Interactions between Dyes and Polyelectrolytes: Effect of Polymer–Polymer Interactions

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Synopsis

The competition between methyl orange dye and various polymers [gelatin, poly(vinyl alcohol), polyacrylamide, etc.] for the binding sites on quaternized poly(1-vinylimidazole) in aqueous solutions was studied. The method used was based on a well-known effect of dissolved polyelectrolytes on the rate of diffusion of solutes through semipermeable membranes. The final results are expressed as the ratio of $C_1''(\text{bound})/C_1'(\text{bound})$, where $C_1''(\text{bound})$ is the amount of the solute adsorbed to a mixture of two polymers and $C_1'(\text{bound})$ is the amount of solute bound to a single polymer. In the case of quaternized poly(1-vinylimidazole) it was found that as much as 15% of the solute bound to the polymer can be replaced by another, "nonadsorbing" polymer.

INTRODUCTION

Polymer/solute interactions are important for many practical uses of polymeric substances. The interactions occurring between a single polymer and a single solute have been studied extensively in order to elucidate, e.g., the binding of dyes to polyelectrolytes,[1] the structural effects of polyelectrolytes on binding,[2] the energy transfer between bound dyes,[3] etc. More complex systems where a degree of competition exists between two or more solutes for "binding sites" on the polymer are less well understood.[4] The competition between a low-molecular-weight solute (such as a dye) and a polymer for the "binding sites" in ternary polymer/polymer/solute systems has not, as far as we know, been examined in detail. In this investigation we make use of a well-known effect of dissolved polyelectrolytes on the rate of diffusion of solutes through a semipermeable polymer film to address this problem.

The diffusion in one direction through a plain sheet of thickness l having the surface concentrations of the solute, C_1 and C_2, is given, at a steady state, by the expression $d^2C/dx^2 = 0$ provided the diffusion coefficient D is constant. After integration using the limits as given by the conditions of $x = 0$ and $x = l$, the flux F across the membrane can be expressed, for a unit area, as

$$F = -D\,dC/dx = -D(C_1 - C_2)/l \qquad (1)$$

Since, according to Fick's first law the amount (M) of diffusant that is transported through the surface having an area (S) of the membrane is given by

$$\frac{dM}{dt} = -DS\frac{dC}{dx} = -DS\frac{C_1 - C_2}{l} \qquad (2)$$

The plot of M as a function of t reaches an asymptote having a slope m,

$$m = -DS\frac{C_1 - C_2}{l} \equiv F \tag{3}$$

For $C_1 >> C_2$, $C_1 - C_2 \approx C_1$, therefore, for a unit area

$$F = DC_1/l \tag{4}$$

We can arrange an experiment where the total concentration of the solute, C_1 is constant and when using the same membrane, the thickness l, and the diffusion coefficient of the solute can be assumed to be constant.

Now, when a polymer is added to the dissolved solute, the amount of free dye in solution may change due to the binding of the solute to the polymer, and a different flux of the "free" solute through the membrane is observed:

$$F' = DC_1'/l \tag{5}$$

The "free" solute concentration C_1' can be calculated employing the expression obtained by combining eqs. (4) and (5),

$$C_1' = C_1\frac{F'}{F} \tag{6}$$

It is then a trivial matter to calculate the amount of solute bound to the polymer (i.e., solute$_{bound}$ = solute$_{total}$ − solute$_{free}$)

We can extend this to a ternary mixture of a solute and two polymers. Let us consider the case where one polymer binds the solute, but the binding between the second polymer and the solute is negligibly small. The observed flux F'' of the solute, as caused by the "free" solute concentration C_1'', now reflects the binding competition between the solute and the second polymer for the sites on the first polymer:

$$F'' = DC_1''/l \tag{7}$$

and

$$C_1'' = C_1'\frac{F''}{F'} \tag{8}$$

It is of course important that the membrane is permeable to the solute but not to the polymers used. Further, some interaction of the membrane with the solute and the polymers can be expected which could modify the permeability of the membrane. This can be minimized by efficient stirring.

