

Dimensionless Groups for the Sorption of Dye and Other Ions by Polymers. II. Hydrochloric Acid, C.I. Acid Blue 25, and Polyamides with an Excess of Basic Groups

RALPH MCGREGOR^{1*} and TOSHIRO IJIMA²

¹Department of Textile Engineering, Chemistry and Science, North Carolina State University, Box 8301, Raleigh, North Carolina 27695-8301, and ²Laboratory of Dyeing Chemistry, Department of Textiles, Jissen Women's University, Osakaue 4-1-1, Hino, Tokyo 191, Japan

SYNOPSIS

The equations of a generalized Donnan model have been used in dimensionless form to describe and analyze the sorption of hydrochloric acid and of C.I. Acid Blue 25 by polyamide fibers containing an excess of basic groups. The method is applicable to a wide variety of ionic sorption systems, and removes some of the restrictions of earlier treatments of the problem. Acid-base reactions, ion exchange processes, electrolyte sorption, and both ion binding and zwitterion formation have been considered.

INTRODUCTION

In Part I,¹ the equations of a generalized Donnan model²⁻⁴ for the sorption of ions by polymers were simplified by assuming inorganic co-ion exclusion: i.e., by ignoring the concentrations of free inorganic ions in the equation of electrical neutrality for the polymer. The equations were then reduced to dimensionless forms, and used to describe the sorption of hydrochloric acid and anionic dyes by different polymeric materials.

The analysis in Part I considered several partial treatments of the topic which have received much attention in the literature.^{5,6} Here the treatment is extended to include specific ion binding, zwitterion formation, anion exchange competition, and electrolyte sorption, without restricting the discussion to limited regions of the sorption isotherms, and without restricting the ratio of the concentrations of acidic and basic end groups in the polymer, as has long been customary.^{5,6} Sumner has recently offered a general approach to the theory of dyeing which is closely related to the present work,⁷ because the same basic thermodynamic ideas underlie both analyses of the problem.⁸ Crespo et al. have also

discussed many of the topics addressed here.^{6,9} The dimensionless group approach, however, offers a number of advantages in obtaining, interpreting, and displaying experimental data.^{1,10-12}

The equilibrium ionic distribution equations take the general form¹⁻⁴

$$C_i^f = \lambda^{z_i} \cdot K_i \cdot C_i^s \quad (1)$$

where λ is the Donnan distribution coefficient which takes account of electrical effects, z_i is the electrical charge on ion i including sign, and the ionic distribution coefficient K_i includes chemical and osmotic effects on the ion distribution. C_i^f is the concentration of ion i in the fiber, and C_i^s is the concentration in solution.

Electrical neutrality in the fiber requires that

$$\sum_i z_i C_i^f + \sum_k B_k^+ - \sum_j A_j^- = 0 \quad (2)$$

B_k^+ is the concentration of the k 'th type of ionized basic groups in the polymer, and A_j^- is the concentration of the j 'th type of ionized acidic groups.

THEORETICAL

Simple Donnan Model

For brevity, only data for polyamides containing an excess of basic groups are considered here, though

* To whom correspondence should be addressed.

the equations to be presented are more generally applicable. A future paper will examine amphoteric polymers with an excess of acidic groups. For clarity, only systems containing a small number of singly charged anions and cations will be discussed. The polymer is assumed initially to have only a single type of basic group and a single type of acidic group. Mathieson and Whewell found it necessary to assume the existence of two distinct types of acidic groups in wool, when discussing the uptake of acids, but this was not required for a nylon 66 fiber with an excess of acidic groups.¹³

The ions present are the cations M^+ and H^+ , and the anions D^- , X^- , and OH^- , as in Part I,¹ except for the substitution of the general metal cation symbol M^+ for the specific symbol Na^+ .

The dye anion D^- is chosen as the reference ion because it is of primary interest, and its concentrations in the fiber and in solution are easily measured.

For the cations

$$\begin{aligned} C_H^f &= \lambda \cdot K_H \cdot C_H^s \\ C_M^f &= \lambda \cdot K_M \cdot C_M^s \end{aligned} \quad (3)$$

For the anions

$$\begin{aligned} C_D^f &= \left(\frac{1}{\lambda}\right) \cdot K_D \cdot C_D^s \\ C_X^f &= \left(\frac{1}{\lambda}\right) \cdot K_X \cdot C_X^s \\ C_{OH}^f &= \left(\frac{1}{\lambda}\right) \cdot K_{OH} \cdot C_{OH}^s \end{aligned} \quad (4)$$

If the concentration B_0 of basic groups in the polymer is taken as a reference value for dimensionless concentration variables, we can use the relative dye concentration θ_D

$$\theta_D = \frac{C_D^f}{B_0} \quad (5)$$

to define the Donnan distribution coefficient λ

$$\lambda = \frac{K_D \cdot C_D^s}{B_0 \cdot \theta_D} \quad (6)$$

and obtain dimensionless expressions for the free cation concentrations θ_H and θ_M of the type

$$\theta_H = \frac{K_H \cdot K_D \cdot C_H^s \cdot C_D^s}{B_0^2 \cdot \theta_D} \quad (7)$$

For the free anion concentrations θ_X and θ_{OH} in the fiber, the corresponding equations take the form

$$\theta_X = \theta_D \cdot \frac{K_X \cdot C_X^s}{K_D \cdot C_D^s} \quad (8)$$

If there is no binding of M^+ , D^- , or X^- , then only the hydrogen ion is bound, as in Part I.¹ This defines a simple Donnan sorption model, and eq. (2) can then be written in the equivalent dimensionless form

$$\frac{1}{1 + \left(\frac{\theta_D}{P_{1B}}\right)} + P_{7B} \cdot \frac{P_{1B}}{\theta_D} = \frac{P_5}{1 + \left(\frac{P_{1A}}{\theta_D}\right)} + P_2 \cdot \theta_D \quad (9)$$

