

The Sorption of Ions by Polyamides

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Synopsis

An analysis is given of the principal thermodynamic factors that influence the distribution of an ion between a macroscopically homogeneous polymer phase and a second homogeneous phase and a general method is proposed for the computation of the equilibrium ion sorptions in well-defined model systems. Particular attention is paid to the sorption of ions by polymers containing ionizable groups and the method is used to clarify some of the current problems in the theoretical explanation of the mechanism of sorption of acid dye anions by polyamide fibers. The method is applicable in principle to any dyeing system in which the fiber phase may be regarded at equilibrium as a macroscopically homogeneous, equipotential volume.

INTRODUCTION

Many different models have been proposed for the mechanism of sorption of acid dye anions by polyamides.¹⁻¹⁰ Although several of these models can give a comparatively good description of the shape of the sorption isotherms in the "amine dyeing" region, they are generally oversimplified to facilitate calculation and their molecular basis is often uncertain.^{11,12}

The amine endgroups of the fiber play a key role in these models, but the explanations offered for the importance of these groups are varied. No satisfactory explanation has yet been offered for the experimentally observed dependence of the equilibrium dye sorptions on the amine endgroup contents of different polymers, at different pH values and for dye anions of differing ionic charge and "affinity."

There is considerable interest at the present time in the deliberate modification of the nature and concentration of the endgroups or side chain groups in a polymer in order to obtain special effects in dyeing.

It therefore seemed useful, both theoretically and practically, to attempt to formulate the problem in a general way in order to compute the behavior to be expected of a given model system and to illustrate the importance of factors such as the "affinity" of the dye anion, the charge on the dye anion, and the pH at which dyeing occurs.

In this paper we present a theoretical model which embodies a minimum of assumptions about the mechanism of sorption and which appears to be able to explain many of the features of the sorption of ionic dyes by substrates that contain ionizable groups.

THEORETICAL

List of Symbols

| | |
|---|--|
| A_j concentration of basic groups of type j in the fiber | K_i partition coefficient for ion i |
| A_j^+ concentration of ionized basic groups of type j in the fiber | K_1 partition coefficient for hydrogen ion ($i = 1$) |
| B_k concentration of acidic groups of type k in the fiber | λ Donnan coefficient |
| B_k^- concentration of ionized acidic groups of type k in the fiber | \ln natural logarithm |
| C^+ net concentration of positive charges on the fiber as a consequence of the ionization of fiber groups | μ_i^{of} standard chemical potential of ion i in fiber |
| C_i^f concentration of ion i in fiber | μ_i^{os} standard chemical potential of ion i in dyebath |
| C_i^s concentration of ion i in dyebath | $-\Delta\mu_i^0 \equiv (\mu_i^{os} - \mu_i^{of})$ "standard affinity" for the distribution of ion i between phases f and s |
| C_1^f hydrogen ion concentration in fiber ($i = 1$) | $-\Delta\mu_i^0$ "apparent standard affinity" |
| C_1^s hydrogen ion concentration in dyebath ($i = 1$) | $\Delta P \equiv (P^f - P^s)$ pressure difference between phases f and s |
| exp exponential function; $\exp(x) = e^x$ | $\Delta\varphi \equiv (\varphi^f - \varphi^s)$ electrical potential difference between phases f and s |
| F the Faraday | R the gas constant |
| $F(\lambda)$ function of λ | T absolute temperature |
| $F'(\lambda)$ derivative of $F(\lambda)$ | \bar{v}_i partial molar volume of ion i (assumed independent of pressure P) |
| γ_i^f an activity coefficient for ion i in fiber | z_i charge on ion i (including sign) |
| γ_i^s an activity coefficient for ion i in dyebath | K_{A_j} dissociation coefficient for basic group A_j |
| | K_{B_k} dissociation coefficient for acidic group B_k |

Basic Equations

Distribution of an Ion Between Two Phases

The distribution of an ion i between two uniformly accessible and homogeneous phases f and s may be described by the following equation¹²:

$$\frac{C_i^f}{C_i^s} = \exp \left\{ -\frac{\Delta\mu_i^0 + \bar{v}_i\Delta P + z_i F\Delta\varphi + RT \ln(\gamma_i^f/\gamma_i^s)}{RT} \right\} \quad (1)$$

Surface adsorption on any phase at the interface is ignored. It has been assumed that the chemical ($\Delta\mu_i^0$), mechanical ($\bar{v}_i\Delta P$), and electrical ($z_i F\Delta\varphi$) work terms may be separated and that activity coefficients, for example, may be defined for each single ionic species.¹³

Only a certain fraction of a fiber volume is accessible to any given ion, and so it is necessary to introduce structure factors χ_i into eq. (1) to take account of such effects.

