent of dye losses from such occurrences as fading or precipitation somewhere in the apparatus out of the flow path. Such losses occurred for Congo Red and Acridine Orange in salt solutions.

After the preliminary experiment, the circulatory systems were rinsed and the dialysis cell was connected to them. Baselines were reestablished while solvent was circulating. Then, dye permeant was added to the retentate compartment.

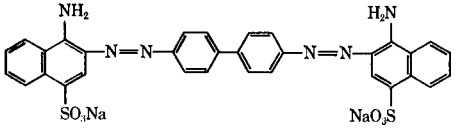
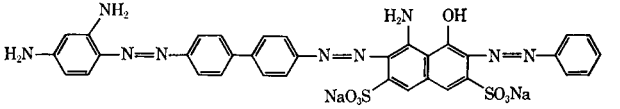
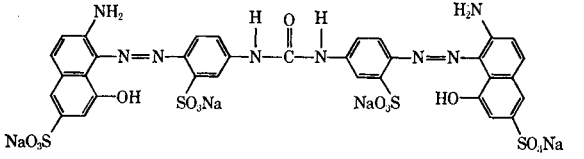
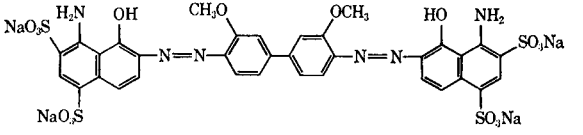
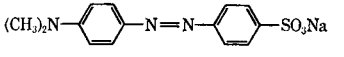
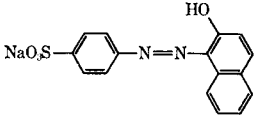
Calculations

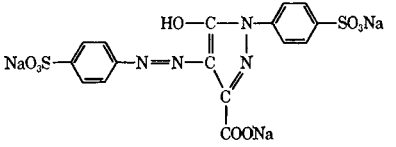
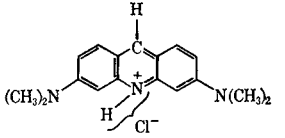
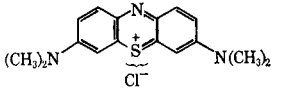
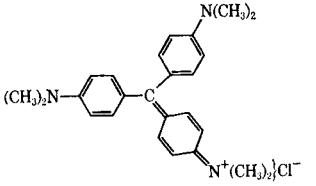
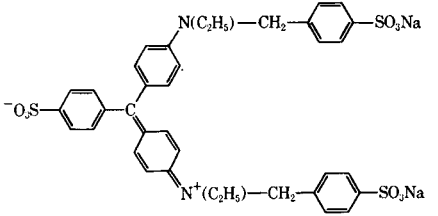
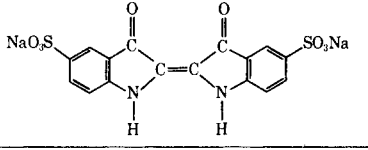
Permeation coefficients $D'K$ were calculated from the diffusate traces by the following equation based on Fick's law of diffusion and $S \propto C$ (C is dye concentration):

$$(D'K) = \left(\frac{lV_2}{A}\right)[S_1(t) - S_2(t)]^{-1}\left(\frac{dS_2}{dt}\right), \quad (1)$$

where D' = diffusion coefficient in the membrane in cm² sec^{-1}, K = partition coefficient between membrane and solution phases, V_2 = volume of

TABLE I
Dyes

Dye name	Color Index No.[a] and Source	Dye structure
Congo Red	CI 22120 Eastman Kodak Co.	
Chlorazol Black E	CI 30235 Eastman Kodak Co.	
Solantine Pink 4BL	CI 25380 Allied Chem. Corp.	
Sky Blue 6BX	CI 24410 E.I. du Pont de Nemours & Co.	
Methyl Orange	CI 13025 Eastman Kodak Co.	
Orange II	CI 15510 Eastman Kodak Co.	

Tartrazine	CI 19140 Eastman Kodak Co.	
Acridine Orange	CI 46005 Eastman Kodak Co.	
Methylene Blue	CI 52015 Eastman Kodak Co.	
Crystal Violet	CI 42555 Eastman Kodak Co.	
Light Green SF	CI 42095 Eastman Kodak Co.	
Indigo Carmine	CI 73015 Eastman Kodak Co.	