If we assume that the "free" solute concentration C_1 is the same as the total concentration of the solute, C, we can express the amount of solute bound to the polymer as

$$C_1'(\text{bound}) = C - C_1' = C - C\frac{F'}{F} \tag{9}$$

Similarly, the amount of solute bound to two interacting polymers will be

$$C_1''(\text{bound}) = C - C_1'' = C - C\frac{F''}{F} \tag{10}$$

The ratio of the amount of solute bound to one polymer to the amount of solute bound to a mixture of two polymers, $C_1'(\text{bound})/C_1''(\text{bound})$, is then a measure of interaction between the two polymers and represents a fraction of the solute molecules displaced from the first polymer by the competing second polymer:

$$\frac{C_1''(\text{bound})}{C_1'(\text{bound})} = \frac{C(1 - F''/F)}{C(1 - F'/F)} = \frac{F - F''}{F - F'} \tag{11}$$

EXPERIMENTAL

Materials. Methyl orange dye (Eastman Kodak Co.) was purified by repeated crystallization from methanol to constant molar absorptivity (a_{420} = 1.9×10^4 dm^3 mol^{-1} cm^{-1}). Dextran (Sigma Chemical Co., $\overline{M}_n = 5 \times 10^5$ dalton), polyacrylamide (Cyanamer P26, Cyanamid Co; $\overline{M}_n > 6 \times 10^6$ dalton), and poly(vinyl alcohol) (Elvanol 7130, DuPont Co., $\overline{M}_n = 7.6 \times 10^3$ dalton) were used as received. Poly(1-vinyl-3-hydroxyethylimidazolium chloride)$_1$-co-(1-vinylimidazole)$_9$ was prepared by reacting poly(1-vinylimidazole) with 2-chloroethanol, and purified by ultrafiltration (the membrane cut off about 5×10^3 dalton). The extent of quaternization was determined by titrating the halide counterion with silver nitrate. The number-average molecular weight $\overline{M}_n$ of the polymer was 4.5×10^3 dalton, $\overline{M}_w = 1.9 \times 10^4$ dalton. The molecular weights [as poly(ethylene glycol) equivalents] of all the polymers were determined by aqueous gel-permeation chromatography. A blend of photographic bone gelatin was used. The intrinsic viscosity of the blend was measured in $2M$ aqueous KCNS at 25°C, and the molecular weight was calculated using the equation of Williams et al.[5] The value of $\overline{M}_w = 2.1 \times 10^5$ dalton was obtained.

Membrane. A pure cellulose membrane filter (Schleicher and Schüll, RC51; nominal pore size < 0.005 μm) was used as a membrane. The filter was washed in deionized water before each measurement; in between the measurements the membrane was kept in a 50 vol % ethanol/water solution.

The *transport* of methyl orange through the membrane was investigated using the experimental set up described previously.[6] The increase in the transmittance with time at wavelength $\lambda = 420$ nm in the downstream compartment of the cell was measured using the Brinkmann Dipping Probe Colorimeter Model PC/600D equipped with a 2 cm stainless steel probe tip. The upstream compartment of the cell was filled with 20 cm^3 of $1 \times 10^{-3}M$ aqueous solution of the dye. The effective nominal area of the membrane was 6 cm^2. The diffusion cell was housed in an electrically heated aluminium block, and the temperature of the solutions within the cell was maintained at 45 $\pm$ 0.5°C during the steady-state part of the measurement. Both compartments of the cell were stirred using magnetic stirrer bars at about 400 rev min^{-1}.

RESULTS AND DISCUSSION

Methyl orange dye has been used extensively in the studies of polymer–solute interactions. Its behavior in solutions and its binding to polymers are well documented. The tendency of ionic azo dyes to aggregate in aqueous solutions is well recognized. For methyl orange, however, the deviations from Beer's law at the concentrations from 10^{-3} to $10^{-6}M$ are quite small.[7] In our measurements the aggregation of the dye could have an effect on the flux of the dye through the membrane. The data in Figure 1 show that for the concentrations of free dye employed in our measurements, the plot of dye flux against its concentration is approximately linear. This indicates that the aggregation of the dye need not be considered.

The details of the binding interactions between dyes and polymers are still not fully understood. Some early work of Liu and Gregor[8] and the more recent contributions by Tan and Sochor[9] suggest that the main driving forces for binding between methyl orange and imidazole-containing polymers in water are the electrostatic and Van der Waals interactions between the solute and polymer, together with the stacking of the bound dye molecules. Further, the variations in entropy and in hydration caused by binding are also thought to be important in the overall binding process. According to Takagishi et al.,[10] the most striking feature of the process is the sharp increase in binding on increasing the dye concentration suggesting cooperative interactions in the binding.

