

Dimensionless Groups for the Description of Sorption Equilibria in Dyeing with Anionic Dyes. I. Inorganic Co-Ion Exclusion

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Synopsis

The equations of a general Donnan Model have been simplified and used to describe the equilibrium sorption of anionic dyes by fibers containing acidic and basic groups. By examining simple situations, the dependence of the sorption behavior on specific dimensionless groups of variables has been clarified. This approach emphasizes common features of different ionic dyeing systems, it can be applied in graphical methods of data analysis, and it has potential applications in process control.

INTRODUCTION

A generalized Donnan model for the sorption of ionic dyes by solid polymers can be based on the assumption that each ionic species i in the solution follows an ionic distribution equation of the type

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

in which C_i^f is the equilibrium concentration in the fiber, C_i^s is the equilibrium concentration in the solution, z_i is the ionic charge on the ion, including sign, and K_i is an ionic distribution coefficient. The Donnan coefficient λ is related to the equilibrium electrical potential difference between the polymer and the solution.¹ The ionic distribution coefficients are dimensionless if the same concentration units are used in the fiber and in the solution.

In addition to the condition of electrical neutrality in the solution

$$\sum_i z_i C_i^s = 0 \quad (2)$$

the ion concentrations in the fiber must satisfy the electrical neutrality condition

$$F(\lambda) = \sum_i z_i \cdot \lambda^{z_i} \cdot K_i \cdot C_i^s + \sum_k \frac{B_k}{1 + (K_{B_k}/\lambda \cdot K_1 \cdot C_1^s)} - \sum_j \frac{A_j}{1 + (\lambda \cdot K_1 \cdot C_1^s/K_{A_j})} = 0 \quad (3)$$

B_k is the concentration of the k th type of basic group in the polymer, and K_{B_k} is its internal dissociation coefficient. K_{A_j} is the dissociation coefficient of the j th type of acidic group in the polymer, and A_j is the concentration of that group. The index $i = 1$ is reserved for the hydrogen ion. Equations (1)–(3) form a general basis for describing or predicting the behavior of ionic dyeing systems,¹ except insofar as the specific roles of the solvent water and the polymer matrix are concerned, but their implications are not obvious: additional insight can come from the examination of simple special cases of eqs. (1)–(3), with the aid of dimensionless groups of variables.^{2,3} For example, the analysis of experimental data for sorption equilibria involving cationic dyes has recently been based on graphical methods using dimensionless groups.^{3,4}

Here, the dimensionless group method is extended to the sorption of anionic dyes by amphoteric polymers containing fixed basic and acidic groups. In order to obtain simple models, and to clarify the effects that may be found, it is necessary to classify the different dyeing systems and to make assumptions that are not mandated by the more general model.

THEORETICAL

The dye solution may contain the sodium salt NaD or the free acid HD of a monosulfonic acid dye, together with a strong electrolyte NaX, and a strong acid HX or the alkali NaOH. These components are assumed to be fully dissociated into the corresponding ions H^+ , Na^+ , D^- , X^- , and OH^- .

The analysis is restricted to situations in which the fiber phase contains very low concentrations of free inorganic cations, as a consequence of the positive charge on the polymer and the low substantivity of these cations. This situation is favored when the basic groups are relatively strongly basic and the acidic groups are relatively weakly acidic, as in wool and most polyamides.⁵⁻⁷ The concentrations of the free hydrogen and sodium ions in the fiber can then be neglected in the electrical neutrality condition for the fiber phase, even though the hydrogen ion continues to play a key role in determining the states of ionization of the acidic and basic end groups in the fiber. This situation will be referred to as inorganic co-ion exclusion, and is most likely to occur when the solution is neutral or acidic and all the inorganic ion distribution coefficients are small.

An Excess of Basic Groups, $B_0 > A_0$

Condition of Electrical Neutrality

The basic group concentration is B_0 , and the acidic group concentration is A_0 . Because the fiber contains an excess of basic groups and the solution is assumed to be acidic or neutral, the acidic groups in fibers such as wool and polyamides will be essentially fully dissociated.⁵⁻⁸ The initial stages of sorption of an anionic dye will be equivalent to the titration of the excess of basic groups by the dye acid HD.^{6,7} Equation (3) reduces to the form

$$\frac{B_0}{1 + (K_B/\lambda \cdot K_H \cdot C_H^s)} = A_0 + C_D^f + C_X^f + C_{OH}^f = A_0 + P_2 \cdot C_D^f \quad (4)$$

The dimensionless group P_2 defines the degree of ion exchange competition for sorption by the polymer, between the dye anion and the inorganic anions.

$$P_2 = 1 + \frac{K_X \cdot C_X^s}{K_D \cdot C_D^s} + \frac{K_{OH} \cdot C_{OH}^s}{K_D \cdot C_D^s} \quad (5)$$