The first term on the left in eq. (9) is the dimensionless expression for B^+/B_0 . The dimensionless group P_{1B} determines the concentration of charged basic groups, as in Part I,¹ and so is a natural parameter to use for the analysis of experimental behavior when the polymer contains an excess of basic groups, which are titrated first by acids.

$$P_{1B} = \frac{K_H \cdot K_D \cdot C_H^s \cdot C_D^s}{K_B \cdot B_0} \quad (10)$$

K_B is the internal dissociation coefficient of the ionized basic groups.

The next term $P_{7B} \cdot P_{1B}/\theta_D$ on the left hand side of eq. (9) gives the total free cation concentration in the polymer $\theta_H + \theta_M$. The new parameter P_{7B} determines the relative concentrations of free M^+ and H^+ ions in the polymer. This product term was neglected in Part I,¹ where the analysis assumed inorganic co-ion exclusion.

$$P_{7B} = \frac{K_B}{B_0} \cdot \left(1 + \frac{K_M \cdot C_M^s}{K_H \cdot C_H^s}\right) \quad (11)$$

The total concentration (dimensionless) of positive charges in the polymer given by the left hand side of eq. (9) must be balanced by the total concentration of negative charges given by the right hand side. The first term on the right hand side of eq. (9) is the dimensionless concentration of charged acidic groups A^-/B_0 . The ratio of acidic to basic group concentrations is given by P_5

$$P_5 = \frac{A_0}{B_0} \quad (12)$$

The dimensionless group P_{1A} determines the charge on this acidic group, as in Part I,¹ where subscript 1 refers to hydrogen ion binding.

$$P_{1A} = \frac{K_H \cdot K_D \cdot C_H^s \cdot C_D^s}{K_A \cdot B_0} \quad (13)$$

K_A is the internal dissociation coefficient for the acidic group.

Since the experimental data will be related initially to P_{1B} rather than to P_{1A} , it is convenient to introduce the dimensionless ratio P_9 of the acidic and basic group dissociation coefficients,

$$P_9 = \frac{K_A}{K_B} = \frac{P_{1B}}{P_{1A}} \quad (14)$$

when specifying the parameters for a calculation. P_{1A} in eq. (9) is replaced by the quantity P_{1B}/P_9 .

The last term on the right-hand side of eq. (9) gives the dimensionless total free anion sorption $\theta_D + \theta_X + \theta_{OH}$ by the polymer. The dimensionless group P_2 reflects the relative uptakes of X^- , OH^- and D^- ions, and represents anion exchange competition with the dye anion for sorption by the fiber. As in Part I,¹ we define

$$P_2 = 1 + \frac{K_X \cdot C_X^s}{K_D \cdot C_D^s} + \frac{K_{OH} \cdot C_{OH}^s}{K_D \cdot C_D^s} \quad (15)$$

The theoretical model represented by eqs. (9)–(15) is more general than, but closely related to, the Donnan models developed long ago by Peters and Speakman,¹⁴ and by others.^{5,6} Although the model of Mathieson and Whewell¹³ is based on polyelectrolyte theory, and introduces useful molecular concepts, the essential mathematical content of that model appears to us to be formally a special case of eq. (9),^{15,16} contrary to the opinions expressed by Zaikov et al.⁶ Mathieson and Whewell also neglect the excess of acidic groups in their nylon fibers. They introduce a variable dissociation coefficient K_A to explain experimental data for wool.¹³

Specific Ion Binding

If the dye anion is assumed to bind to the charged basic groups, forming a new component B^+D^- of the system, as in the Gilbert-Rideal type of approach,¹⁷⁻¹⁹ the extent of binding can be specified by an internal dissociation coefficient K_{BD} for the

bound complex B^+D^- , or by the dimensionless group

$$P_{8BD} = \frac{K_{BD}}{B_0} \quad (16)$$

Similarly, the extent of binding of X^- to form the new component B^+X^- can be defined using an internal dissociation coefficient K_{BX} , or the dimensionless group

$$P_{8BX} = \frac{K_{BX}}{B_0} \quad (17)$$

The expression for the fraction of charged basic groups, which forms the first term in eq. (9), becomes more complicated, but can still be expressed in terms of the concentration θ_D of free or unbound dye anion,

$$\frac{B^+}{B_0} = \frac{1}{1 + \frac{\theta_D}{P_{1B}} + \frac{\theta_D}{P_{8BD}} \cdot P_{8XD}} \quad (18)$$

by introducing the dimensionless group P_{8XD} which determines the relative degree of binding of X^- and D^- ions

$$P_{8XD} = 1 + \frac{P_{8BD} \cdot K_X \cdot C_X^s}{P_{8BX} \cdot K_D \cdot C_D^s} \quad (19)$$

Since there may also be cation binding of M^+ to the charged acidic groups of the fiber, as postulated by Crespo et al.,^{6,9} an internal dissociation coefficient K_{AM} for the species A^-M^+ can be introduced, through the dimensionless variable P_{8AM}

$$P_{8AM} = \frac{K_{AM}}{B_0} \quad (20)$$

However, the first term on the right hand side of eq. (9) may still be written as a function of θ_D

$$\frac{A^-}{B_0} = \frac{1}{1 + \frac{P_{1A}}{\theta_D} \cdot P_{8MH}} \quad (21)$$

by introducing the dimensionless group P_{8MH} to define the relative extent of binding of M^+ and H^+ ions to A^- .

$$P_{8MH} = 1 + \frac{K_A \cdot K_M \cdot C_M^s}{K_{AM} \cdot K_H \cdot C_H^s} \quad (22)$$

When eq. (9) is modified in this manner, it can be solved to determine the concentrations of free or unbound ions in the fiber. The internal binding equations must then be applied to obtain the concentrations of bound ions, before calculation of the total ion concentrations in the fiber.