In view of the dependence of the structure of a polymer on its previous history and on the immediate conditions of experiment, it might be argued that the application of simple thermodynamic treatments to such systems is unsound. If we bear this reservation in mind and recognize that the structure factors χ_i will in general be complex functions of the previous history of the polymer and of the prevailing experimental conditions, we may nevertheless use these factors in a formal sense and rewrite eq. (1) in the form

$$\frac{C_i^f}{C_i^s} = \exp \left\{ -\frac{\Delta\mu_i^0 + \bar{v}_i\Delta P + z_i F\Delta\varphi + RT \ln (\gamma_i^f/\gamma_i^s) + RT \ln \chi_i}{RT} \right\}. \quad (2)$$

For simplicity in what follows, we define "apparent standard affinity" as follows:

$$-\overline{\Delta\mu_i^0} \equiv -\{\Delta\mu_i^0 + \bar{v}_i\Delta P + RT \ln (\gamma_i^f/\gamma_i^s) + RT \ln \chi_i\} \quad (3)$$

and a partition coefficient by

$$K_i \equiv \exp\{-\overline{\Delta\mu_i^0}/RT\} \quad (4)$$

If we now define a Donnan coefficient in the form

$$\lambda \equiv \exp \left\{ -\frac{F\Delta\varphi}{RT} \right\}, \quad (5)$$

it is possible to rewrite eq. (2) in the simple form

$$C_i^f = \lambda^{z_i} K_i C_i^s. \quad (6)$$

The distribution of any ion between the two phases depends on the electrical potential difference between the two phases, through the factor λ^{z_i} , so that the sign and magnitude of the charge on the ion (z_i) is one fundamental parameter determining the sorption behavior.

The partition coefficient K_i is the remaining fundamental parameter and is related to the "apparent standard affinity" $-\overline{\Delta\mu_i^0}$ by eq. (4). It is clear from eq. (3) that neither $-\overline{\Delta\mu_i^0}$ nor K_i will in general be constants—they will vary with experimental conditions through the terms in the parentheses in eq. (3). These terms make it possible in principle to define the effects of polymer structure, of interactions between the components of the system, and of aggregation or special adsorption phenomena on the sorption behavior; only the standard chemical potential difference $-\Delta\mu_i^0$ in eq. (3) is by definition a constant for a given temperature T .

In separating the electrical terms from the other terms, it becomes implicit that any differences in the distribution of the ionic groups in a dye molecule will be reflected as differences in the "affinity" factors $-\overline{\Delta\mu_i^0}$ and K_i , since z_i remains constant.

We may use the two parameters z_i and K_i as the determining factors for the sorption of any ion by any polymer, but we must also consider the role played by the ionizable groups in the fiber.

So as to obtain the simplest possible model, we shall assume initially that

there are no specific binding forces between the ionizable groups of the polymer and any other ion except the hydrogen ion. The theory is readily modified to take such interactions into account, and we wish to see if such a modification is really necessary.

Instead, we assume that the ionizable groupings are important only insofar as they affect the charge on the fiber and must be included in the electrical neutrality conditions. Since some potentially ionizable groupings may be inaccessible or ineffective by virtue of their occlusion in the more ordered regions of the polymer, it may be necessary to introduce additional structure factors to take account of this effect. This complication has been ignored in setting up this preliminary simple model of the sorption process.

Electrical Neutrality in Phases f and s

The condition of electrical neutrality in the dyebath or solution phase s requires that

$$\sum_i z_i C_i^s = 0. \quad (7)$$

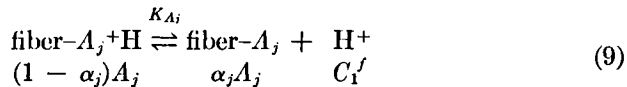
For electrical neutrality in the fiber phase f we require that

$$C^+ + \sum_i z_i C_i^f = 0 \quad (8)$$

where C^+ , the net positive charge on the polymer matrix as a consequence of the ionization of fiber groupings, is a function of the hydrogen ion concentration C_1^f in the fiber.