P_2 is analogous in form to the corresponding parameter P_2 for the sorption of a cationic dye by a fiber containing only a single acidic group, as described elsewhere.³

To ensure that the remaining dimensionless groups in this paper describe by subscript essentially the same effects as do those in Ref. 3, a new dimensionless group P_5 is introduced here, out of numerical sequence.

$$P_5 = A_0/B_0 \quad (6)$$

Rearrangement of eq. (4) to give an expression for the Donnan coefficient λ , when followed by the introduction of P_5 and the relative dye sorption $\Theta_D = C_D^f/B_0$, and by the combination of variables to give the new dimensionless group P_1 , where

$$P_1 = \frac{K_H \cdot K_D \cdot C_H^s \cdot C_D^s}{K_B \cdot B_0} \quad (7)$$

gives

$$\lambda = \frac{K_B \cdot (P_5 + P_2 \cdot \Theta_D)}{K_H \cdot C_H^s \cdot (1 - P_5 - P_2 \cdot \Theta_D)} \quad (8)$$

Substitution for λ from the ionic distribution equation $C_D^f = (1/\lambda) \cdot K_D \cdot C_D^s$ leads to the expressions

$$\frac{\Theta_D \cdot (P_5 + P_2 \cdot \Theta_D)}{(1 - P_5 - P_2 \cdot \Theta_D)} = P_1 \quad (9)$$

and

$$\Theta_D = \frac{-(P_5 + P_1 \cdot P_2)}{2P_2} \left\{ 1 - \left[1 + \frac{4 \cdot P_1 \cdot P_2 \cdot (1 - P_5)}{(P_5 + P_1 \cdot P_2)^2} \right]^{1/2} \right\} \quad (10)$$

The Fiber Contains Only a Basic Group

If there is only a basic group, $P_5 = 0$, and eqs. (9) and (10) become formally identical to the dimensionless equations for the sorption of a cationic dye by

a fiber containing a single acidic group [eqs. (10) and (11) of Ref. 3], though the definitions of P_2 and P_1 are different.

If the product $P_1 \cdot P_2$ of eq. (10) is very small, the ionization of the basic groups will change as the dye acid HD is sorbed, and

$$\Theta_D = (P_1/P_2)^{1/2} \quad (11)$$

so that Θ_D varies as the square root of P_1 when P_2 is held constant: This is shown in Figure 1 by the initial slopes of the theoretical plots of $\log \Theta_D$ against $\log P_1$, for selected constant values of P_2 .

If $P_1 \cdot P_2$ is very large, the basic groups will be fully protonated, and changes in dye sorption will be determined entirely by ion-exchange processes. The dye uptake is now independent of P_1 but inversely proportional to P_2

$$\Theta_D = (1/P_2) \quad (12)$$

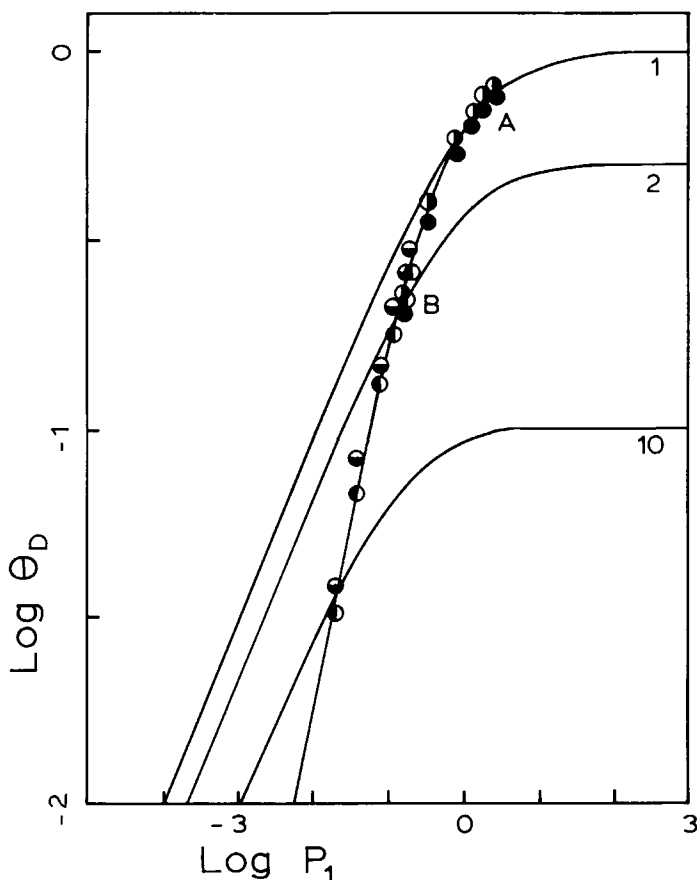


Fig. 1. Sorption curves for polymer with a basic group only. The numbers near the curves are for P_2 . The data points are for aminopolypropylene and Orange 1 at 91°C (●) and 76°C (○) and for Orange 8 at 91°C (●) and 76°C (○).¹³

as can be seen from the limiting levels of Θ_D at high values of P_1 in Figure 1. It follows from eq. (12) and the definition of P_2 that

$$\frac{\Theta_D}{1 - \Theta_D} = \frac{1}{P_2 - 1} = P_3 \quad (13)$$

Neglecting the hydroxyl ion concentration,

$$P_3 = \frac{K_D \cdot C_D^s}{K_X \cdot C_X^s} \quad (14)$$

and P_3 is formally analogous to parameter P_3 of Ref. 3.