Ion Pairs and Zwitterions

The concept of ion-pair formation implied by the ion binding equations raises the issue of ion-pair formation in general. The possible existence of ion-pairs such as M^+D^- , and M^+X^- ,^{6,9} and of additional electrically neutral components such as HD and HX,^{11,20} both in the polymer and in the solution, makes the discussion of even a nominally simple system very complex.^{6,9}

These possibilities are recognized, but not explicitly included here. Simple models which include the uptake of undissociated acids have been discussed elsewhere.¹¹ This mode of uptake represents an alternative mechanism which can produce effects very similar to those produced by the electrolyte sorption considered later in this paper.¹¹

Zwitterion formation has been discussed by Wall and Beresiewicz,¹⁹ and others,^{5,6} but there is some vagueness in the use of the term. It is not always clear whether zwitterions represent a distinct chemical component of the system, such as a contact ion pair, or adjacent, electrostatically interacting acidic and basic groups, or merely the mutual co-existence of protonated amino groups and ionized carboxyl groups in a water-saturated polyamide.

It therefore seems useful to explore the consequences of the hypothesis that zwitterion ion pairs B^+A^- exist in the fiber and can be treated as a distinct component of these systems.

An internal dissociation coefficient K_{ZW} can be introduced for the postulated dissociation equilibrium between the zwitterion ion pairs and unpaired acidic (A^-) and basic (B^+) groups. The corresponding dimensionless parameter is K_{ZW}/B_0 . The analysis can be made for the basic model of eq. (9), but requires the simultaneous solution of the three equations given in the appendix for $[B^+]/B_0$, for $[A^-]/B_0$, and for θ_D . This was achieved for assigned values of P_{1B} , P_2 , P_5 , P_{7B} , P_9 , and of $K_{ZW}/B_0 = P_{10}$, by an iterative method.

APPLICATION TO EXPERIMENTAL DATA

Sorption of Hydrochloric Acid by Nylon 66

Estimation of Dissociation Coefficients and Ionic Distribution Coefficients

Wall and Beresiewicz could find no satisfactory explanation for their experimental data on the sorption of hydrochloric acid, in absence of added potassium chloride, by an undrawn nylon 66 fiber (Nylon I) with a large excess ($P_5 = 0.19$) of basic groups.¹⁹ So far as we are aware these data have never been explained.

Figure 1 compares the data which these authors obtained for their nylon I fiber at 14°C with theoretical curves generated using eq. (9). The data were

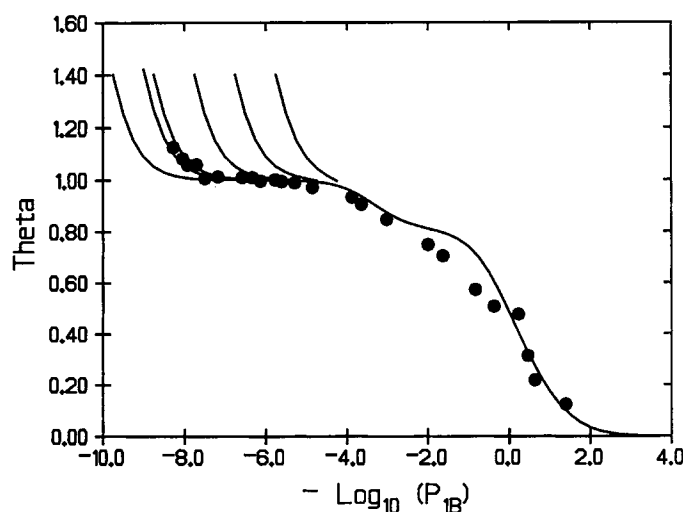


Figure 1 Sorption of hydrochloric acid at 14°C by nylon I of Wall and Beresiewicz.¹⁹ The titration curve is calculated using eq. (9) with $P_2 = 1$, $P_5 = 0.19$, $P_9 = 2320$ and, (moving from left to right for $\theta > 1$), for the electrolyte sorption parameter values $P_{7B} = 1 \times 10^{-10}$, 6×10^{-10} , 1×10^{-9} , 1×10^{-8} , 1×10^{-7} , and 1×10^{-6} .

plotted as θ_{Cl} values on the ordinate axis against $-\log_{10} a_H^S \cdot a_{Cl}^S$ as abscissa, where a is activity, and then displaced laterally to obtain a fit to the theoretical curve at lower θ values, as discussed for the use of $\log_{10} \theta_{Cl}$ as ordinate in Part I.¹

Figure 1 has $-\log_{10} P_{1B}$ as abscissa and therefore resembles a conventional pH titration curve. This comparison includes corrections for nonideal behavior in solution. No attempt was made to optimize the fit to the data in the second stage of back titration of the ionized acidic groups: the theoretical curve was generated using an independent estimate of $P_9 = 2320$ based on the data in Table III of Part I.¹ Since the system was free from competing anions, $P_2 = 1$.