Binding is also a competitive process. It has been shown[10] that the addition of other solutes such as urea and KCl lowers the affinity of various polye-
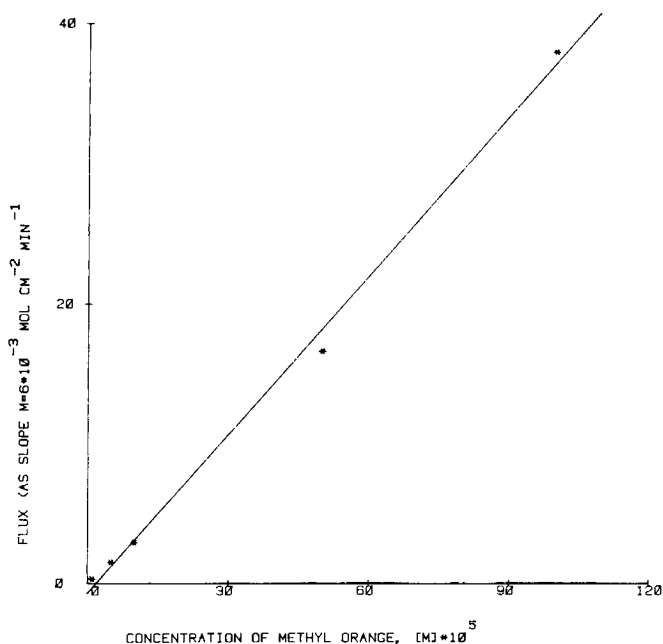

Fig. 1. The dependence of the flux of methyl orange dye on the dye concentration. Correlation coefficient = .998.

lectrolytes towards methyl orange dye. With increasing urea concentration (1–4M), the extent of binding decreases, and the occurrence of cooperativity is no longer evident at high urea concentrations.

It is the aim of this report to examine the binding between a polymer (P_1) and a dye (D) as modified by the presence of another polymer (P_2). In our case, polymer P_1 interacts strongly with the dye, while the second polymer P_2 does not. We estimated the competitive action of the second polymer on the binding process from the changes in the concentration of free dye in solution, as determined by measuring the flux of the dye across an inert membrane. We showed in the Introduction that the measure of interaction between the two polymers is, in this context, expressed by the relative amount of the solute bound to the polymers [eq. (11)]. The influence of the individual polymers on the flux of methyl orange through the cellulose membrane is shown in Table I.

The total concentration C of methyl orange in these experiments was 9.1 $\times$ 10^{-4} mol dm^{-3}, and the flux of the dye through the membrane was relatively high ($F = 1.25 \times 10^{-5}$ mol cm^{-2} min^{-1}). As expected, the addition of polymers to the dye solution changed the value of solute flux. It can be seen from the results that only the polymers that could, due to their chemical structure, be expected to adsorb the dye, i.e., the quaternized poly(1-vinylimidazole) and to some extent the parent poly(1-vinylimidazole) show a large effect on the flux of the solute dye through the membrane. As anticipated, the magnitude of the polymer effect depends on its concentration (cf. Fig. 2). The other polymers used in this study adsorb the dye very little (gelatin) or not at all.

It is of much more interest to examine the effect of such "nonadsorbing" polymers on the outcome of the adsorption of methyl orange to the quaternized poly(1-vinylimidazole). The results are given in Table II.

Our interpretation of the results is based on the thesis that the second polymer (P_2) competes with the solute dye for the "binding sites" on the first (P_1) polymer. In principle, changes in the chain dimensions of the binding polymer caused by the changes in the composition of the solution could lead to different binding equilibria. The effect of ionic strength and pH on the chain dimensions of the quaternized poly(1-vinylimidazole) was

TABLE I
Effect of Various Polymers on the Flux of Methyl Orange Dye through RC51 Pure Cellulose Membrane in Water

Polymer	Polymer concn. (wt %)	Flux (slope $m \times 10^3$)	"Free" solute C'_1 ($\times 10^4$) (M)
No polymer	—	60.0	9.1
Quaternized poly(1-vinylimidazole)	0.61	4.3	0.66
Poly(1-vinylimidazole)	0.59	28.7	4.38
Gelatin	0.61	48.2	7.36
Dextran	0.59	60.0	9.1
Poly(vinyl alcohol)	0.61	60.0	9.1
Polyacrylamide	0.088[a]	60.0	9.1