Such ion exchange processes will lead to a simple Langmuir sorption isotherm for the dye, if the competing anion concentration C_X^s is held constant while C_D^s is varied.

In intermediate situations, the sorption isotherm will reflect some combination of ion-exchange competition and titration of the basic group. Experiments in which P_2 is held constant while P_1 is varied offer the possibility of estimating P_2 and P_3 independently of P_1 .

When data are obtained at a constant pH in a buffer system, P_2 is not constant: A decrease in P_1 then represents a decrease in the concentration of the acid anion or dye anion, with a corresponding increase in competition from the buffer anion. A new dimensionless parameter P_4 can be used in this situation, so defined that

$$P_1 \cdot P_2 = P_1 + P_4 \quad (15)$$

and

$$P_4 = \frac{K_H \cdot K_X \cdot C_H^s \cdot C_X^s}{K_B \cdot B_0} \left(1 + \frac{K_{OH} \cdot C_{OH}^s}{K_X \cdot C_X^s} \right) \quad (16)$$

Neglecting the hydroxyl ion concentration,

$$P_3 = (P_1/P_4) \quad (17)$$

P_4 will remain constant in this type of experiment if $K_H \cdot K_X/K_B$ is constant.

An Excess of Acidic Groups, $A_0 \geq B_0$

For polyamides containing an excess of acidic groups over basic groups, the uptake of simple acids,^{7,12,16} and of anionic dyes,^{5,16} supports the idea that the basic groups will be essentially fully protonated in neutral or acidic aqueous solutions. The electrical neutrality condition becomes

$$\frac{A_0}{1 + (\lambda \cdot K_H \cdot C_H^s/K_A)} = B_0 - P_2 \cdot C_D^f \quad (18)$$

with P_2 as defined in eq. (5). Equation (18) will apply only at pH values low enough to ensure that the cations are the co-ions in the system. Retaining the previous definition of P_5 , and proceeding as before, it follows that

$$\frac{\Theta_D \cdot (P_5 - 1 + P_2 \cdot \Theta_D)}{(1 - P_2 \cdot \Theta_D)} = P_1 \quad (19)$$

and

$$\Theta_D = -\frac{(P_5 - 1 + P_1 \cdot P_2)}{2P_2} \left\{ 1 - \left[1 + \frac{4P_1 \cdot P_2}{(P_5 - 1 + P_1 \cdot P_2)^2} \right]^{1/2} \right\} \quad (20)$$

Since the sorption behavior is now dependent on the titration of the acidic group, P_1 is dependent on K_A :

$$P_1 = \frac{K_H \cdot K_D \cdot C_H^s \cdot C_D^s}{K_A \cdot B_0} \quad (21)$$

When $A_0 = B_0$, as is approximately true for some regular-dyeing nylon 6 polymers, and for wool, eqs. (19) and (20) also become formally identical with eqs. (10) and (11) for cationic dyeing in Ref. 3. Equation (15) leads to a new but analogous definition of P_4 :

$$P_4 = \frac{K_H \cdot K_X \cdot C_H^s \cdot C_X^s}{K_A \cdot B_0} \left(1 + \frac{K_{OH} \cdot C_{OH}^s}{K_X \cdot C_X^s} \right) \quad (22)$$

In terms of the existing parameter P_2 and the newly defined parameters P_1 and P_4 , the expected behavior for $A_0 = B_0$ is formally identical with that shown in Figures 1 and 2 for a solid polymer containing only a single basic group B and with that shown in Figure 1 of Ref. 3 for the sorption of a cationic dye by a fiber containing only a single acidic group.

GRAPHICAL ANALYSIS OF EXPERIMENTAL DATA

Independence and Uses of Dimensionless Groups

P_1 , P_2 , P_3 , P_4 , and P_5 are not truly independent dimensionless groups, because they share common parameters and concentration variables.

For a model system in which all parameters such as K_H , K_D , K_A , and K_B are constants, selected groups such as P_1 and P_2 can be changed independently by appropriate control of the ion concentrations in solution. The use of P_1 and P_2 is then equivalent to testing the experimental data against this simple model.

