The Graphical Evaluation of Ionic Dye Sorption Isotherms Using Dimensionless Groups

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Synopsis

A graphical method is proposed for the analysis of experimental data on the equilibrium sorption of ions by charged polymers. The method uses dimensionless groups of variables, which are based on a generalized Donnan theory. Graphical comparisons of theoretical curves with experimental data-point sets permit rapid estimation of theoretical parameters. The use of dimensionless groups clarifies the complex interactions between the individual sorption variables. This simple procedure consists of relative lateral and vertical displacements of the data point graphs and the theoretical graphs along their coordinate axes. The graphical comparisons help to reveal the nature of departures from the basic theoretical model. Examples of the method are given for oxycellulose/methylene blue and polyacrylonitrile polymer/cationic dye systems.

INTRODUCTION

The equilibrium sorption of ions by solid polymers, from aqueous solutions, can be described in a formal sense on the basis of a generalized macroscopic Donnan model.[1] In this model, each ionic species i is assumed to follow an ionic distribution equation of the type

$$C_i^f = \lambda^{z_i} K_i \cdot C_i^s \tag{1}$$

in which C_i^f is the ion concentration in the polymer or fiber, and C_i^s is the concentration in the external solution. z_i is the electrical charge on ion i, including sign. λ is a Donnan distribution coefficient related to the equilibrium electrical potential difference between the polymer phase and the solution phase. The individual ionic distribution coefficient K_i contains all the effects that modify the ionic distribution, other than macroscopic electrical effects.

In the simplest version of the model, the acidic and basic groups in the polymer are assumed to take part in internal acid–base dissociation equilibria, and to generate fixed electrical charges in the polymer. The condition of electrical neutrality in the polymer takes the form

$$F(\lambda) = \sum_i z_i \lambda^{z_i} K_i C_i^s + \sum_k \frac{B_k}{1 + \left(K_{B_k}/\lambda K_1 C_1^s \right)}$$

$$- \sum_j \frac{A_j}{1 + \left(\lambda K_1 C_1^s / K_{A_j} \right)} = 0 \tag{2}$$

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and for electrical neutrality in the solution

$$\sum_i z_i C_i^s = 0 \tag{3}$$

The ion index $i = 1$ is reserved for the hydrogen ion, which directly modifies the degree of dissociation of each type of acidic or basic group. B_k is the concentration in the polymer of the kth type of basic group of dissociation coefficient K_{B_k}. A_j is the concentration in the polymer of the jth type of acidic group, of dissociation coefficient K_{A_j}.

Theoretical sorption isotherms can be calculated if numerical values can be assigned to the following parameters,

$$
\begin{aligned}
z_i, \qquad & i = 1, 2, \ldots, n \\
K_i, \qquad & i = 1, 2, \ldots, n \\
A_j, \qquad & j = 1, 2, \ldots, nj \\
K_{A_j}, \qquad & j = 1, 2, \ldots, nj \\
B_k, \qquad & k = 1, 2, \ldots, nk \\
K_{B_k}, \qquad & k = 1, 2, \ldots, nk
\end{aligned}
\tag{4}
$$

and if the solution concentrations C_i^s are known. The calculations require the solution of eq. (2) for the unknown parameter λ, followed by the use of eq. (1) to calculate the C_i^f. This procedure must be followed for each change in the solution concentrations C_i^s, or in any of the parameters of eqs. (4).

Although this procedure is general, flexible, and gives useful information, it is far from transparent in its workings. In particular, it is very difficult to recognize the complex interactions of changes in the input parameter values, and each computation requires significant effort.

For these reasons we have tried to develop simple graphical procedures for testing experimental data against the predictions of this model, and for establishing the numerical values of key parameters. As an example of our approach, we shall consider the sorption of cationic dyes by oxycellulose and acrylic polymer fibers.

THEORETICAL

The first step is to use eqs. (1)–(3) to describe a simple system, and to rearrange the resultant equations so that appropriate *dimensionless groups* of variables can be seen to determine the equilibrium dye sorption behavior.[2] The second step is to use these dimensionless groups to generate "master curves" against which the experimental data can be compared.

Systems in Which Co-Ion Exclusion Occurs

If the polymer contains a concentration A_0^- of fixed ionized groups, then the ratio $(A_0^-/K_X C_X^s)$ will determine the extent to which an anion X^- is excluded from the polymer by the electrostatic effects of co-ion exclusion.

Let us consider a simple solution containing an acid HX, a sodium salt NaX, and a cationic dye salt DX, in which a polymer containing a single acidic group of concentration A_0 is immersed. If we assume that the anion X is excluded from the fiber (i.e., *co-ion exclusion* occurs), then eq. (2) reduces to

$$\frac{A_0}{1 + (\lambda K_H C_H^s / K_A)} = C_H^f + C_D^f + C_{Na}^f = C_D^f \cdot P_2 \tag{5}$$

in which the *dimensionless group* P_2,

$$P_2 = 1 + \frac{K_H C_H^s}{K_D C_D^s} + \frac{K_{Na} C_{Na}^s}{K_D C_D^s} \tag{6}$$

represents ion-exchange competition between the dye cation D^+ and the inorganic ions H^+ and Na^+.