There were no metal cations present, so that the acid sorption in excess of the basic end group content ($\theta_{Cl} > 1$) predicted by eq. (9) is attributed to electrolyte sorption of the hydrochloric acid.

The experimental data in the intermediate range of θ_{Cl} deviate strongly from the theoretical curve. Possible explanations for this will now be examined.

Anion Binding

Figure 2 shows the experimental data from Figure 1, together with theoretical curves for different values of the bound anion dissociation parameter P_8 of eq. (16), which here refers to chloride ion binding only because this is the only anion present. The abscissa is now $\log_{10} P_{1B}$, to focus attention on the role

of the ionic or activity product for the acid, rather than on the role of pH alone.^{11,21,22}

In agreement with Wall and Beresiewicz,¹⁹ the assumption of anion binding does not explain the sorption of hydrochloric acid in the absence of potassium chloride. It provides in fact a poorer fit to the data than does eq. (9).

It is interesting to note that the binding assumption gives steeper curves for the initial titration of the basic group, but then gives curves of lower slope for the subsequent second stage of back titration of the acidic group, if the curve from eq. (9) without anion binding is taken as the reference.

The Parameter P_5

The analysis of a polyamide for the concentrations of acidic and basic end groups can be difficult, and not all of the acidic and basic groups in the polymer may be accessible to the hydrochloric acid.¹

Figure 3 shows the experimental data at 14°C, plotted now against theoretical curves from eq. (9) for different values of the ratio P_5 of acidic groups to basic groups. The bounding curves for a single basic group only ($P_5 = 0$), and for equal concentrations of basic and acidic groups ($P_5 = 1$), have the same shape,¹ but are displaced relative to each other by more than 3 log units along the abscissa.

Figure 3 shows clearly that accuracy in the difficult measurements of the accessible acidic and basic end group concentrations of a polymer is essential

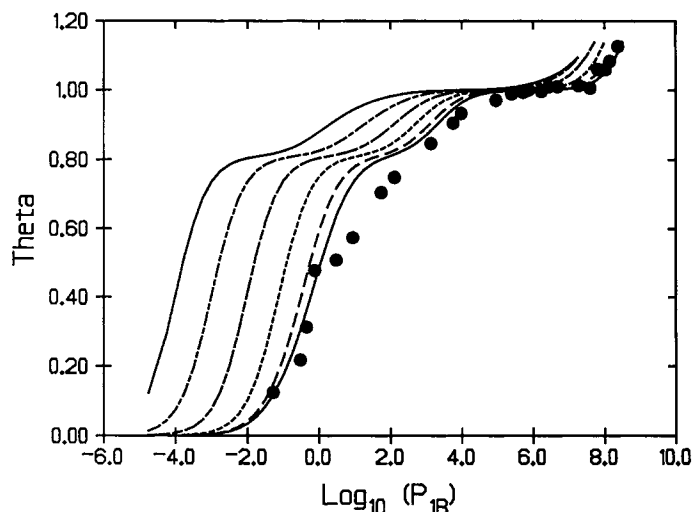


Figure 2 Predicted effects of chloride anion binding. The data of Figure 1 are plotted in reversed mode, and compared with curves calculated from eq. (9) and modified to include anion binding of chloride ion to charged basic groups. The same values of P_2 , P_5 , and P_9 , with $P_{7B} = 6 \times 10^{-10}$, are used as in Figure 1. Moving from right to left, the anion binding dissociation parameters P_8 for each curve are $P_8 = \infty$ (solid line, calculated for zero binding), and $P_8 = 10, 1, 0.1, 0.01, 0.001, \text{ and } 0.0001$ (solid line).

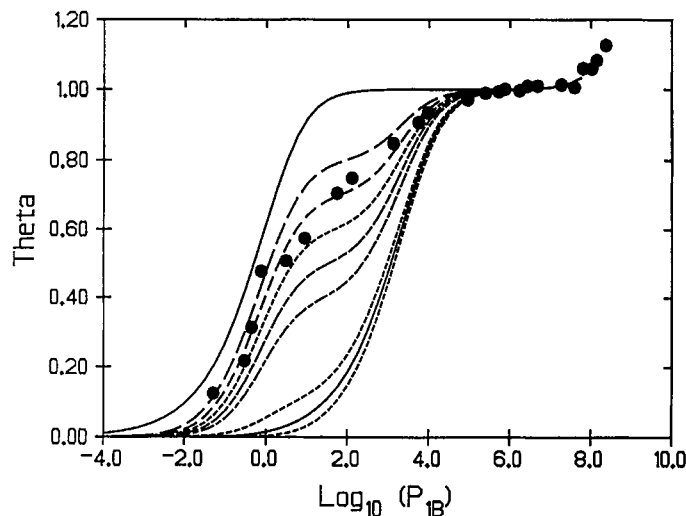


Figure 3 Predicted effects of the ratio P_5 of acidic groups to basic groups. The data and the main parameters are the same as for the zero binding curve in Figure 2, but now P_5 takes the following values as one moves from top to bottom of the graph: $P_5 = 0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.9, 1.0,$ and 1.1 .

for reliable theoretical analysis, and that both the acidic and the basic groups must be taken into account in the analysis of these problems.

Zwitterion Formation

Figure 4 shows the same 14°C -data, compared this time with theoretical curves from the equations in the Appendix for an approach to zwitterion for-

mation based on the law of mass action, and including the creation of a new ion-pair component of the system.