Possible advantages in the use of parameters such as P_1 and P_2 are in their representation of distinct effects common to different systems, in emphasizing common mathematical structures in the analysis of these systems, in facilitating the graphical analysis and interpretation of experimental data, and in the avoidance of unwarranted assumptions about individual parameters through making explicit the dependence of the basic group titration behavior, for ex-

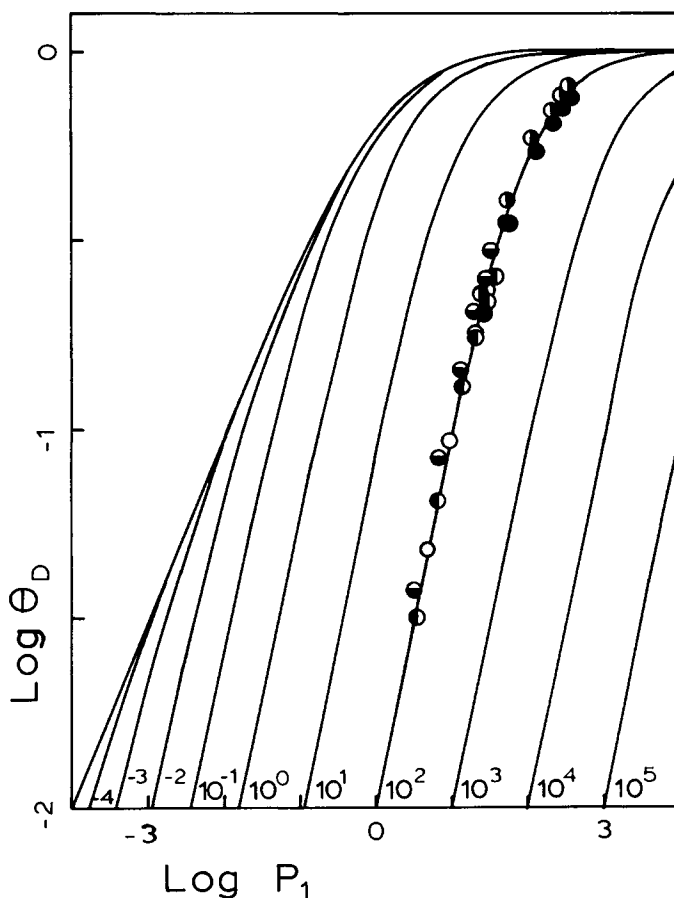


Fig. 2. Polymer with a basic group only: dependence on P_4 . The numbers assigned to the curves are for P_4 . Only the exponent is shown for some curves. The data from Figure 1 are replotted for the ion-exchange assumption, using the same symbols as given for Figure 1, and with the addition of data for Cibalan Grau BL at 76°C (○).¹³

ample, on each one of the specific parameters and concentration variables that constitute P_1 .

In addition, the numerical ranges of the dimensionless groups P_1 – P_5 are normalized on scales that are common to all other systems. Systems which have similar values for their dimensionless groups should behave similarly.

Graphical Method of Data Analysis

The graphical method³ proceeds as follows: the experimental data are reduced to graphical plots of $\log C_D^f$ as ordinate against $\log(C_H^s \cdot C_D^s)$ as abscissa, using the same scales as theoretical plots of $\log \Theta_D$ against $\log P_1$. The experimental data plots are then superimposed on the theoretical plots.

Vertical shifts of the data plots adjust for limited accessibility of the acidic and basic groups in a polymer. The basic groups in solid polyamides are not always completely available to the anions of acids,⁷ nor to chemical reagents such as 2,4-dinitrofluorobenzene.⁹ The basic group concentrations accessible

to HCl in the undrawn nylons of Ref. 7 ranged from 84 to 87% of the basic group concentrations determined by titration of the dissolved polymer. The accessibility of the basic groups in crystalline nylon 6 films to 2,4-dinitrofluorobenzene ranged from 95 to 77%, decreasing with increasing polymer crystallinity.⁹

When the vertical adjustment has been made, lateral shifts of the experimental curves to fit a given theoretical curve will lead to a correspondence between the theoretical $\log P_1$ abscissa scale and the experimental $\log(C_H^s \cdot C_D^s)$ abscissa scale. It is then possible to calculate $K_H \cdot K_D/K_B$, or $K_H \cdot K_D/K_A$, because the vertical shifts have determined B_0 .

The groups $K_H \cdot K_D/K_B$ and $K_H \cdot K_D/K_A$ are all that can be determined without additional information or assumptions. This approach makes explicit the dependence of the behavior on all of the parameters K_H , K_D , and K_B or K_A , and thus reveals the mutual interactions of assumptions about any one of these parameters.

The focusing of attention on the concentration product $C_H^s \cdot C_D^s$ accommodates some of the criticisms that have been made of the Donnan theory of wool dyeing.^{10,11} The graphical method is intended to facilitate the understanding and interpretation of experimental data by its presentation against a visual background of alternative patterns of behavior, and to provide estimates of parameter values.