If we rearrange eq. (5) to give an expression for

$$\lambda = \frac{K_A \left(A_0 - P_2 \cdot C_D^f \right)}{P_2 \cdot C_D^f \cdot K_H C_H^s} \tag{7}$$

we can then substitute for λ from eq. (1) for the dye cation

$$C_D^f = \lambda K_D C_D^s \tag{8}$$

The introduction of the dimensionless relative dye sorption

$$\theta_D = C_D^f / A_0 \tag{9}$$

then leads to the simple dimensionless equations

$$\frac{\theta_D^2}{1 - P_2 \cdot \theta_D} = \frac{P_1}{P_2} \tag{10}$$

and

$$\theta_D = -\frac{P_1}{2} \left[1 - \left(1 + \frac{4}{P_1 \cdot P_2} \right)^{1/2} \right] \tag{11}$$

in which the new dimensionless group P_1 appears:

$$P_1 = \frac{K_A K_D C_D^s}{A_0 K_H C_H^s} \tag{12}$$

The dimensionless group P_1 determines the titration behavior of the acidic group A_0. For example, if P_1 is very large, the acidic groups A_0 will be fully

ionized as $A_0^- = A_0$. Then eq. (5) becomes

$$A_0 = C_D^l \cdot P_2 \tag{13}$$

or

$$\theta_D = 1/P_2 \tag{14}$$

which represents a sorption isotherm of a Langmuir shape. From the definition of P_2 in eq. (6) it is possible to rewrite eq. (14) in the forms

$$\theta_D = \frac{P_3}{1 + P_3} \tag{15}$$

and

$$\frac{\theta_D}{1 - \theta_D} = P_3 \tag{16}$$

in which the new dimensionless group P_3 appears:

$$P_3 = \frac{K_D C_D^s}{K_H C_H^s} \tag{17}$$

The Langmuir form of the behavior is clearly recognizable in eqs. (16) and (17), which have been further simplified for competition between the dye cation D^+ and the hydrogen ion only.

Somewhat more generally, the dimensionless product $P_1 \cdot P_2$ of eq. (11) can be rearranged to give the result

$$P_1 \cdot P_2 = P_1 + \frac{K_A}{A_0} \left\{ 1 + \frac{K_{Na} C_{Na}^s}{K_H C_H^s} \right\} = P_1 + P_4 \tag{18}$$

in which the new dimensionless group P_4

$$P_4 = \frac{K_A}{A_0} \left(1 + \frac{K_{Na} C_{Na}^s}{K_H C_H^s} \right) \tag{19}$$

represents the relative importance of ion-exchange competition by the sodium and hydrogen ions in the solution.

In the absence of detailed measurements of the inorganic ion distributions between the solution and the polymer it is a useful simplification to assume that

$$K_{Na} = K_H = K_X = K_I \tag{20}$$

In this case, some of the errors induced by this assumption will appear in K_A.

It is clear that dimensionless groups have a tendency to proliferate and that the most appropriate groups for a given problem have to be identified before

they can be used. Systematic approaches to this problem have been discussed in detail by other authors.[3-5] For experiments in which the dye cation concentration in solution is varied, while C_{Na}^s and C_H^s are held constant, the three parameters θ_D, P_1, and P_4 are convenient to use: Their manner of use will be explained later.

Systems in Which Electrolyte Sorption Occurs

When co-ion exclusion breaks down, the anion X^- is able to enter the fiber. Since this anion must be electrically neutralized by an equivalent concentration of the counterions H^+, Na^+, and D^+, this is equivalent to the sorption of some mixture of the three electrolytes HX, NaX, and DX. This phenomenon is described as *electrolyte sorption*.

When there is no electrolyte sorption, there is no means of separating the ion-exchange distribution coefficient K_I^D into unique values of K_I and K_D, except on the basis of uncertain assumptions.

When electrolyte sorption occurs, the anion X^- enters the solid polymer, and must be electrically neutralized by an equivalent quantity of cations in the polymer. We have, for example,

$$C_X^f = (1/\lambda)K_X C_X^s \cong (1/\lambda)K_I(C_H^s + C_{Na}^s + C_D^s) \qquad (21)$$

But from eq. (8)

$$C_D^s = \lambda K_D C_D^s$$

and so

$$C_D^f \cdot C_X^f \cong K_D \cdot K_I \cdot (C_H^s + C_{Na}^s + C_D^s)C_D^s \qquad (22)$$

Similarly,

$$C_{Na}^f \cdot C_X \cong K_I^2(C_H^s + C_{Na}^s + C_D^s)C_{Na}^s \qquad (23)$$

so that direct measurements of C_D^f, C_X^f, and C_{Na}^f can lead to well-defined numerical values of both K_D and K_I.[6] In practice, the assumption that $K_{Na} = K_H = K_X = K_I$ will be the weak point of this argument. Precise studies will require the determination of the K_i for each type of ion present. Procedures for this have been discussed elsewhere.[7]

It can be far from obvious that electrolyte sorption has occurred, since the recognition of the effect requires a careful comparison with the behavior to be expected in the absence of electrolyte sorption. If, however, there is only one type of acidic group in the polymer, one type of electrolyte sorption becomes immediately recognizable as "overdyeing," which is a dye cation sorption in excess of the known acidic group content of the polymer. In this situation, which is characterized by values of $\theta_D > 1$, the degree of overdyeing at a given value of the parameter P_1 will depend on the *product* $K_D \cdot K_I$, so that different theoretical curves will now be generated when different numerical values are assigned to K_I or K_D. In this way, K_I can be estimated from the high concentration dyeing data alone.[8] Increases in the sodium ion concentration in the dyebath, for example, will tend to *increase* the sorption of dye by

the fiber when $\theta_D > 1$. This is in contrast to the tendency of increases in sodium ion concentration to *decrease* the dye ion sorption at $\theta_D < 1$, in the *ion-exchange* region of behavior.