[a] See reference 10.

diffusate compartment, A = area of membrane exposed to permeant solution, l = swollen membrane thickness, S_1 = height of recorder trace from retentate (corr. by scale factor), S_2 = height of recorder trace from diffusate, and t = time.

$D'K$ was calculated from the diffusate trace instead of the retentate trace. The latter includes dye disappearance factors other than those due to diffusion, e.g., dye binding to the membrane.

The permeation coefficients of a dye in water and in salt solution through a Nuclepore membrane filter (General Electric Co.) were compared and the differences taken as an indication of the effect of salt on the free diffusion of the dye. Nuclepore contains about 7% void volume in the form of straight-through pores 0.5 μ in diameter and is unswollen in water and in salt solution. There is no interaction, ionic or otherwise, between the dyes and the polycarbonate porous diaphragm so that the dyes diffuse freely through it. (The pores are too big for molecular sieve effects with the dyes even if they are aggregated to fairly high degrees.) Therefore, since there is no tortuosity in the diffusion path through Nuclepore, the partition coefficient K of the permeability coefficient $D'K$ is simply the volume fraction of the membrane available to diffusion, i.e., 0.07. $D'K = 0.07D'$, and D' simply equals D_0, the free diffusivity in water. The diffusion coefficient D_0 of Orange II in water is calculated to be 100×10^{-7} cm²/sec. This value is not out of order with Valko's[13] datum, 79.9×10^{-7} cm²/sec, differing perhaps because of an erroneously low estimate of the Nuclepore void volume. Our value of D_0 for Acridine Orange is 82.5×10^{-7} cm²/sec. These values and the diffusion coefficients in salt solution are listed in Table II.

TABLE II
Permeability of Poly(vinyl Alcohol) (PVA) and Nuclepore Membranes to Orange II and Acridine Orange in H_2O and in NaCl Solution

Dye	Dye concn. $\times 10^5$, g/ml	Solvent	v_2 of PVA	$D'K \times 10^7$, cm²/sec		$D \times 10^7$, cm²/sec	$(D'K)_{PVA}/D$
				PVA	Nuc.		
Orange II	3.3	H_2O	0.357	2.10	7.03	100	0.021
		1.0N NaCl	0.396	14.2	4.79	68.4	0.208
Acridine Orange	2.1	H_2O	0.373	32.1	5.77	82.5	0.389
		1.0N NaCl	0.392	7.49	1.66	23.7	0.316

Difficulties with Salt Solutions of Dyes

Water solutions and 0.1N salt solutions of Congo Red were stable, and the dialysis experiments were carried out without significant dye losses to the apparatus. However, Congo Red at a concentration of 2.9×10^{-5} g/ml in 0.5N salt solutions generally precipitated. (The time interval for a fresh solution to precipitate varied. Some precipitated in 2 to 6 hr, and one did not precipitate at all.) Precipitation occurred somewhere in the

apparatus (in the liquid end of the pump, we think) in a dialysis control experiment with the Nuclepore membrane in the 0.5*N* NaCl solution, and this experiment was ruined. In a dialysis experiment with the PVA membrane and the same solvent, however, most of the dye moved into the membrane within 1 hr, as evidenced by the intense color of the membrane, and so not much precipitated in the apparatus.

There was severe dye loss in the dialysis experiments with Acridine Orange in salt solutions (1.0*N*). At dialysis equilibrium with both Nuclepore and PVA membranes, the sum of dye amounts in retentate and in diffusate was only half the amount originally added. The driving force for the dialysis due to dye concentration was therefore decreasing more rapidly than in a straightforward experiment, so that the calculated $D'K$ represents a lower limit. $D'K$ is calculated from the data during the first 80 min of the experiment (which is the procedure for all the experiments) and should be low by less than 50%.

Experiments with Congo Red or Acridine Orange in salt solutions were followed by a prolonged water rinse of the apparatus. After these experiments, while the baseline with pure solvent was being established for the next experiment, a fresh PVA membrane in the dialysis cell scavenged Congo Red or Acridine Orange from the apparatus and became lightly colored. Evidently, water did not always rinse these dyes thoroughly from the apparatus, trace amounts remaining adsorbed in it.

There was no dye loss with Orange II.

