Diffusion Coefficients of Direct Dyes in Chitosan

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SYNOPSIS

Diffusion coefficients for direct dyes (C. I. Direct Red 81, Green 26, Blue 75, and Black 22) in Chitosan films are determined to be 4.48×10^{-11} to 4.54×10^{-10} cm^2/at 60°C and pH 9. A method for producing chitosan films is described.

INTRODUCTION

Chitosan [poly(1-4)-2-amino-2-deoxy-β-D-glucan] is a crystalline, structural polysaccharide, usually prepared by purification and N-deacetylation of chitin from natural sources. Chitosan has a chemical structure similar to cellulose, but exhibits many properties different from cellulose. In fact, due to the presence of amino groups, chitosan is considerably more chemically versatile than is cellulose.

Chitosan is readily solution-spun into fibers or films, as is cellulose.[1,2] The dye sorption properties of cellulose are very well known and characterized.[3] However, dyeing data reported for chitosan fibers and films appears to be limited to one study of a few food colorants.[4] We have found that chitosan can easily be dyed with direct, acid, fiber reactive, and other dye classes. The purpose of this paper is to characterize diffusion coefficients of direct dyes in chitosan.

MATERIALS

Chitosan was prepared from practical grade chitin from crabshells (Sigma, C-3132, lot 36F0116) by Horton and Lineback's method.[5] Two hundred grams of chitin was heated in 2L of 50% (w/w) NaOH for 2 h at 100°C under nitrogen (to avoid oxidation). The reaction mixture was cooled to room temperature, then the chitosan was recovered,

rinsed twice in methanol, and once in acetone and dried. The sample was treated exactly as above a second time to achieve maximum N-deacetylation, rinsed (as above), and dried. Three batches of chitosan (each yielding about 125 g) were prepared in this way.

Chitosan films were cast from 5% polymer solutions in 90% aqueous formic acid. Formic acid is a convenient volatile solvent that yields clear and flexible chitosan films. The chitosan/formic acid solutions were filtered through a 7-micron-pore-size sintered metal frit using the polymer extrusion cylinder on a Bradford wet spin unit. Films were cast with a doctor knife onto smooth glass plates and allowed to dry at room temperature. They were then removed from the glass and soaked overnight in 0.05 M sodium methoxide in methanol to regenerate the free amine form. This regeneration procedure does not disturb the morphology of the film, as an aqueous treatment might.

The N-acetyl content of the sample was determined by two methods: IR spectra and potentiometric titration. From these data, a percent N-acetyl of 51.2 was calculated, i.e., 48.8% free amine.

Film thickness was determined with a micrometer. The chitosan films used in this experiment were 1.27×10^{-3} cm thick. The cellulose (control) films were 5.00×10^{-3} cm thick. Cellulose film, used as a control in these dye diffusion experiments, was obtained from Flexcel Corp. (mill roll #524187009).

The dyes used are listed in Table I. Pyrazol Fast Red 8BL (Direct Red 81), Pyrazol Fast Blue 2GL (Direct Blue 75), and Pyrazol Black G (Direct Black 22) were obtained from Sandoz Chemicals Corporation. Solophenyl Green BL (Direct Green 26) was

Table I Direct Dyes for Which Diffusion Coefficients Were Measured

Dye (C.I. Direct)	Color Index Constitution	Molecular Weight
Red 81	28160	699
Green 26	34045	1320
Blue 75	34220	1127
Black 22	35435	1131

obtained from Ciba-Geigy Corporation. All dyes were commercial product samples and used without purification.