Perhaps it should be noted that the more-hydrophobic fibers have low water sorptions, and that this water may not behave as normal liquid water. The environment of the ions in the water-saturated polymer may change as θ_D increases, so that the K_I value determined from overdyeing data may not apply precisely at low θ_D values.

The mathematical analysis becomes much more complicated when electrolyte sorption occurs, since the equation for electrical neutrality in the fiber [eq. (2)] is now a cubic equation. The parameters $\log \theta_D$ and $\log P_1$ are, however, still useful for the graphical plots. The fractional electrolyte sorption θ_X is

$$\theta_X = \frac{C_X^f}{A_{01}} = \frac{K_D \cdot K_I \cdot C_D^s}{A_{01} C_D^f}(C_H^s + C_{Na}^s + C_D^s) \tag{24}$$

and so the relative contribution from electrolyte sorption is determined by the dimensionless group

$$\frac{\theta_X}{\theta_D} = K_D \cdot K_I \left(\frac{C_D^s}{C_D^f}\right)^2 \left(1 + \frac{C_H^s}{C_D^s} + \frac{C_{Na}^s}{C_D^s}\right) \tag{25}$$

We note that electrolyte sorption increases greatly in importance as the dye concentration C_D^s increases in the system, for any given numerical value of the product $K_D \cdot K_I$. This effect becomes most pronounced near $\theta_D = 1$.

It is clear from eq. (25) that electrolyte sorption can become significant not only at high sodium ion concentrations but also at low pH values in these systems.

Systems with More Than One Type of Acidic Group

When there is more than one type of acidic group in the polymer, for example, in an acrylic polymer, it is convenient to calculate θ_D for the polymer relative to the concentration A_{01} of the most strongly acidic group, and to base the parameter P_1 on A_{01} and on K_{A1}.

Then the behavior becomes dependent also on new dimensionless ratios such as

$$p = K_{A2}/K_{A1} \tag{26}$$

and

$$q = A_{02}/A_{01} \tag{27}$$

and now overdyeing may have more than one origin. It is necessary to decide the relative contributions of electrolyte sorption, and of the additional acidic groups, to overdyeing.

The direct determination of all of the ion concentrations in the polymer is always the best approach, but is not always possible. Failing this, studies of

the effects of pH and of electrolytes on the sorption isotherms can help to assign the proper weight to each type of effect. Expressed differently, the numerical values of the parameters p, q, and K_I (or $K_D \cdot K_I$) must be established.

The computations can no longer be carried out so simply. It is necessary to use the general approach of eqs. (1)–(3) for calculation of theoretical curves, but the output data can still be grouped conveniently in terms of the parameters $\log \theta_D$, $\log P_1$, and P_4, for example.

GRAPHICAL EVALUATION OF SORPTION ISOTHERM DATA

Systems in Which Co-Ion Exclusion Occurs

The primary graphical variables are $\log \theta_D$ (or θ_D) as ordinate, and $\log P_1$ as abscissa. The log–log plots are preferable when particular attention is directed to the low concentration data, or when graphical corrections for errors in the acidic group concentration A_0 must also be made.

The experimental sorption isotherm data points are first plotted on common scales with $\log_{10}\theta_D$ as ordinate and $\log_{10}(C_D^s/C_H^s)$ as abscissa. For our purposes, the errors involved in equating the solution pH to $-\log_{10}C_H^s$ appear to be unimportant. The experimental data points are plotted on normal 18×24 cm, mm ruled graph paper.

Theoretical curves of $\log_{10}\theta_D$ as ordinate against $\log_{10}P_1$ as abscissa are generated from eq. (11), for example, for different constant values of the parameter P_4 (since $P_1 \cdot P_2 = P_1 + P_4$), and plotted on the same scales on semitransparent 18×24 cm, mm ruled graph paper. Figure 1 shows such curves, together with an experimental set of data points which has been reproduced at two different locations A and B in Figure 1 by lateral translation of the data-point graph across the theoretical graph. The theoretical curve for $P_4 = 0.01$ is a reasonable fit to the shape of the data-point graph at lower dye concentrations. The data-point graph is clearly different in shape from the theoretical curves for the higher values of P_4, at location A.