RESULTS

Congo Red and Other Anionic Azo Dyes

Figure 1 shows sketches of the recorder responses to the dialysis experiments with Congo Red as dye permeant (at an initial concentration of 2.9×10^{-5} g/ml), PVA as membrane, and distilled water and 0.1*N* NaCl solution as solvents. The retentate traces show that the transport of Congo Red from water into the PVA membrane was relatively slow (although the membrane appeared considerably dyed in a few hours), and less than half entered the membrane by 16 hr. In contrast, Congo Red moved into the membrane much faster in the presence of salt. The diffusate traces show that little dye appeared downstream after 16 hr in either experiment. Therefore, in both cases, the dye appears immobilized in the membrane.

In order to determine whether the membrane upon saturation with dye will yield substantially more dye to the downstream compartment, the experiment in 0.1*N* NaCl solution was repeated and carried further by discrete additions of more dye solution. The last dye addition apparently saturated the membrane. The binding curve, shown in Figure 2, was generated from the data. At the end of the experiment, there was 4.65×10^{-6} mole of dye in the membrane (which contained 1.50×10^{-2} g poly-

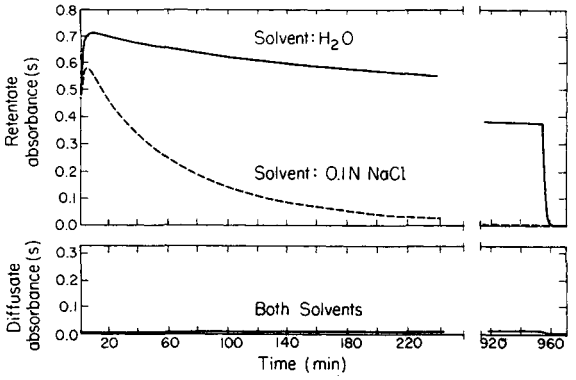


Fig. 1. Decrease of absorbances with time in the retentate compartment of the dialysis cell and increase of absorbances in the diffusate compartment as Congo Red was transported into PVA membranes in H_2O in one experiment and in 0.1*N* NaCl in another.

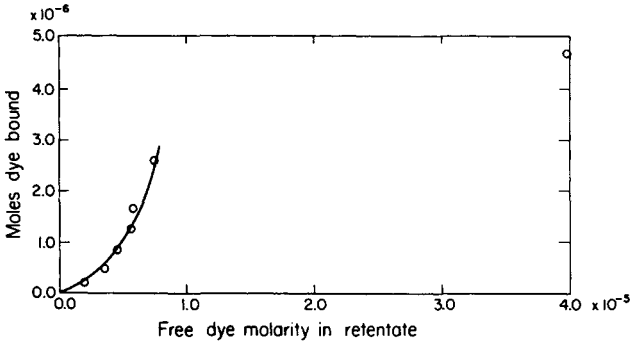


Fig. 2. Moles of Congo Red bound to the PVA membrane vs. free dye concentration. Solvent was 0.1*N* NaCl.

mer), 1.01×10^{-6} in the retentate, and 0.0675×10^{-6} in the diffusate. This shows that even at saturation, PVA will not yield an appreciable amount of Congo Red to the downstream compartment.

Four other anionic azo dyes, Chlorazol Black E (initial concentration 3.02×10^{-5} g/ml), Sky Blue 6BX (1.03×10^{-5} g/ml), Solantine Pink (0.822×10^{-5} g/ml), and Direct Orange R (2.01×10^{-5} g/ml), were found to bind to PVA membranes during dialysis with distilled water as solvent. In no case was dye observed visually in the downstream compartment by 16 hr. The azo dyes Methyl Orange (2.06×10^{-5} g/ml) and tartrazine (3.08×10^{-5} g/ml) did not bind to nor rapidly permeate PVA membranes.

Dyes of Other Classes

A short survey of the dialytic behavior of examples of various classes of dyes through PVA membranes with water as solvent showed that anionic dyes permeated PVA membranes only very slowly, whereas cationic dyes

permeated the membranes relatively rapidly. The anionic dyes surveyed were Light Green SF (a triphenylmethane dye at an initial concentration of 2.06×10^{-5} g/ml), Indigo Carmine (4.12×10^{-5} g/ml) and Orange II (a nonbinding azo dye at 3.29×10^{-5} g/ml). These chromophore-bearing anions did not dye the membranes more than a tinge, if at all.