APPARATUS

The diffusion coefficient for each dye was determined from steady-state diffusion experiments using Daynes' time-lag method.[6,7] The diffusion cell used was a standard electrochemical H-cell, model C-600 (The Electrosynthesis Co., Inc.), as illustrated in Figure 1. Films of cellulose or chitosan were used as the membrane separating the dye compartment from the blank side of the H-cell. A 2 L beaker served as an expansion tank for the dye compartment of the

H-cell in order to provide an "infinite" dye bath to maintain constant dye concentration on the diffusant side of the polymer film. Two Masterflex peristaltic pumps were employed to provide a constant circulation of dye solution between the dye compartment of the H-cell and the 2 L beaker. Diffusion of dye through the polymer film was monitored with the aid of a Diano Match Scan II continuous double-beam spectrophotometer. A third Masterflex pump provided continuous circulation of the solution contained in the blank compartment of the H-cell through a flow cell housed in the spectrophotometer. The solution contained in the dye compartment of the H-cell was stirred vigorously throughout the experiment by an impeller-type glass stir rod. Both the H-cell and 2 L beaker were maintained at 60°C
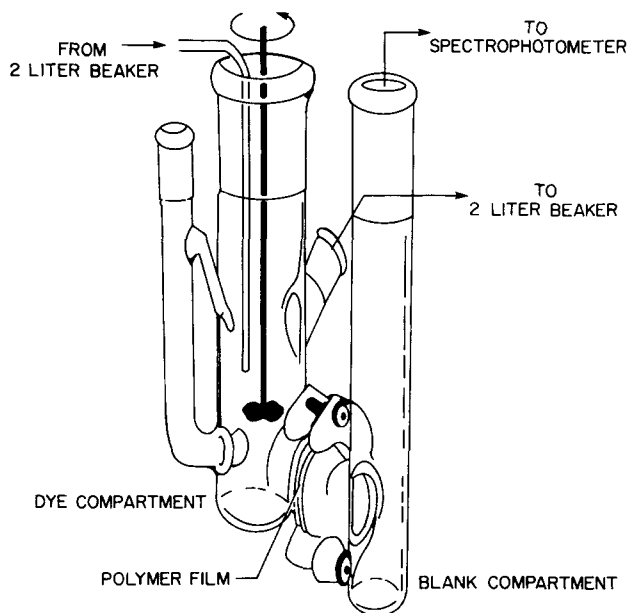
DIFFUSION APPARATUS

Figure 1   The diffusion cell used was a standard electrochemical H-cell, Model C-600 (The Electrosynthesis Co., Inc.).

by the use of two Haake, model F3-CH, thermostated circulating baths.

PROCEDURE

Chitosan (or cellulose) film was placed over the 2.1 cm diameter opening between the two compartments of the H-cell and sealed tightly with the aid of a

rubber O-ring gasket and metal clamp to prevent leakage. Both compartments of the H-cell were filled with pH 9 buffer solution (0.2 mol/L boric acid and 0.1 mol/L sodium hydroxide) and the film allowed to condition overnight.

The H-cell was then emptied, and 80 mL of fresh buffer solution was added to the blank compartment and 60 mL to the dye compartment. After positioning the H-cell in the constant temperature bath, it was allowed to equilibrate at 60°C. Two liters of 0.1 g/L dye in buffer solution was prepared and placed in the expansion tank in the second circulating constant temperature bath at 60°C. The stirrer and peristaltic pump controlling the circulation of the buffer solution in the blank compartment through the flow cell in the spectrophotometer were then turned on. The circulation flow was held constant at 250 mL/min.

To begin each experiment, 40 mL of 0.25 g/L dye in buffer solution was quickly added to the dye compartment that already contained 60 mL of buffer solution. At the time of addition, the third Masterflex pump controlling circulation of dye solution between the 2 L expansion tank and the H-cell was activated. The flow rate was 225 mL/min.

Spectrophotometric scans were taken at frequent time intervals. The concentration of diffused dye was computed from the absorbance maximum using previously prepared calibration curves according to the Beer Lambert Law. This concentration multiplied by the volume of the solution gave the amount of diffused dye, A_D.