For the comparison shown at location B in Figure 1, the ordinate at $\log(C_D^s/C_H^s) = 0$ in the data-point graph is coincident with the ordinate at the location $\log_{10}P_1 = -0.68$ in the theoretical graph. Since

$$\log P_1 = \log(K_A \cdot K_D/A_0 \cdot K_H) + \log(C_D^s/C_H^s) \qquad (28)$$

the dimensionless group $(K_A \cdot K_D/A_0 \cdot K_H) = 0.209$. Note that at first sight only this dimensionless group has been determined. But, since the calculation of θ_D requires knowledge of the acidic group content $A_{,}$, it is clear that eq. (28) gives us the numerical value of the group $K_A \cdot K_D/K_H$ directly. To the extent to which we have found the best fit in Figure 1 at point B, we can say that we have also determined the parameter P_4. But from eq. (19)

$$K_A = A_0 \cdot P_4 / \left[1.0 + (K_{Na} \cdot C_{Na}^s/K_H \cdot C_H^s)\right]$$

$$\cong A_0 \cdot P_4 / \left[1.0 + (C_{Na}^s/C_H^s)\right]$$

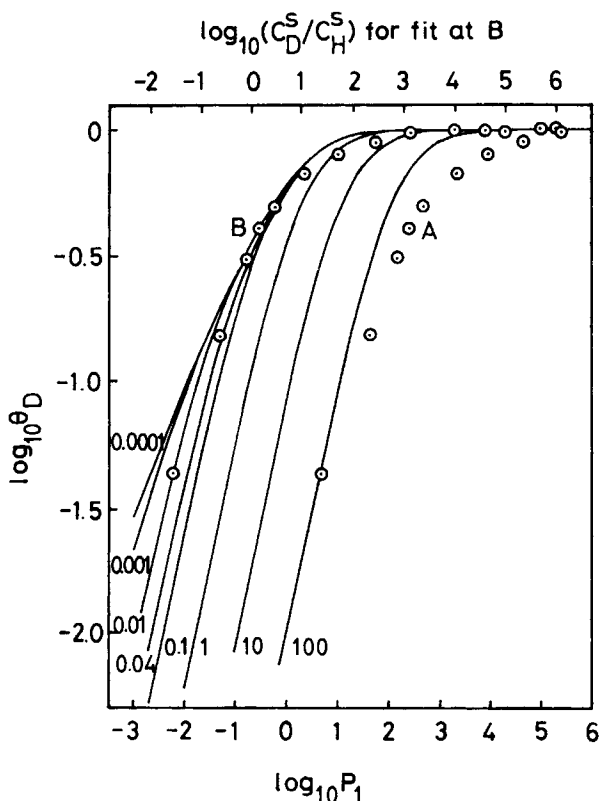so that subject to the approximation $K_{Na} = K_H$, we can also determine K_A.

Fig. 1. Theoretical sorption isotherms in the log θ_D/log P_1 coordinate system. The numbers on the curves are the numerical values of the parameter P_4. The computations are for the sorption of methylene blue by an alkaline hypobromite oxycellulose containing a single acidic group at concentration $A_0 = 0.213$ mol/kg.[9] The conditions assumed are $C_H^s = 1 \times 10^{-4}$ mol/L, $C_{Na}^s = 12.5 \times 10^{-3}$, with C_D^s varying over a wide range. The ratio $K_D/K_{Na} = 625$, in accordance with Davidson's data (Figure 3 of Ref. 9). K_I was set at 0.001 to obtain a good approximation to co-ion exclusion over the dye concentration range of interest. The data points are from Table VI and Figure 2 of Ref. 9: They are used here for illustrative purposes only. Since A_0, C_H^s, and C_{Na}^s were fixed, the different values of P_4 were obtained by assigning different values to the acidic group dissociation coefficient K_A.

The dimensionless ratio K_D/K_I is therefore determinable, but we can go no further than this on the basis of the information given. It is *not* possible to determine K_I and K_D separately without additional information or assumptions. This difficulty is not always recognized.

The slopes of the linear sections of the lines at low θ_D values are quite sensitive to the parameter P_4 when P_4 is small. For large values of P_4 and P_1, these linear sections all have the same slope because now the acidic groups are fully ionized at all times, and we are really dealing with cation exchange processes only. At low values of P_4 and P_1 we have some combination of acidic group titration and cation exchange: The acidic group ionization changes as θ_D changes, so that the behavior is much more complex than it appears at first sight.
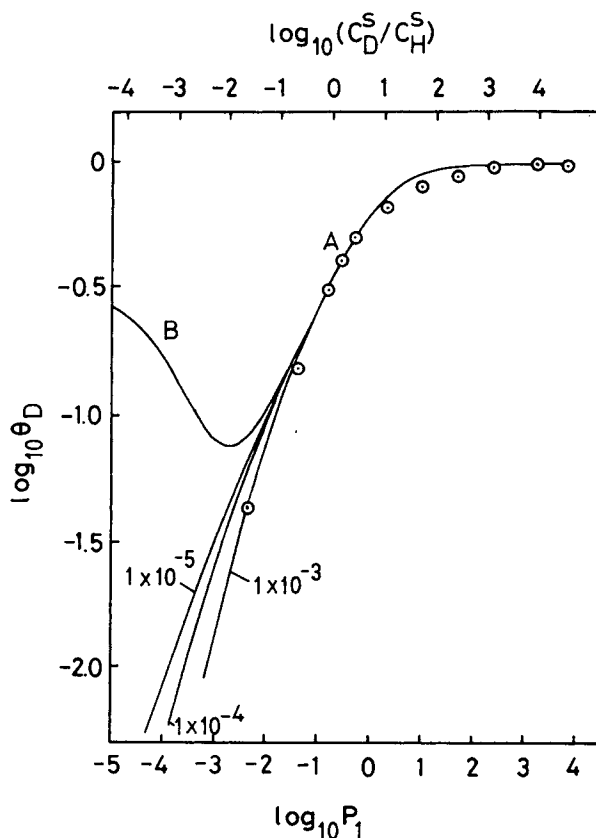
Fig. 2. Graphical comparison of experimental data with theory. The computations are for the hypobromite oxycellulose of Figure 1, but now $C_D^s = 1 \times 10^{-3}$, $C_{Na}^s = 12.5 \times 10^{-3}$, and C_H^s varies from 1×10^{-9} to 1×10^{-1}. The numbers adjacent to the curves give the numerical values of K_A for each curve. $K_I = 0.001$, except for curve B, for which $K_I = 0.1$, and $K_A = 1 \times 10^{-5}$. The data points are from Figure 2 and Table VI of Ref. 9, and have been made coincident with the theoretical curves at point A. The ratio $K_D/K_I = 625$, as in Figure 1.