Once the parameters P_2 , P_5 , and B_0 are known, it is of course possible, for example, to use standard linear regression analysis on plots of $\log P_1$ against $\log C_H^s \cdot C_D^s$ to obtain statistical estimates of $K_H \cdot K_D/K_B$ or $K_H \cdot K_D/K_A$, where P_1 is now calculated from the experimental data using the expression on the left hand side of eq. (9) or eq. (19).¹²

Amino Polypropylene

The graphical method will first be applied to the data of Ferrini and Zollinger for the dyeing of amino polypropylene with acid and premetallized dyes.¹³ Their data for Orange 8 have been made coincident with the curve for $P_2 = 1$ in region A of Figure 1, as outlined above. The measured basic group content of the polymer (0.66 mol/kg) could be used for B_0 . The data for Orange 1 were made coincident with the Orange 8 data in region B, using the same B_0 value. The combined data define an average curve which deviates increasingly from the basic group titration curve for $P_2 = 1$ as P_1 decreases, suggesting a variable competing anion effect.

The dyeing data were obtained at a constant pH of 3.73 in a buffer system containing 0.05 *M* sodium acetate, so that for these data a decrease in P_1 represents a decrease in dye concentration, with a corresponding increase in competition from the acetate buffer anion. The dimensionless parameter P_2 is not constant in this type of experiment.

Figure 2 shows theoretical curves for the new parameter set P_1 and P_4 . The data from Figure 1 can be superimposed on Figure 2 and displaced laterally to give a reasonable fit to any of the curves for $P_4 \geq 1$ in Figure 2, so that there is no basis for estimating P_1 and P_4 separately.

The curve for $P_4 = 100$ is the first curve in Figure 2 to approximate closely the requirement for pure anion exchange that $\Theta_D = 0.5$ when $P_3 = 1$, and $P_1 = P_4$. The data for Orange 8, Orange 1, and Cibalan Grau BL have been made

coincident with this curve to illustrate the general goodness of fit. The data for Orange 2 are not shown because they agree so closely with the data for Orange 1 that they would confuse the plot. Detailed curve fitting for each data set gives the parameter estimates of Table I.

As an example of the graphical procedure, when the $\log C_D^f$ versus $\log C_H^s \cdot C_D^s$ data plot for Orange 8 at 76°C is fitted to the curve for $P_4 = 100$ in Figure 2, the ordinate for $\log P_1 = 0$ coincides with the ordinate for $\log(C_H^s \cdot C_D^s) = -8.80$, and so $\log(K_H \cdot K_D/K_B \cdot B_0) = 8.80$.

This result is based on the assumption that $P_4 = 100$, but, since $\log(C_H^s \cdot C_X^s) = -5.03$ for the acetate buffer solution, this assumption gives $\log(K_H \cdot K_X/K_B \cdot B_0) = 7.03$, and so $K_D/K_X = 58.9$ for Orange 8 at 76°C. The same result is also obtained from the curves for higher P_4 values since they are all displaced one log unit to the right in Figure 2 for each log unit of increase in P_4 .

This tortuous procedure can obviously be avoided by assuming the validity of the ion-exchange model and using eqs. (13) and (14) as the basis for determination of K_D/K_X . This simpler alternative may however fail to reveal the potential uncertainty of the ion-exchange assumption.

It is not possible to determine the products $(K_H \cdot K_D/K_B \cdot B_0)$ and $(K_H \cdot K_X/K_B \cdot B_0)$ without additional experiments, but the assumption that this is a pure anion exchange process leads to interesting estimates of the ratios K_D/K_X for the dye anions and the acetate anion.

The data in Table I are in agreement with Ferrini and Zollinger's analysis, which also used the anion exchange assumption but was based on the determination of Langmuir isotherm constants K_L from standard Scatchard plots of C_D^f/C_D^s against C_D^f .¹³ These authors converted their K_L data into apparent standard affinities for the dyeing processes.

The anion exchange processes of Table I are exothermic, and the nonaggregating dye Orange 8 behaves very differently from all the other dyes, which show a much lower ability to compete with the acetate anion for uptake by the amino polypropylene. The K_D/K_X values are much smaller than would be expected for the same dyes and the less hydrophobic polyamide fibers, as implied by the data in Table III.

K_L in Table I is the Langmuir isotherm constant which would be obtained if the site content were constant for all dyes and equal to B_0 , as required by the ion-exchange assumption. Figure 2 in Ref. 13, however, shows Scatchard plots which extrapolate to lower site contents as the substantivity of the dye for the aminopolypropylene decreases, so that, for these dyes, P_1 is probably smaller than required by the ion exchange assumption, and the dye sorption is probably determined by some mixture of basic group titration and anion ex-

TABLE I
Anion Exchange Parameters for Acid Dyes and Acetate Anions in Amino-Polypropylene¹³

Dye	Temp (°C)	K_D/K_X	$K_L = (K_D/K_X \cdot C_X^s)$
Orange 8	76	59	1,180
	91	47	936
Orange 1	76	5.9	118
	91	4.5	90
Cibalan Grau BL	76	7.4	147

change. Alternatively, the basic groups may be less accessible to the dyes of lower substantivity.