Ionization of Fiber Groups

Basic Groups. We postulate the dissociation equilibrium



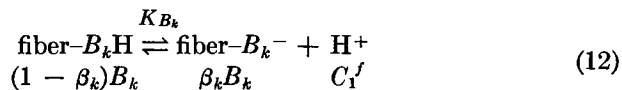
where α_j is the fraction of basic groups of type j which is uncharged or unionized, and

$$A_j^+ = (1 - \alpha_j)A_j \quad (10)$$

is the concentration of charged basic groups of type j . It follows that

$$A_j^+ = \frac{C_1^f A_j}{C_1^f + K_{A_j}}. \quad (11)$$

Acidic Groups. We assume the dissociation equilibrium



where β_k is the fraction of acid groups of type k which is ionized and

$$B_k^- = \beta_k B_k \quad (13)$$

is the concentration of charged acidic groups of type k . It is possible to show that

$$B_k^- = \frac{K_{B_k} B_k}{K_{B_k} + C_1^f} \quad (14)$$

Total Positive Charge on Polymer Matrix. We have

$$C^+ = \sum_j A_j^+ - \sum_k B_k^- \quad (15)$$

with A_j^+ and B_k^- given by eqs. (11) and (14), respectively.

In the preceding equations, the fiber is regarded as a macroscopically homogeneous equipotential volume. The dissociation coefficients K_{A_j} and K_{B_k} need not necessarily be constants since they include the effects of the activity coefficients which may be defined for the hydrogen ions in the fiber and for the ionized groups themselves.

The ionizable groups may be in an environment which is very different from a normal aqueous environment. Consequently K_{A_j} and K_{B_k} may have very different values from those characteristic of comparable ionizable groups in aqueous solution.

Equilibrium Sorption Behavior

The problem of determining the equilibrium sorption of any ion may be formulated as follows: In a given experimental situation, the partition coefficients K_i , the ionic charges z_i , the solution concentrations C_i^s , the dissociation coefficients K_{A_j} and K_{B_k} , and the ionizable group concentrations A_j and B_k will have definite values.

The equilibrium sorption of any ion is determined by all of these factors, together with the electrical potential difference $\Delta\varphi$ (through the parameter λ).

The essential problem is to find the value of λ for which eq. (8) is satisfied, i.e., we must solve the equation

$$F(\lambda) = \sum_i z_i \lambda^{z_i} K_i C_i^s + \sum_j \frac{\lambda K_1 C_1^s A_j}{\lambda K_1 C_1^s + K_{A_j}} - \sum_k \frac{K_{B_k} B_k}{K_{B_k} + \lambda K_1 C_1^s} = 0. \quad (16)$$

If the only unknown in eq. (16) is λ , the equation may be solved for λ by standard methods such as the Newton-Raphson iterative process.¹⁴ If λ is known, the equilibrium concentrations C_i^f may be calculated using eq. (6).

In principle it is possible to take into account the concentration-dependence of all of the factors in eq. (16), and the approach is general enough to be applied to any system in which ionic species distribute themselves between a macroscopically homogeneous polymer and some other homogeneous phase. It is assumed here that surface adsorption is unimportant, and this may not be a valid assumption in some systems of very high specific surface area.

Application of the Method

Computations have been made on an IBM 1800 computer using a Fortran IV program for a variety of model systems. For simplicity, the parameters K_i , K_{A_j} , and K_{B_k} have been treated initially as constants, though this is not a necessary restriction. The results of these computations will be discussed in detail in later publications, but to illustrate the usefulness of the proposed approach, we present here some preliminary calculations for a model system for the sorption of an acid dye by polyamide fibers of differing endgroup contents.

It is assumed that the dyebath contains only the free acid of the dye, together with sodium hydroxide in differing amounts to obtain different pH values. The dye anion concentration in the dyebath is held constant at 10^{-3} g-ions/l. and the dyebath pH varies from 3 to 12.

The dye anion is monobasic ($z = -1$) and the sorption of the dye anion is calculated for different values of the dye anion "affinity," as represented by K values of 1, 10, 100, 1,000, and 10,000. It is assumed that all the inorganic ions have negligible "affinity" for the polymer ($K_i = 1$).