The theoretical curves can readily be superimposed on the data plots. The general patterns of the data, relative to those of the theoretical curves, are clearly seen, and greatly facilitate assessment of the appropriate numerical value of P_4, for example. In addition, deviations from the model are clearly seen, and can suggest modifications to the model to better represent the data. The choice of P_4 can be verified by analysis of data from experiments in which C_{Na}^s is deliberately varied while C_H^s and C_D^s are held constant. Once P_4 has been determined, we can calculate K_A.

When data comparisons are made for a range dyes, it is easy to see if all the dyes follow a common isotherm shape. In this case a series of simple lateral displacements of the theoretical curve is made until each set of the data points has been fitted. Direct comparisons of the two abscissa scales as before give the ratio K_D/K_I for each dye in the series.

Figure 2 shows a data comparison for a different, but related situation. In experimental studies of the sorption of methylene blue by oxycelluloses,

Davidson[9] carried out an experiment in which C_{Na}^s and C_D^s were held constant while the solution pH was varied from pH 9 to pH 1.4.

Since P_4 now varies with each change in solution pH, it is perhaps surprising that the log θ_D/log P_1 plot continues to be useful. The average value of P_4 will, however, still depend on the parameter K_A, so that theoretical calculations for different K_A values should predict different average patterns of behavior.

The theoretical curves in Figure 2 show clearly distinguishable behavior patterns at lower θ_D and lower P_1 values, as the numerical value assumed for K_A is changed. For K_A values from 10^{-3} to 10^{-5}, which is probably the range of most interest here, the theoretical curves are indistinguishable in shape at the higher θ_D values. The data-point set in Figure 2 defines a curve which agrees best at low θ_D values with the curve for $K_A = 10^{-3}$.

On the other hand, the data fit at point A in Figure 2 requires that $(K_A \cdot K_D/A_0 \cdot K_H) = 0.20$, in essential agreement with Figure 1. Davidson's studies of the effects of the sodium ion concentration on the uptake of methylene blue were made at pH 7.9, and require that $K_D/K_I = 625$, so that if this value also applies at lower pH values we have $K_A/A_0 = 3.2 \times 10^{-4}$. Since $A_0 = 0.213$ mol/kg, the acidic group dissociation coefficient $K_A = 6.8 \times 10^{-5}$.

This large discrepancy between the two estimates of K_A is associated with a large difference in both θ_D and P_1. It may be due to a large decrease in K_D/K_I at low dye concentrations, which has been observed in a related system,[6] or to a specific effect of low pH values. Low pH values may cause changes in the state of ionization of the dye cation, leading to changes in effective ionic charge.

When the same data are plotted in the θ_D/log P_1 coordinate system, the deviations at low θ_D values tend to be visually underestimated in importance.

The curve labeled B in Figure 2 was calculated for $K_A = 1 \times 10^{-5}$ and $K_D/K_I = 625$, and for $K_I = 0.1$, a value of K_I which may be reasonable for a cotton fiber. The curve B predicts a high degree of electrolyte sorption at low P_1 values, i.e., at low pH values. Since this type of experimental behavior was not observed by Davidson for this particular fiber, either K_I for cotton oxycellulose is much smaller than 0.1, or the ratio K_D/K_I does indeed decrease markedly at low θ_D values and low pH, as suggested above, or both effects occur together.

Direct measurements of the sorption of all the ions in the system provide the best, and perhaps the only method of resolving this type of question.

Systems in Which Electrolyte Sorption Occurs

The addition of a neutral salt such as NaCl introduces both anions and cations into the dyeing system. When co-ion exclusion holds, the main effect of salt addition is to reduce the dye cation uptake by cation exchange competition. This is clearly shown in Figure 3 of Davidson's paper,[9] and is predicted by the effects of parameter P_2.