Plotting the amount of dye diffused vs. time gave graphs as shown in Figure 2. When a steady-state diffusion was reached, i.e.,
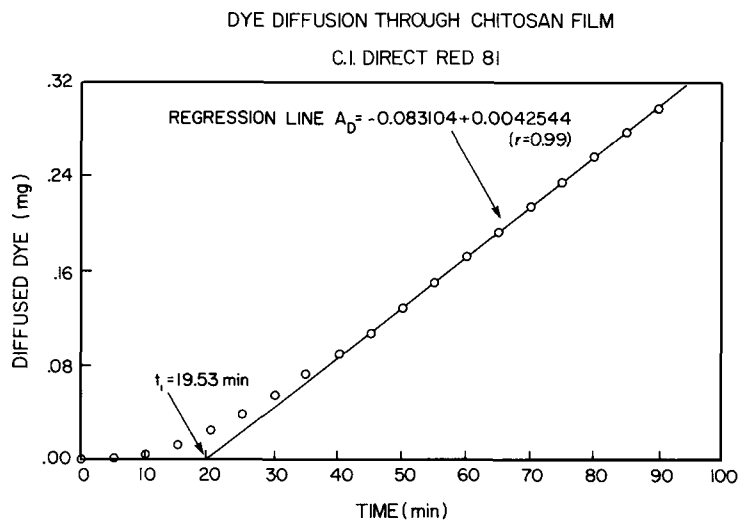
DYE DIFFUSION THROUGH CHITOSAN FILM

C.I. DIRECT RED 81

REGRESSION LINE A_D = -0.083104+0.0042544
(r=0.99)

t_i =19.53 min

Figure 2   The diffusion coefficient for each dye was determined from steady-state diffusion using Daynes' time lag method.[6,7]

Table II   Direct Dye Diffusion in Cellulose and Chitosan at 60°C, pH 9

Dye (C.I. Direct)	Film Type	Thickness (cm)	Time Lag[a] (s)	Diffusion Coefficient (cm²/s)
Red 81	Cellulose	5.00×10^{-3}	9744	4.25×10^{-10}
Red 81	Chitosan	1.27×10^{-3}	1209	2.22×10^{-10}
Green 26	Chitosan	1.27×10^{-3}	6000	4.48×10^{-11}
Blue 75	Chitosan	1.27×10^{-3}	3182	8.45×10^{-11}
Black 22	Chitosan	1.27×10^{-3}	592	4.54×10^{-10}

[a] Averages are reported; duplicated runs gave time lags reproducible within ±3%.

$$\frac{dA_D}{dt} = \text{constant}$$

the time lag was determined by extrapolation as shown in Figure 2.

RESULTS AND CONCLUSIONS

Time lags for passage of direct dyes through films were used to calculate the diffusion coefficients using

$$D = \frac{(\Delta l)^2}{6t_l} \qquad (1)$$

where D is the diffusion coefficient, Δl is the film thickness, and the t_l is the time lag.[6,7] Determinations of time lags were replicated typically within 2–3%.

Data were fitted by linear least squares to give values for t_l as shown in Figure 2. In that case, the equation of the least-squares fit is

$$A_D = -0.083104 + 0.0042544t \quad (r = +0.99)$$

where A_D is the amount of dye diffused in milligrams, t is the elapsed time in minutes, and r is Pearson's product moment correlation coefficient. Extrapolating this to $A_D = 0$ gives $t = t_l$ or

$$t_l = \frac{0.083104}{0.0042544} \text{ min} = 1172 \text{ s}$$

A second determination under the same conditions gave $t_l = 1246$ s. Averaging the two and using eq. (1) gave a value of $D = 2.22 \times 10^{-10}$ cm²/s in this case. Other determinations are shown in Table II.

The diffusion coefficient for C. I. Direct Red 81 obtained in this manner agreed well with previously reported values for cellulose.[8] Under these experimental conditions, the diffusion coefficients of direct dyes in chitosan films varied from 4.48×10^{-11} cm²/s to 4.54×10^{-10} cm²/s. These are somewhat lower but within the same order of magnitude as diffusion coefficients for the same direct dyes in cellulose films.[8] Other preliminary studies have shown that the affinities of direct dyes for chitosan films are at least as great as (and usually greater than) the affinities of these dyes for cellulose. (That work is being prepared for publication). This being the case, one may reasonably expect to be able to develop for chitosan suitable commercial dyeing processes that are similar to processes currently used for cellulose.

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