This hypothesis does not provide a good explanation of the experimental data in the middle range of θ_{cl} values. It is obvious that a very low dissociation coefficient ($P_{10} \ll 0.0001$) for the zwitterion complex would either eliminate the second stage of back-titration of the acidic groups, or greatly increase the

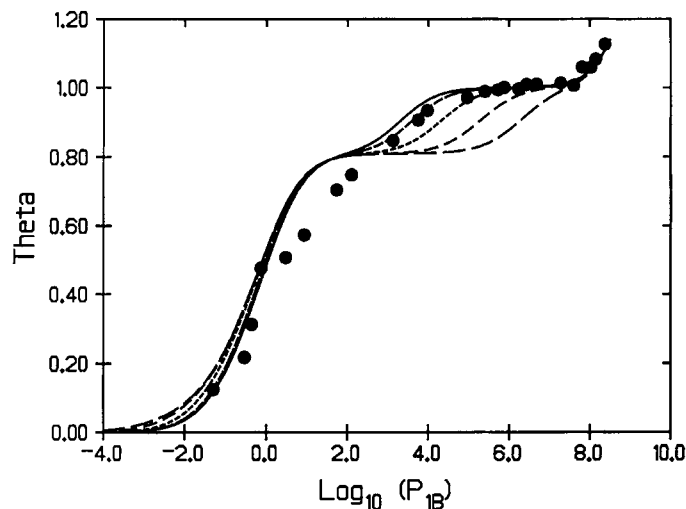


Figure 4 Predicted effects of zwitterion complex formation. The data and the basic parameter values remain the same as for Figure 3, but as the zwitterion dissociation parameter P_{10} takes the values $P_{10} = 0.0001, 0.001, 0.01, 0.1, 1.0,$ and $10,000$, the upper curves move from right to left while the lower curves move in the opposite direction.

apparent value of the acidic group dissociation coefficient (i.e. of $P_9 = K_A/K_B$).

It is interesting that the effects of this type of zwitterion formation would also extend to the initial stage of titration of the excess basic groups, and so lead to errors in the calculation of K_B from the data at low theta values.

A Distribution of Dissociation Coefficients

Davidson noted that the sorption of methylene blue by acidic oxycelluloses could not be explained by assuming the existence of acidic groups with only a single dissociation coefficient.²³ It was obvious from our own analysis of that system that it would be necessary to assume the existence of at least two types of acidic groups with different dissociation coefficients in the alkaline hypobromite oxycelluloses in order to obtain a completely satisfactory fit to the experimental data shown in Figures 1 and 2 of an earlier publication.¹² The deviations between theory and experiment observed in that work¹² are analogous to those under discussion here. Some acrylic fibers also appear to contain at least two types of acidic groups, with markedly different dissociation coefficients.

The highly unbalanced end group content characteristic of nylon I of Wall and Beresniewicz, data

from which are shown in Figure 1, can often be obtained by using polymerization terminators which introduce an additional type of basic group into the polymer. The end-group composition of this nylon indicates that it was not typical of the commercial products available at the time of the original work, but was probably an experimental fiber.²⁴

In the absence of any other obviously acceptable explanation for the data, we adopted the hypothesis that a fraction $\beta_1 = 1 - P_5$ of the total basic group concentration B_0 consists of amino groups which are more basic in character than the remaining basic groups, which have a higher dissociation coefficient. The latter groups are presumed to be contributed by a polymerization modifier, or to be in a different local environment from the other basic groups. The equations used in this analysis are given in the Appendix. The principal parameter values for P_5 and P_9 were based on data from Part I,¹ and since there are no other competing anions, $P_2 = 0$. Figure 5 shows that this hypothesis can generate curves which reproduce very well the general trends in the data of Wall and Beresniewicz, obtained at three different temperatures in the absence of potassium chloride. Even the anion sorption in excess of the basic end-group content is well described by the electrolyte sorption term.

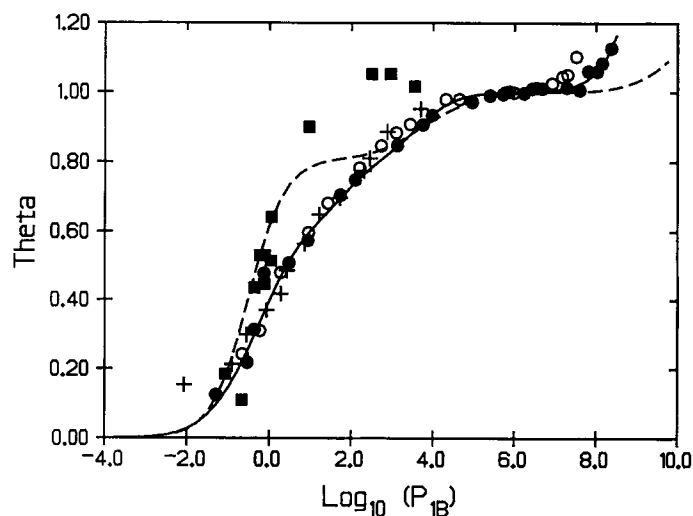


Figure 5 Data tests assuming two types of basic groups. The solid curve is calculated for $P_2 = 1$, $P_5 = 0.19$, $P_{7B} = 6 \times 10^{-10}$, as in the previous figures; here we have assumed that a fraction equal to 0.19 of the total basic group concentration B_0 consists of basic groups with a dissociation coefficient greater by a factor of 100 than that for the major fraction of basic groups. The parameter P_9 is also set equal to 500. The experimental data, in the absence of potassium chloride, are taken from Wall and Beresniewicz¹⁹: (●) at 14°C, (○) at 35°C and (+) 50°C; (■) data obtained in the presence of 0.2M potassium chloride at 25°C. These last are fitted better at the lower θ_{Cl} values by the curve from Figure 2 for $P_8 = 0.01$, based on anion binding.