At high values of P_1, the acidic groups will be fully ionized, and eq. (14) will hold. It follows from eq. (14), and from eq. (6) for P_2, that the fractional dye sorption θ_D will tend to reach a limiting value that is *less* than unity at high
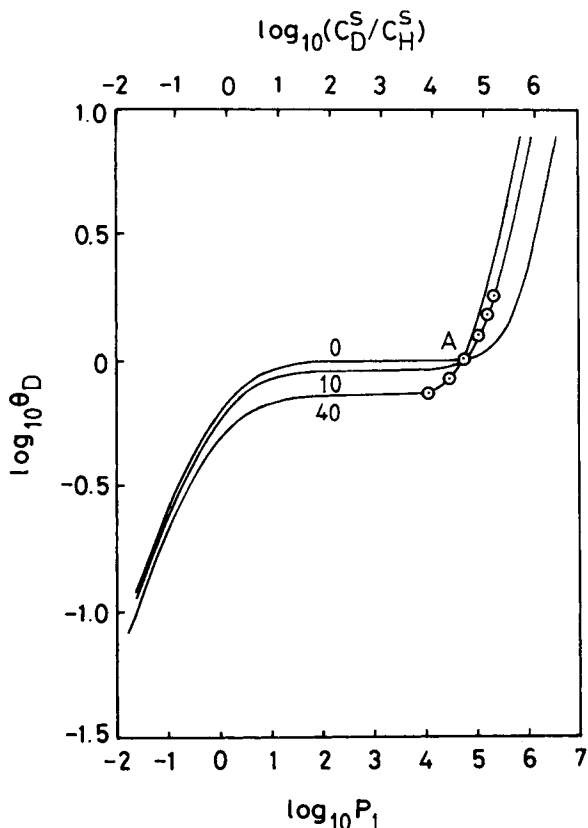
$$\log_{10}(C_D^S/C_H^S)$$

Fig. 3. Complex effects of added electrolytes. The calculations are for $A_0 = 0.0066$ mol/kg, $K_A = 6.8 \times 10^{-5}$, $C_H^s = 1.27 \times 10^{-8}$, $K_D/K_I = 110$, and for $K_I = 0.1$. C_D^s was varied over a wide range, for specified constant values of the ratio C_{Na}^s/C_D^s, to simulate the experiments in Figures 4 and 5 of Ref. 9. The data points shown are taken from these figures, and were used to establish the parameter values for the experiment at $C_{Na}^s/C_D^s = 40$. The numbers adjacent to the curves give the numerical values of this ratio for each curve.

P_1 values, if the dimensionless ratios

$$\left(K_H \cdot C_H^s/K_D \cdot C_D^s \right) \quad \text{and} \quad \left(K_{Na} \cdot C_{Na}^s/K_D \cdot C_D^s \right)$$

are sufficiently large.

For the limiting θ_D value of Figure 2 of Davidson's paper we have $C_H^s = 1 \times 10^{-8}$, $C_{Na}^s/C_D^s = 12.5$, $K_D/K_I = 625$, and $C_D^s = 1 \times 10^{-3}$. For these values, $P_2 = 1.02$, and $\theta_D = 0.98$. The experimental uncertainty is such that this reduction in θ_D is unlikely to be noticed.

A new and different effect was observed when Davidson studied the effect of the ratio C_{Na}^s/C_D^s on the sorption of methylene blue by an "acid-washed scoured cotton."[9] At low dye concentrations, increases in C_{Na}^s/C_D^s reduced the dye sorption by the cellulose, but at high dye concentrations the reverse was observed: increases in the ratio C_{Na}^s/C_D^s increased the dye uptake. This was attributed by Davidson to a dual mechanism of dye uptake. Some of the dye was assumed to interact with the carboxyl groups of the cellulose, and some of

the dye was assumed to interact with the hydroxyl groups of the cellulose by a mechanism "similar in nature to the absorption of direct dyes by cellulose."[9]

Figure 3 shows theoretical calculations for different values of the ratio C_{Na}^s/C_D^s, and for plausible initial assumptions about the other parameters. Point A identifies a transition from θ_D values less than 1 to θ_D values greater than 1. This transition naturally occurs at $\theta_D = 1.0$, but rather surprisingly it also occurs at essentially the same P_1 value for each value of the ratio C_{Na}^s/C_D^s in Figure 3.

To the left of point A we see the plateau behavior predicted by eq. (14). To the right of point A we see very clearly the predicted consequence of the breakdown of co-ion exclusion, which is additional dye uptake by electrolyte sorption.

Note that the common intersection point at A is predicted to occur at $\theta_D = 1$, which raises doubts about Davidson's estimates of A_0 for this fiber. We have therefore assumed that $A_0 = 0.0066$ mol/kg, and have not used the lower value of 0.0057 mol/kg given by Davidson.[9]

Figure 4 has been generated for a constant value of the ratio $C_{Na}^s/C_D^s = 40$, but for different assumptions about K_I. The ratio K_D/K_I was held constant at a numerical value of 110, and we note that all the computations define a single, common curve as P_1 increases up to the plateau level. As the numerical value assigned to K_I increases, the onset of electrolyte sorption moves to lower P_1 values, but the curve shapes in the overdyeing region are essentially the same. Note that overdyeing is now defined not by a dye cation uptake in excess of $\theta_D = 1$, but by a dye cation uptake in excess of the lower, limiting θ_D value predicted by eq. (14).