The cationic dyes surveyed were Methylene Blue (a thiazine dye at an initial concentration of 1.54×10^{-5} g/ml), Crystal Violet (a triphenylmethane dye at 1.03×10^{-5} g/ml), and Acridine Orange (2.05×10^{-5} g/ml). These dyes permeated the membranes rapidly in spite of being retained in various amounts by the membranes. Crystal Violet dyed the membrane intensely, Methylene Blue rather intensely, and Acridine Orange only moderately.

Orange II and Acridine Orange

In Figure 3 are drawn the retentate and diffusate traces of the permeants Orange II and Acridine Orange through PVA membranes in H_2O. Table II lists permeability coefficients $D'K$ for the experiments calculated from the diffusate traces using eq (1). The anionic dye Orange II permeated very slowly ($D'K = 2.10 \times 10^{-7}$ cm²/sec), whereas the cationic dye Acridine Orange permeated rapidly ($D'K = 32.1 \times 10^{-7}$ cm²/sec). Note that the experiment with Orange II had not yet come to dialysis equilibrium in 900 min (15 hr). Also note the short delay in appearance of Acridine Orange downstream of the membrane in the diffusate compartment and that after dialysis equilibrium had been achieved, there was some loss of dye from the solution in the diffusate compartment. The delay of cationic dye permeation of the membrane (which we also saw with negative gelatin membranes) we attributed to the effect of the Donnan potential. The dye cations must first diffuse into and fill the membrane to a degree con-

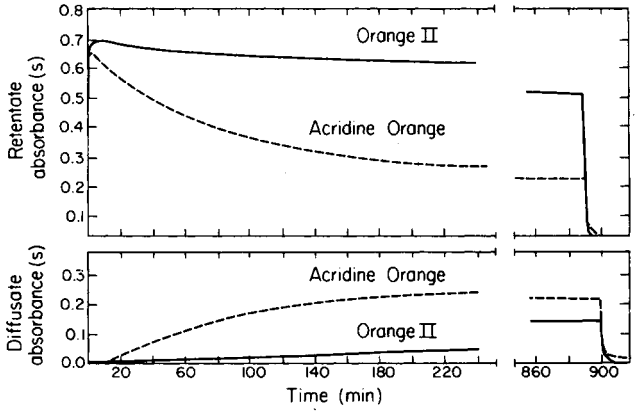


Fig. 3. Decrease of absorbances with time in the retentate compartment of the dialysis cell and increase of absorbances in the diffusate compartment as Orange II and Acridine Orange permeated PVA membranes. Solvent was water in each experiment.

trolled by the Donnan potential before they are released from the membrane at its downstream (diffusate) side. The PVA membrane appeared colored to a moderate intensity by the Acridine Orange.

The experiments with the Nuclepore membrane show the dyes to have relatively similar diffusivities in water. They would be expected to have similar permeabilities in the PVA membrane unless there were charge or other hindrances. In order to subdue any electrical hindrances to diffusion, the dialyses were rerun in 1.0*N* NaCl solution.

In the presence of the added electrolyte, Orange II permeated PVA much more rapidly, and Acridine Orange much more slowly, than in water. These are expected shifts in $D'K$ for permeation governed by electrostatic forces between ionic dye and polyanionic membrane. In analyzing these data, however, the effect of the salt in the solvent on the free diffusivity of the dyes, shown by the control experiments with Nuclepore (see Table II), must be taken into account. The difference in the ratio $(D'K)_{PVA}/D$ in the two solvents reflects the effect of solvent on the dye–membrane interaction. These ratios for the two dyes tend to converge in 1.0*N* NaCl toward a common value, which is governed primarily by the tortuosity in the membrane. The salt was very effective in subduing electrostatic repulsion between the PVA membrane and Orange II, but its success in altering the interaction of the membrane with Acridine Orange is less pronounced. In the latter case, the reduced permeability coefficient through PVA is partially accounted for simply by the salt effect on the free diffusivity of the dye.

There was no large change from the result in water in the coloration of the membranes by the dyes in the presence of salt.

Deionized PVA

The PVA membranes for the above studies were prepared directly by dissolution and coating of Elvanol 71.30 without further purification. The ash content specification of the Elvanol is $\leq 1\%$ (calculated as Na_2O).[11]

One per cent of inorganic impurities present in our PVA membranes would cause a charge density of 0.1*M*. This is in the realm of weak ion exchange behavior.