Polyamides

Table II summarizes the end group contents of the polyamides to be discussed in the following sections of this paper, as determined by titration of dissolved polymer. The isotherm tests are based on the effective end group contents obtained when A_0 and B_0 are multiplied by the fractional accessibility values given in Table II.

The use of such accessibility corrections can lead to error if the effects shown at high P_1 values in Figure 1, or in Figure 3, are present but not recognized to be so, and the observed plateaus are used to estimate accessibility.

The "deep-dyeing" polyamides often contain an excess of basic groups over acidic groups. If anion exchange competition is negligible, then $P_2 = 1$ and eq. (10) predicts the behavior shown in Figure 3 for different values of the acidic to basic group ratio P_5 , for $P_5 < 1$.

In reality, there will be a gradual transition from the first stage of titration of the excess of basic groups to the second stage of back titration of the ionized acidic groups, so that at best an inflexion in the sorption curve will be seen, rather than the clear plateaus at high P_1 values in Figure 3. In addition, the onset of electrolyte sorption at high P_1 values will further complicate the picture,^{1-3,7} not to mention the possibility of protonation of the amide groups.⁷

Wall and Beresiewicz could find no satisfactory theoretical explanation of their experimental data for the first stage of the sorption of hydrochloric acid at 14°C for polyamide 1.⁷ These data have been plotted to the left in Figure 3 to make clear the deviations from the present model, and to avoid confusing the other data comparisons. To obtain the parameter estimates for $K_H \cdot K_D / K_B$ in Table III, the data were fitted to a curve for $P_5 = 0.19$ at $\log \Theta_D = -0.5$, using the observation by Wall and Beresiewicz that only 84% of the acidic and basic groups are accessible to the acid. The values in parenthesis in Table III were obtained by linear extrapolation of plots of $\log K_H \cdot K_D / K_B$ against $1/T(K)$.

The data of Iijima et al.¹² for the sorption of ethane sulfonic acid at 50°C by polyamide 2 fit the theoretical curve for $P_5 = 0.18$ in Figure 3 quite well. The graphical estimate of $K_H \cdot K_D / K_B$ in Table III is close to that obtained independently from a linearized data plot.¹²

TABLE II
Polyamide Polymer Characteristics

Number	Polyamide	$10^3 \times A_0$ (meq/kg)	$10^3 \times B_0$ (meq/kg)	P_5	Access. fraction	Ref.
1	Undrawn 66 fiber	27	142	0.190	0.84	7
2	Undrawn 6 film	16.4	92.4	0.178	1.00	12
3	Drawn 6 fiber	21.3 ± 0.25	65.8 ± 2.2	0.324	1.00	14
4	Drawn 6 fiber	57.3 ± 0.25	50.0 ± 2.5	1.15	0.84	14
5	Drawn 6 fiber	75.3 ± 0.3	19.2 ± 0.8	3.92	0.94	14
6	Undrawn 66 fiber	73	42	1.74	0.87	7