A nonlinear least squares curve fitting procedure was used to determine the parameter values shown in Table I. The coefficients of determination ranged from 0.969 to 0.997.

When there is no sorption of acid in excess of the basic end group concentration B_0 , it is possible to determine only the composite quantity $K_H \cdot K_{Cl}/K_B$ for the basic group.¹

However, when the ion sorption exceeds B_0 it is possible to determine the parameter P_{7B} , and this permits the estimation of both the basic group dissociation coefficient K_B , and the ionic distribution coefficient product $K_H \cdot K_{Cl}$. Separate estimates of K_H and K_{Cl} can be obtained only through additional assumptions, or by the adoption of a specific convention for assigning individual ionic distribution coefficients.²⁶

The confidence limits on the parameter K_{21} are large, but the order of magnitude is clear. To maintain objectivity, parameter restraints were used based on the data from Part I,¹ and on the hypothesis for β_1 stated earlier. Free adjustment of all parameters was not permitted.

For comparison with the approach of Mathieson and Whewell,¹³ the fiber end-group concentrations were based on the water-swollen volume of the fibers, assuming a density of 1.14 g/mL.

On this basis the average ionic distribution coefficient for hydrochloric acid is $(K_H \cdot K_{Cl})^{1/2} = 0.85$ at 14°C, and 0.92 at 34.7°C. These data are close to unity, which supports the assumption that the water-swollen volume of the fiber is an appropriate reference volume for calculations based on a simple Donnan model.¹³ On the other hand, only the ratio K_B/B_0 can be determined from the present data, and the concentration units assigned to B_0 determine the conclusions reached about K_B and the average ionic distribution coefficient $(K_H \cdot K_{Cl})^{1/2}$.

For the most basic group we then find that $pK_B = 10.2$ at 14°C, and 9.4 at 34.7°C. An Arrhenius plot extrapolation of the data for $\log_{10} K_H \cdot K_{Cl}/K_B$ gives

an estimate of $pK_B = 10.6$ at 0°C, on the assumption that $K_H \cdot K_{Cl} = 1$. Hexamethylene diamine at 0°C has $pK_a = 11.19$ in water.²⁷ There is a difference of the order of 2 units in pK_B between the two types of basic groups assumed to be present in the Nylon I. Differences of this order of magnitude can be found in aqueous solution at 25°C between aliphatic amines such as *n*-hexylamine ($pK_a = 10.56$) and amines such as morpholine ($pK_a = 8.33$), 2,4-dimethyl imidazole ($pK_a = 8.36$), and several other amines.²⁷ The high temperature dependence of pK_B in Nylon I fibers makes accurate comparison difficult, but the above data show that the present results are not unreasonable.

If it is assumed instead that the accessible volume fraction of the fiber is 0.080,²¹ then B_0 increases from 0.136 mol/L to 1.70 mol/L, and at 34.7°C $pK_B = 8.3$ and $(K_H \cdot K_{Cl})^{1/2} = 12$. This is a very different picture, requiring very high local concentrations within the fiber, and implying significant specific interactions of the inorganic ions with the water-swollen polymer matrix. The real situation is probably somewhere between the two limiting calculations given above, but nevertheless the experimental data for both high and low theta values at all temperatures are well represented by eq. (9), modified for the presence of two types of basic groups.

We are not aware of any previous attempts to use dimensionless groups in this manner, to extract independent information on dissociation coefficients and ionic distribution coefficients from the analysis of different regions of the same titration curves or sorption curves for polymers or other materials.

Sorption of Hydrochloric Acid in Presence of Potassium Chloride

In Figure 5 the data for the first stage of sorption of hydrochloric acid by nylon I of Wall and Beresiewicz, at 25°C in presence of 0.2 mol/L potassium

Table I Nonlinear Least Squares Parameter Estimates^a

Temperature (°C)	$\text{Log}_{10} \left(\frac{K_H \cdot K_{Cl}}{K_B} \right)$	P_{7B}	$K_H \cdot K_{Cl}$	K_B	$(K_H \cdot K_{Cl})^{1/2}$
14	10.01	5.2×10^{-10}	0.72	7.1×10^{-11}	0.85
34.7	9.28	3.3×10^{-9}	0.84	4.5×10^{-10}	0.92
50	8.73	—	—	—	—

^a The data are based on the water-swollen volume of the fibers, assuming $B_0 = 0.136$ mol/L for the total concentration of basic groups, and $\beta_1 = 1 - P_5 = 0.81$ for the fractional concentration of the more basic amino groups. The dissociation coefficient ratios for the two types of basic groups were found to be $K_{21} = 150$ at 14°C, 80 at 34.7°C, and 240 at 50°C. The ratio for the dissociation coefficients of the acidic groups and the most basic groups was set at $P_9 = 2360$ at 14°C, 1030 at 34.7°C, and 597 at 50°C.¹

chloride,¹⁹ are better represented at low θ_{Cl} values by a theoretical curve assuming anion binding, as pointed out by Wall and Beresiewicz, and deviate strongly from the other data for nylon I obtained in absence of potassium chloride.

Further exploration of this problem will be combined in a later paper with a discussion of other titration curves in presence of potassium chloride.