An Elvanol 71.30 solution was vigorously stirred in the presence of ion exchange resins in bead form in order to remove inorganic impurities, and perhaps adsorbed sulfate and acetate anions, so that a membrane formed from the solution would not retain the impurities. (PVA is known to adsorb many anions, acetate ions,[6] thiocyanate,[4,14] surfactant ions,[3,15] and possibly sulfates.[16,17]) The ion exchange beads were Amberlite IR120 and IRA 400 (Mallinckrodt Co.) used in the hydrogen and hydroxide forms, respectively.

The permeability coefficients of Orange II and Acridine Orange through a membrane made from the deionized solution were determined and compared to those through the membrane made from an untreated solution (see Table III). It is evident that the deionizing treatment removed some anions from the PVA membrane, but did not reduce its charge to zero.

TABLE III
Permeability of Untreated PVA and Deionized PVA Membranes to Orange II and Acridine Orange in H_2O

Dye	$D'K \times 10^7$, cm²/sec	
	Untreated PVA	Deionized PVA
Orange II	2.10	5.20
Acridine Orange	32.1	22.1

DISCUSSION

The anionic character of PVA membranes appreciably slowed down the transport of anionic dyes through the membranes. Congo Red and some other anionic azo dyes bound to the membranes despite the negative charges on both dye and polymer molecules. Congo Red appeared immobilized within the membrane because it entered the membrane but was not transmitted to the downstream compartment.

Salt subdued the electrostatic repulsion between a nonbinding anionic dye such as Orange II and the PVA membrane so that the dye was transported through the membrane more rapidly. In the case of the binding dye, Congo Red, movement into the membrane was increased appreciably in the presence of salt, whereas transport out of the membrane was not influenced. The added electrolyte probably exercised two influences on the binding process: a reduction in electrostatic repulsion between dye molecules and membrane surface and a decrease in dye affinity for the aqueous phase made evident by increased dye aggregation.[13] Under these influences, the solubility of the dye in the membrane phase was increased.

It would be interesting to know more about aggregation in Congo Red. Although the transport of Congo Red into the PVA membrane was so slow that less than half of it entered the membrane in 16 hr when the initial dye concentration was 2.9×10^{-5} g/ml (and water was the solvent), all of the dye disappeared from the retentate compartment into the membrane in 16 hr when the initial dye concentration was 1.0×10^{-5} g/ml. At a still lower concentration, 0.57×10^{-5} g/ml, Congo Red simply disappeared in the apparatus when a Nuclepore membrane was used. Apparently, diluting the solution forced the dye to disaggregate, but the monomer (or higher-mer) was unstable in water and adsorbed to almost anything it contacted.

A second, more convincing piece of evidence that Congo Red is considerably aggregated even in water is provided by the following experiments. While small anionic azo dyes such as Methyl Orange and Orange II permeate a Metricel PEM membrane of cellulose triacetate (Gelman Instrument Co.), which is claimed in the 1969 Gelman catalog to have a pore size of 0.0075 μ, Congo Red will not permeate PEM either in water or 0.1N NaCl solution. The PEM membrane has a "cutoff" to permeation by neutral molecules of molecular weight around 3000.[12] The molecular weight of Congo Red is 696. On the other hand, Congo Red permeated the Nuclepore of 0.5 μ in pore size. $(D'K)_{\text{Nuc}}$ was 2.54×10^{-7} cm²/sec in water and

2.12×10^{-7} cm²/sec in 0.1N salt solution. From these data, D_0 (in water only) is calculated to be 36.3×10^{-7} cm²/sec, and D (in 0.1N salt) is calculated to be 30.3×10^{-7} cm²/sec.

SUMMARY

In water, anionic dyes permeated PVA membranes only very slowly, whereas cationic dyes permeated these membranes relatively rapidly. This behavior is typical of membranes that have fixed negative charges. Two sources of such charges are possible in commercial PVA: carboxyl endgroups and strongly adsorbed salt anions. Despite the presence of these fixed negative charges (which ought to repel dissolved anions exterior to the swollen membrane), Congo Red and certain other anionic azo dyes are strongly bound to PVA membranes. The attractive forces between these dyes and PVA must, therefore, be very large. Certainly they are sufficiently large virtually to immobilize Congo Red in a swollen PVA membrane. Although some of the ions of cationic dye permeants were retained by PVA membranes of opposite charge, not even the best membrane-colorant among them was as effectively immobilized there.

The authors are indebted to Miss Carolyn M. Little and Miss JoAnn Dickerson for performing some of the experiments in this study.

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Received July 24, 1973
Revised September 4, 1973