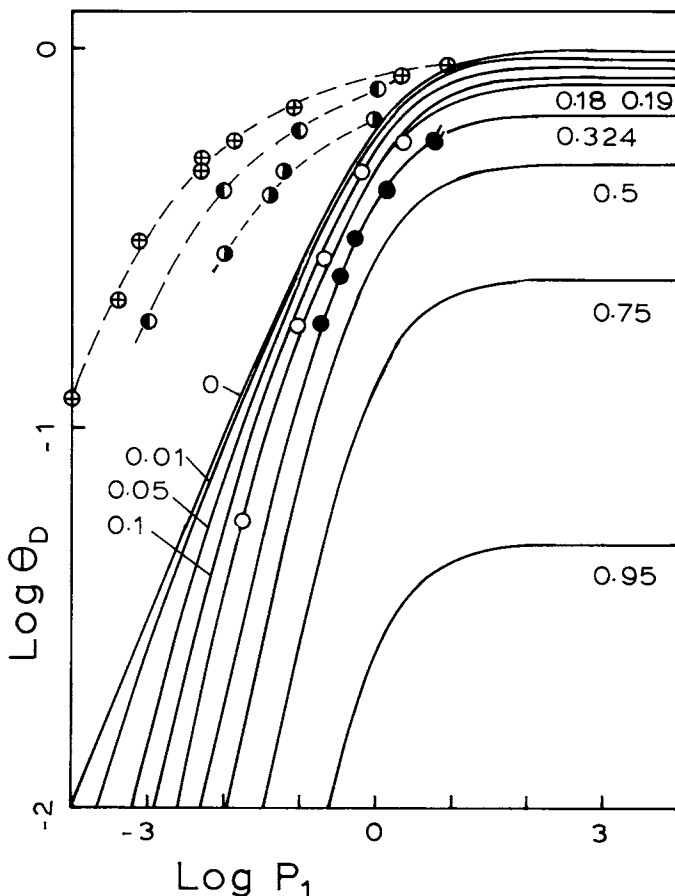


Fig. 3. Polymer with acidic and basic groups, and $B_0 > A_0$. The numbers assigned to the curves are for P_5 , and it is assumed that $P_2 = 1$. At low Θ_D values the curves for $P_5 = 0.18$ and 0.19 are so similar that here only the curve for $P_5 = 0.18$ is drawn. The data points are for hydrochloric acid and polymer 1 at 14°C (\oplus), 34.7°C (\bullet), and 50°C (\bullet)⁷; for ethane sulfonic acid and polymer 2 at 50°C (\circ)¹²; and for C. I. Acid Blue 25 and polymer 3 at 95°C and pH 7.5 (\bullet) and pH 6.1 (\bullet)¹⁴.

Dye sorption measurements at 95°C with C. I. Acid Blue 25 and polyamide 3¹⁴ also agree quite well with the appropriate theoretical curve in Figure 3. In addition, data obtained at pH 7.5 fall on the same curve as data obtained at pH 6.1, confirming the dependence of the behavior on the ionic product $C_H^i \cdot C_D^i$. The estimates of $K_H \cdot K_D / K_B$ for C. I. Acid Blue 25 in Table III are 4 orders of magnitude higher than is estimated for chloride ion at 95°C .

Figure 4 shows theoretical plots of $\log \Theta_D$ against $\log P_1$ for $P_2 = 1$ and for $P_5 \geq 0$. The effects of increases in the acidic to basic group ratio P_5 are most pronounced at low P_1 values and have a great effect on the shape of the sorption isotherm. Low P_1 values can be produced by low dye concentrations, by higher pH values, and by dyes with low distribution coefficients K_D . These are all conditions under which the "differential-dyeing" polyamides, which contain different ratios of acidic and basic groups, show their greatest differences in acid dyeability.¹⁷

TABLE III
 Sorption Parameters for Polyamides

Anion D sorbed	Temp (°C)	Log ($K_H \cdot K_D / K_A$)	Log ($K_H \cdot K_D / K_B$)	Log (K_D / K_{Cl})	Data reference
Chloride	(95)	(5.14)	(7.40)		7
	55.5	5.69			7
	50.0	(5.74)	8.50		7
	34.8	5.91			7
	34.7		8.99		7
	20	6.11			16
	18	6.31			7
	14		9.65		7
Ethane sulfonate	50	4.94		(-0.80)	12
				(-1.66)	12
				(graphical)	
C. I. Acid Blue 25	95	9.54 (5)		(4.40)	14
C. I. Acid Blue 25	95	9.78 (4)		(4.64)	14
C. I. Acid Blue 25	95		11.32 (3)	(3.92)	14

Note: ($K_H \cdot K_D / K_A$) and ($K_H \cdot K_D / K_B$) are calculated for accessible B_0 values based on the weight of the polymer. Data in parenthesis are obtained by interpolation or extrapolation of Arrhenius plots for the temperature dependence of the behavior for hydrochloric acid. The numbers in parentheses after the C. I. Acid Blue 25 data identify the polyamide fiber used (Table II).

The data for C. I. Acid Blue 25 and polyamides 3, 4, and 5 were obtained at 95°C, and pH 6.1 and pH 7.5 in buffered dyebaths 0.012 *M* in phosphate anion.¹⁴ A satisfactory fit for polyamide 4 with $P_5 = 1.15$ in Figure 4 required the assumption that only 84% of the end groups are accessible to dye. The data at pH 6.1 again combined with data at pH 7.5 to define a single pattern of behavior. Polyamide 5 gave a satisfactory fit to the curve for $P_5 = 3.9$ with the assumption that 94% of the end groups in this fiber are accessible to the dye. Since the values of $K_H \cdot K_D / K_A$ in Table III are four orders of magnitude greater than was found for hydrochloric acid, it seems unlikely that ion exchange competition from the inorganic buffer anions was significant in these dyeing experiments.

The data for the sorption of HCl by polyamide 6 were taken from Figure 4 of Wall and Beresniewicz,⁷ and agree well at lower P_1 values with the curve for $P_5 = 1.74$, assuming that 87% of the end groups are accessible as reported by Wall and Beresniewicz. The HCl sorption data drop below the theoretical curve at higher P_1 values, which is consistent with the different theoretical model proposed in Ref. 7.

The data in Figures 3 and 4 confirm the importance of the parameter P_5 in modifying the behavior of the ion sorption processes. This has long been recognized in the scientific literature,^{5-7,12,16} but the graphical plots in Figure 4 show clearly that the effects of increases in P_5 are most pronounced at the lower P_1 values which accentuate the differences between the acid dyeing behavior of the differential dyeing polyamides.¹⁷

Table III summarizes the parameter values obtained from the graphical procedure. The ethane sulfonic acid anion has a lower ionic distribution coefficient than the chloride ion, and K_D for the anion of C. I. Acid Blue 25 is four orders of magnitude greater than that for the chloride ion.