Sorption of C.I. Acid Blue 25 by Nylon 6

Anion Exchange Competition and Electrolyte Sorption

Figure 6 shows experimental data²⁵ for the sorption of C.I. Acid Blue 25 at 95°C by a drawn nylon 6 fiber with an excess of basic end groups (polymer 3 of Table II of Part I).¹

The solid curve is a good fit to the data points, which extend well into the overdyeing region ($\theta_D > 1$), and is calculated from eq. (9) neglecting anion exchange competition from buffer anions in the system (i.e. for $P_2 = 1$), and assuming that only one type of basic group is present.

The experiments were carried out in a phosphate buffer system at pH 7.5 and at pH 6.1, for different dye concentrations. The phosphate anion concentration was constant at 0.012 mol/L, and greatly exceeded the dye anion concentration. In this situation the parameter P_2 of eq. (15) is not constant.

If the hydroxyl ion is neglected, we can introduce the parameter P_4 of Part I¹ to define the extent of anion exchange competition between D^- and X^- ions,

$$P_2 = 1 + \frac{P_4}{P_{1B}} \quad (23)$$

where

$$P_4 = \frac{K_H \cdot K_X \cdot C_H^s \cdot C_X^s}{K_B \cdot B_0} \quad (24)$$

Since this aspect of the calculation is intended to be illustrative only, P_4 has been calculated for an equivalent concentration of 0.012 mol/L of an added salt with the competing anion X^- . For data at pH 6.1, $P_4 = 3.64$, and for data at pH 7.5, $P_4 = 0.145$. It is clear from Figure 6 that the effect of anion exchange competition is much less at pH 7.5 than at pH 6.1.

Only the six data points for the highest θ_D values were obtained at pH 6.1, so that the effects of competition from buffer anions are probably small in this experiment, in agreement with the conclusions in Part I.¹

Competition of this type makes the sorption curve steeper, and might be mistakenly taken as evidence for an anion binding mechanism of sorption.

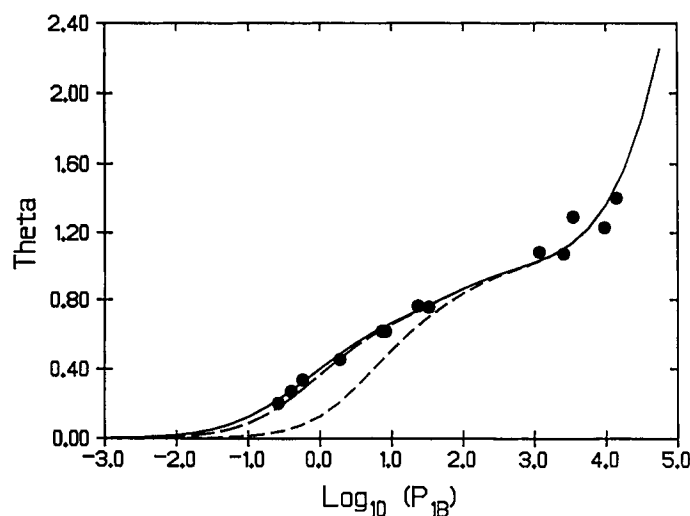


Figure 6 Sorption of C.I. Acid Blue 25 by a nylon 6 fiber at 95°C. The solid line is calculated for a simple Donnan model with only one type of basic group, without anion binding, and for hydrogen ion binding only, with negligible anion exchange competition from buffer anions: $P_2 = 1$, $P_5 = 0.324$, $P_9 = 80$, and $P_{7B} = 5 \times 10^{-5}$. The broken curves take into account anion exchange competition, as discussed in the text. The data are by Fienberg.²⁵

The data for over dyeing, with $\theta_D > 1$, are rather scattered, but the curve calculated for $P_{7B} = 5 \times 10^{-5}$ represents the data reasonably well. If we base calculations on the water-swollen volume of the nylon polymer, and assume that $K_B = 3.6 \times 10^{-8}$ mol/L at 95°C, as would follow from applying the implicit assumptions of Mathieson and Whewell to the extrapolated data for HCl at 95°C in Table III of Part I,¹ we are forced to conclude from the definition of P_{7B} in eq. (11) that the ratio $K_M/K_H = 6 \times 10^{-3}$. The sorption of hydrogen ions is greatly preferred by the fiber to the sorption of sodium and potassium ions.

CONCLUSIONS

The sorption of dye and inorganic ions by polymers can be described using dimensionless groups of variables. Different dimensionless groups represent different aspects of the sorption processes. The effects of changing the numerical value of a given dimensionless group can be clearly shown, and it is not necessary to restrict the analysis to a limited region of a sorption isotherm, or to a limited choice of the ratio of acidic groups to basic groups in the polymer, as has long been customary.

Changes in the numerical value of a given dimensionless group can originate in any of the component variables comprising that group. This is one reason why there are often several different assumptions which can account for the same pattern of experimental behavior, and why controversies arise over issues which cannot in fact be resolved unambiguously without additional data. For example, Mathieson and Whewell were able to account for the uptake of acids by wool by introducing a variable acidic group dissociation coefficient,¹³ and Gilbert and Rideal were able to explain the same data by assuming anion binding to the basic groups in the wool.¹⁷

Examples have been given to show how an examination of all regions of a sorption curve or titration curve can yield the maximum amount of information about the key parameters for a sorption process.

The sorption of hydrochloric acid by a nylon fiber with an excess of basic groups, in the absence of potassium chloride, can be well described by equations and assumptions which are closely related to the polyelectrolyte theory of Mathieson and Whewell.

These same assumptions give a good account of the sorption of an acid dye by a nylon 6 fiber, though

there is evidence that the fiber sorbs hydrogen ions in preference to sodium ions.