The different numerical values assigned to K_I, when the ratio K_D/K_I is held constant, correspond in fact to different values of the product $K_D \cdot K_I$, which determines the degree of electrolyte sorption [eq. (22)]:

$$K_D \cdot K_I = (K_D/K_I) \cdot K_I^2 \qquad (29)$$

To determine K_I from dye sorption date alone, it would be necessary to carry out experiments over a wide range of P_1 values: for example, measurements to locate point A in Figure 4 would make it possible both to estimate the ratio K_D/K_I, and then to select the best-fitting curve for the overdyeing region, which would then determine both K_I and K_D.

The data points in Figure 4 show significant deviations from the predicted curve shapes for overdyeing. The deviations shown in Figure 4 indicate that the ratio K_D/K_I decreases as the degree of overdyeing increases. A similar effect has been observed in a related system.[6]

The curves in Figure 4 show the great sensitivity of the predicted overdyeing behavior to the parameter K_I.

Interestingly, the unusual "overdyeing" behavior predicted by curve B in Figure 2 was observed experimentally by Davidson for the "acid washed scoured cotton" (Fig. 6 of Ref. 9), and attributed by him to an electrolyte effect on the interaction of the dye with hydroxyl groups of the cellulose. The onset of electrolyte sorption depends on the parameter $(A_0^-/K_X C_X^s)$: When this parameter is large, co-ion exclusion is favored, but when this parameter is small, co-ion exclusion breaks down and electrolyte sorption occurs. Ap-
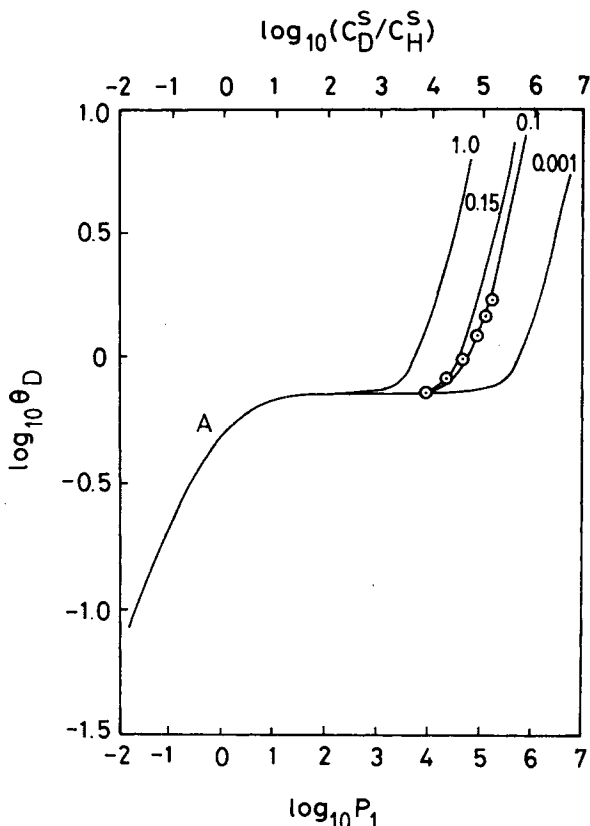
Fig. 4. "Overdyeing" by electrolyte sorption. The calculations of Figure 3 for $C_{Na}^s/C_D^s = 40$ are repeated, for different assumptions about the parameter K. The numbers adjacent to the curves are the numerical values of K for each curve. The data points for $C_{Na}^s/C_D^s = 40$ are taken from Figure 5 of Ref. 9, and have been made to agree most closely with the curve for $K_I = 0.1$.

parently A_0 is so much smaller for the "acid washed scoured cotton" than for the hypobromite oxycellulose that electrolyte sorption occurs at low pH for the former fiber, but not for the latter.

Systems with More Than One Acidic Group

Some acrylic-polymer fibers contain both "strongly acidic" groups and "weakly acidic" groups.[6] Figure 5 shows theoretical curves for the dye sorption by such a fiber. The ratio q of eq. (27) can be determined experimentally by titration of the dissolved polymer, but the parameter p of eq. (26) must generally be determined from the dye sorption data, or from other ion sorption data.