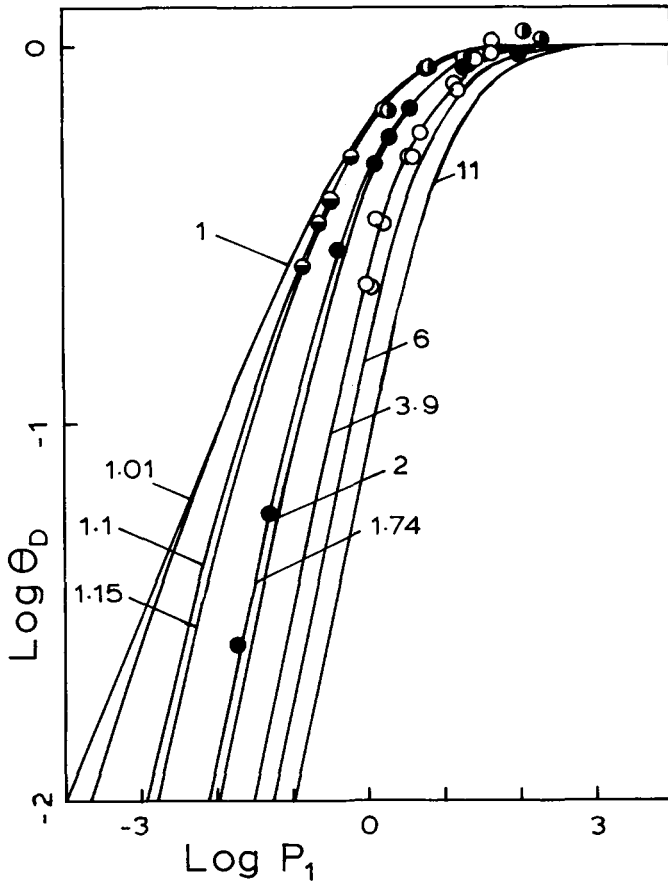


Fig. 4. Polymer with basic and acidic groups, and $A_0 > B_0$. The numbers associated with the curves are for P_5 . It is assumed that $P_2 = 1$. The data are for C. I. Acid Blue 25 and polymer 4 at 95°C, and at pH 7.5 (●) and pH 6.1 (○); for C. I. Acid Blue 25 and polymer 5 at 95°C, and at pH 6.1 (○)¹⁴; and for hydrochloric acid and polymer 6 at 55.5°C (●).⁷

For a nylon 66 fiber of unspecified acidic and basic end group content, and using a different approach, Grieder obtained the estimate $\log K_D = 3.5$ at 95°C for C. I. Acid Blue 25.¹⁵ Grieder's assumption that the inorganic ions are in an internal solution occupying 0.07 l/kg of fiber implies that $K_{Cl} = 0.07$ for concentrations based on the fiber weight, so that $\log K_D/K_{Cl} = 4.7$, in good agreement with the data in Table III for polyamide 4.

Temperature Effects

The tendency for zwitterions to form by mutual ionization of the basic and acidic groups is indicated by the parameter K_z ,⁷

$$K_z = K_A/K_B \quad (23)$$

which can be estimated from the data in Table III. The standard enthalpy change, calculated from the temperature dependence of $K_H \cdot K_D/K_B$ for hydrochloric acid ($\Delta H^0 = -13.5$ kcal/mol) is almost twice that for $K_H \cdot K_D/K_A$ (ΔH^0

= -7.2 kcal/mol). The tendency for zwitterion formation decreases markedly as the temperature increases,⁷ and so the numerical values of $K_H \cdot K_D/K_A$ and $K_H \cdot K_D/K_B$ move closer together. Any inflexion in the sorption curves accompanying a transition from titration of basic groups to titration of acidic groups or vice versa will become more difficult to detect as the temperature increases.

CONCLUSIONS

The data presented in this paper are used primarily to illustrate a graphical method of data analysis, rather than to establish the correctness of a given theoretical approach.

The graphical method of data analysis based on dimensionless groups allows experimental data to be evaluated against a visual background of alternative assumptions, or alternative sorption models, which can be useful. Mathematical features and patterns of behavior common to different ionic sorption models are made clear. In particular the dependence of the sorption behavior on specific groups of parameters is shown, thus making explicit the fact that assumptions about any one of these parameters will necessarily affect the conclusions reached about the others.

The dependence of the sorption of an acid, or of an acid dye, on the properties and solution concentrations of both ions is emphasized, as it should be.^{7,10,12}

The formulation in terms of dimensionless groups keeps in focus those parameters and concentrations about which assumptions must be made, or for which measurement strategies must be devised.

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