APPENDIX

Zwitterion Formation

The three simultaneous equations solved for the zwitterion calculations are as follows.

$$\left(\frac{[B^+]}{B_0}\right)^2 \cdot \alpha + \left(\frac{[B^+]}{B_0}\right) \cdot \left[\left(\frac{K_{ZW}}{B_0} \cdot \alpha \cdot \beta\right) + P_5 - 1\right] - \frac{K_{ZW}}{B_0} \cdot \beta = 0$$

$$\left(\frac{[A^-]}{B_0}\right)^2 \cdot \beta + \left(\frac{[A^-]}{B_0}\right) \cdot \left[\left(\frac{K_{ZW}}{B_0} \cdot \alpha \cdot \beta\right) - P_5 + 1\right] - P_5 \cdot \frac{K_{ZW}}{B_0} \cdot \alpha = 0$$

$$\left(\frac{[B^+]}{B_0}\right) - \left(\frac{[A^-]}{B_0}\right) - P_2 \cdot \theta_D + \frac{P_{1B} \cdot P_{7B}}{\theta_D} = 0$$

where

$$\alpha = 1 + \frac{\theta_D}{P_{1B}}$$

$$\beta = 1 + \frac{P_{1B}}{P_9 \cdot \theta_D}$$

and $K_{ZW}/B_0 = P_{10}$.

Two Types of Basic Groups

The fraction of groups of type 1 is

$$\beta_1 = \frac{B_1}{B_0}$$

The dimensionless electrical neutrality equation is

$$\frac{\beta_1}{1 + \frac{\theta_D}{P_B}} + \frac{1 - \beta_1}{1 + \frac{K_{21} \cdot \theta_D}{P_{1B}}} - \frac{P_5}{1 + \frac{P_{1B}}{P_9 \cdot \theta_D}} - P_2 \cdot \theta_D + \frac{P_{1B} \cdot P_{7B}}{\theta_D} = 0$$

The ratio of the dissociation coefficients for the two types of basic groups is

$$K_{21} = \frac{K_{B2}}{K_{B1}}$$

REFERENCES

1. R. McGregor and T. Iijima, *J. Appl. Polym. Sci.*, **41**, 2769 (1990).
2. R. McGregor and P. W. Harris, *A Chemical Engineering Approach to Dyeing Problems: The Sorption of Acid Dyes by Polyamides*, Research Monograph M-20, Allied Chemical Fibers Division, Petersburg, Virginia, 1969.
3. R. McGregor and P. W. Harris, *J. Appl. Polym. Sci.*, **14**, 513 (1970).
4. R. McGregor, *Diffusion and Sorption in Fibers and Films, Vol. 1, An Introduction with Particular Reference to Dyes*, Academic Press, London, 1974.
5. R. H. Peters, *Textile Chemistry, Vol. III, The Physical Chemistry of Dyeing*, Elsevier, Amsterdam, 1975.
6. G. E. Zaikov, A. P. Iordanskii, and V. S. Markin, *Diffusion of Electrolytes in Polymers*, VSP, Utrecht, 1988.
7. H. A. Sumner, "Thermodynamics of Dye Sorption," Ch. 4 in *The Theory of Coloration of Textiles*, 2nd Ed., A. Johnson, Ed., Society of Dyers and Colourists, Bradford, England 1989.
8. E. A. Guggenheim, *Thermodynamics*, 5th Edn., North-Holland, Amsterdam, 1967.
9. R. Crespo, J. Tomas, R. Areal, and G. Garcia, *An. Quim.*, **71**, 751 (1974).
10. R. McGregor, *Text. Chem. Color.*, **9**, 98 (1977).
11. R. McGregor, *Text. Chem. Color.*, **17**, 17 (1985).
12. R. McGregor, K. Tamura, and T. Iijima, *J. Appl. Polym. Sci.*, **34**, 2777 (1987).
13. A. R. Mathieson and C. S. Whewell, *J. Appl. Polym. Sci.*, **8**, 2029 (1964).
14. L. Peters and J. B. Speakman, *J. Soc. Dyers Col.*, **49**, 63 (1949).
15. R. McGregor, *J. Appl. Polym. Sci.*, **10**, 1973 (1966).
16. V. V. Than, J. H. Petropoulos, and T. Iijima, *J. Appl. Polym. Sci.*, **28**, 2813 (1983).
17. G. A. Gilbert and E. K. Rideal, *Proc. Roy. Soc., A* **182**, 335 (1944).
18. W. R. Remington and E. K. Gladding, *J. Am. Chem. Soc.*, **72**, 2553 (1950).
19. F. T. Wall and A. Beresiewicz, *J. Phys. Chem.*, **60**, 692 (1956).
20. H. Zollinger, *Amer. Dyestuff Reporter*, **54**, 46 (1965).
21. T. Obara, T. Iijima, S. Ikeda, H. Ishikawa, and T. Nakagawa, *J. Appl. Polym. Sci.*, **16**, 2393 (1978).
22. J. A. Kitchener and P. Alexander, *J. Soc. Dyers Col.*, **49**, 63 (1949).
23. G. F. Davidson, *J. Text. Inst.*, **39**, T65 (1948).
24. E. D. Williams, Jr., E. I. DuPont de Nemours & Co., private communication.
25. Unpublished data of L. Fienberg.
26. R. McGregor, *Textile Res. J.*, **42**, 172 (1972); **44**, 43 (1974).
27. R. C. Weast, Ed., *CRC Handbook of Chemistry and Physics*, 54th Ed., CRC Press, Ohio, 1973.

Received April 24, 1991

Accepted August 30, 1991