Since the condition $\theta_D > 1$, where θ_D is based on A_{01}, can arise either from electrolyte sorption or from the presence of A_{02}, or both, the analysis of dyeing data requires care. In some situations direct measurements of the sorption of inorganic ions can be used to estimate K_I, which establishes the contribution from electrolyte sorption.[6] Comparisons of experimental data in
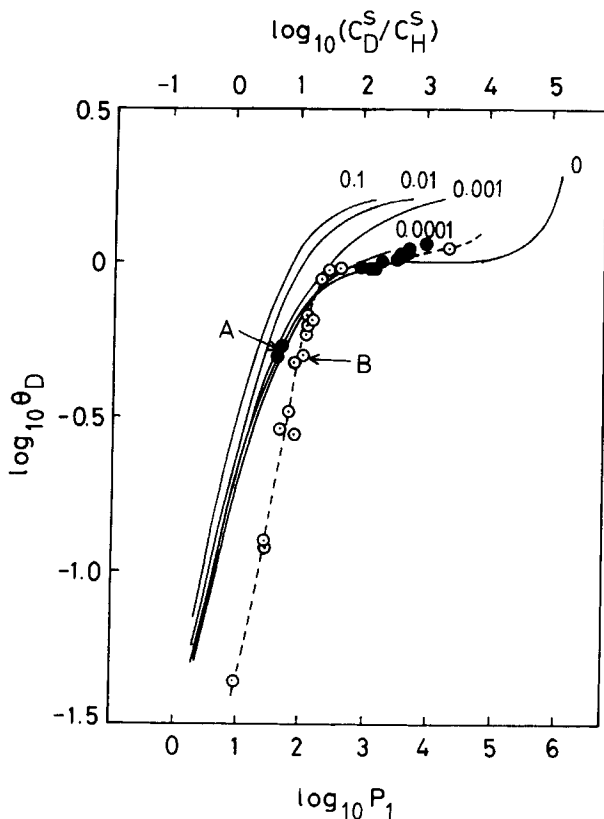
Fig. 5. "Overdyeing" by ionization of a second acidic group. The theoretical curves were calculated for an acrylic polymer with $A_{01} = 0.0311$ mol/kg, $K_{A1} = 1.24 \times 10^{-4}$, $q = 0.675$, $K_I = 0.0106$, $K_D = 53.6$, $C_H^s = 1 \times 10^{-6}$, and $C_{Na}^s = 0.01$ mol/L, for various values of the parameter p. The numbers adjacent to the curves give the parameter p for each curve. These parameter values are taken from the literature.[6] The experimental points (●) are for the oxazine dye of Ref. [8], and are based on unpublished data.[10] The experimental points (⊙) are for C.I. Basic Blue 22.[6,10] In both cases, the dye uptake measurements were made at pH 6, and at 100°C, in an acetic acid/sodium acetate buffer which was 0.01M in sodium acetate.

the $\log \theta_D / \log(C_D^s / C_H^s)$ coordinates with theoretical curves in the $\log \theta_D / \log P_1$ coordinates are still useful.

In Figure 5, the two data points for the oxazine dye at location A have been made to coincide with the theoretical curve for $p = 0.0001$, in accordance with data from Ref. 6. The ordinate at $\log(C_D^s / C_H^s) = 0$ for the data-point graph is then coincident with the ordinate for $\log_{10} P_1 = 0.95$ in the theoretical $\log \theta_D / \log P_1$ graph, so that the ratio $K_A \cdot K_D / A_0 \cdot K_H = 8.91$. We therefore find that $K_D / K_H = 2240$. If $K_H = K_{Na} = K_I = 0.0106$,[6] then $K_D = 23.7$ for the oxazine dye. The data points for this dye are limited in number, but are reasonably consistent with the curve for $p = 0.0001$, so that the overdyeing in this instance is probably largely due to the ionization of the second set of "weakly acidic groups."[6]

The data points for C.I. Basic Blue 22 in Figure 5 behave anomalously. If the two data points at location B are made coincident with the theoretical

curve for $p = 0.0001$, then $K_A \cdot K_D/A_0 \cdot K_H = 3.8$, and $K_D/K_H = 953$. Direct measurements of C_D^i, C_{Na}^i, C_D^s, and C_{Na}^s give $K_D/K_{Na} = 903$ for the uppermost of the two data points at location B in Figure 5. This level of agreement is probably as good as can be expected, and supports the approximation $K_H = K_{Na} = K_I$.

From the ratio $K_D/K_H = 953$, we conclude that, for C.I. Basic Blue 22, $K_D = 10.1$ at θ_D values close to 0.5. Since the data points drop well below the theoretical curve as θ_D decreases, the reason for this may be that the ratio K_D/K_H decreases greatly as θ_D decreases. It has been shown elsewhere that the ratio K_D/K_{Na} decreases in this manner,[6] which supports this suggestion.

The single data point shown for C.I. Basic Blue 22 in the "overdyeing region" is the average of two independent measurements, which also included measurements of C_{Na}^i. The average value of K_D/K_{Na} was 248, corresponding to $K_D = 2.6$ at this level of $\theta_D = 1.1$, assuming that $K_I = 0.0106$.[6] From eq. (25), the ratio $(\theta_X/\theta_D) = 6.4 \times 10^{-4}$, so that electrolyte sorption is negligible: The "overdyeing" can indeed be attributed solely to the ionization of the second set of "weakly acidic groups" in the polymer.[6]

CONCLUSIONS

Direct graphical comparisons of experimental data points with theoretical curves in the $\log \theta_D/\log P_1$ coordinate system are very helpful in understanding the behavior of cationic dyes on polymers containing fixed acidic groups. Simple lateral shifts along the abscissa permit rapid estimation of K_I^D for each point in a data set, or as a "visual average" for the data set as a whole, or for selected regions of the data. Simple vertical shifts on the ordinate permit corrections for the "effective acidic group concentration A_{01}," if such corrections are considered necessary.

The use of dimensionless groups helps to reveal the complex interactions between the sorption parameters, and prevents unwarranted assertions about the individual sorption parameters.

This type of approach is useful for other dyeing systems also, and can be automated at the expense of some complexity in computer graphics programming.

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