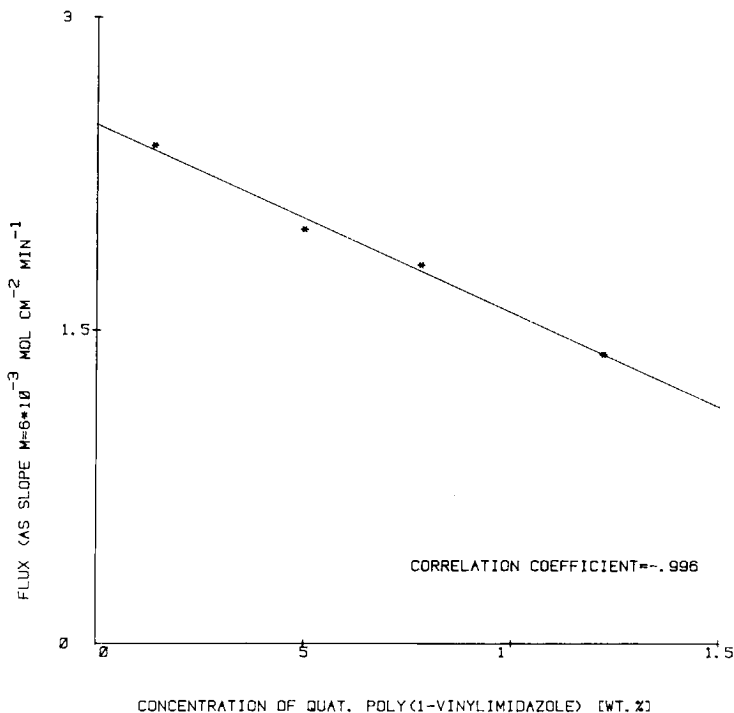[a] Polymer precipitation occurs at a higher concentration.

Fig. 2. The effect of concentration of quaternized poly(1-vinylimidazole) on the flux of methyl orange. Correlation coefficient = .996.

studied by Tan et al.[9] As expected, the chain dimensions (as estimated from the changes in the intrinsic viscosity of solutions) decreased in aqueous salt solutions with increasing ionic strength. At a constant ionic strength, the changes in pH were reported to give rise to "irregular" changes in the intrinsic viscosity. The differences in binding of methyl orange to the polymer at different pH values were large, however, and could not be accounted for by the relatively small changes in chain dimensions. The differences were attributed to counterion competition with the dye ion. We suggest, therefore, that the effect of changes in the ionic strength and the pH of our solutions caused by the addition of the second polymer P_2 is negligible.

As mentioned above, the overall result of a binding process is a combination of several separate, and fundamentally different, interactions. Although our measurements cannot provide much information about the individual steps of such processes, the results give a quantitative estimate of the extent of polymer/polymer interactions taking place in aqueous solutions. The ratio of C_1'' (bound) to C_1' (bound) [(the bound solute in the presence of polymer P_2) to (the bound solute in the absence of P_2)] takes values between 0 and 1, and indicates how much solute is replaced from one polymer by another polymer. In case of quaternized poly(1-vinylimidazole) it appears that as much as 15% of the solute bound to the polymer can be replaced by another polymer (depending on the chemical structure of the second polymer, its concentration, possibly its molecular weight, and the temperature).

TABLE II
Effect of a Second Polymer (P_2) on the Flux of Methyl Orange through RC51 Pure Cellulose Membrane from an Aqueous Solution of Quaternized Poly(1-vinylimidazole) (P_1)

Polymer 2	Polymer 2 concn (wt %)	Flux (slope $m \times 10^3$)	"Free" solute concn $C_1'' (\times 10^4)$ (M)	C_1'' (bound)/ C_1' (bound)
—	—	4.3	0.66	—
Dextran	0.31	5.9	0.91	0.971
	0.56	5.8	0.89	0.973
	1.08	5.8	0.89	0.973
Gelatin	0.14	6.5	1.00	0.961
	0.18	7.4	1.14	0.944
	0.44	8.0	1.23	0.933
	0.80	9.7	1.49	0.903
Poly (vinyl alcohol)	0.08	5.9	0.91	0.971
	0.23	6.9	1.06	0.953
	0.42	7.9	1.21	0.935
Polyacrylamide	0.0044	6.4	0.98	0.962
	0.010	7.8	1.20	0.936
	0.018	8.0	1.23	0.933
	0.026	8.6	1.32	0.923
	0.035	8.9	1.37	0.917
	0.044	10.9	1.67	0.880
	0.050	11.1	1.70	0.877
	0.088	11.8	1.81	0.864

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