Figure 1 shows the predicted dependence of the dye anion sorption on its

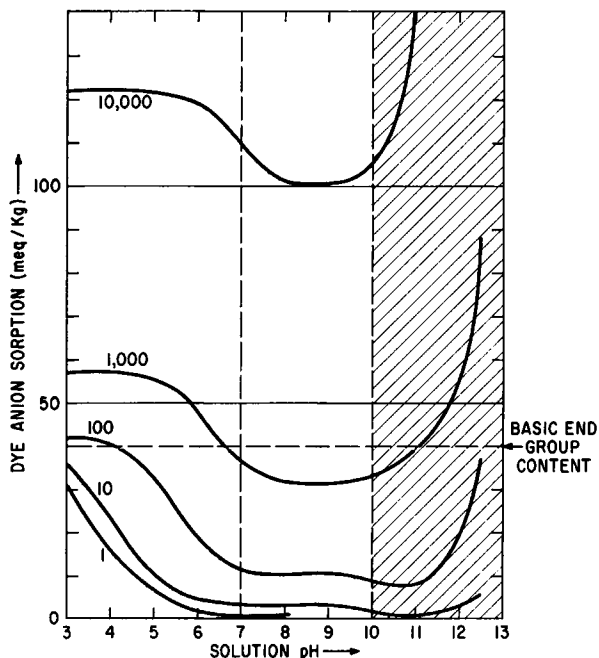


Fig. 1. Dye anion sorption as a function of dye anion affinity and pH. Numbers on curves are K values for the monobasic dye anion ($z = -1$). System contains the free dye acid (HD) and sodium hydroxide to adjust to pH value. Dye anion concentration is held constant at 10^{-3} g-ions/l. The fiber contains 40×10^{-3} equiv./kg of basic endgroups with $K_A = 10^{-10}$ and 40×10^{-3} equiv./kg of acidic endgroups with $K_B = 10^{-5}$. Shaded region includes high pH values which have not normally been used in experimental studies.

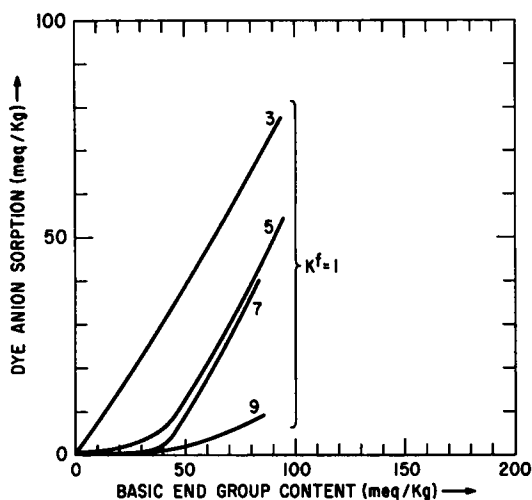


Fig. 2. Dye anion sorptions for different basic endgroup contents, dye anion affinities, and pH values. $K = 1$; numbers adjacent to curves are pH values.

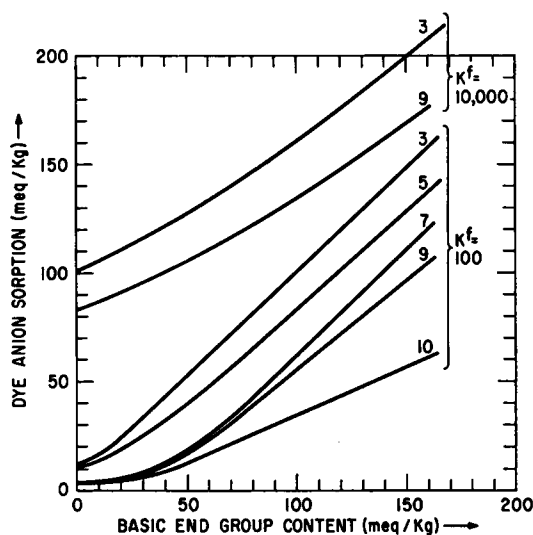


Fig. 3. Dye anion sorptions for different basic endgroup contents, dye anion affinities, and pH values. Upper two curves are for $K = 10,000$; lower curves are for $K = 100$; numbers adjacent to curves are pH values.

“affinity” (K), and on the solution pH, for a fiber which contains 40×10^{-3} equiv./kg of basic endgroups with dissociation coefficient $K_A = 10^{-10}$ and 40×10^{-3} equiv./kg of acidic endgroups with dissociation coefficient $K_B = 10^{-5}$. The possible effect of amide groups has for the present been ignored.

The variation of the dye anion sorption with pH has the anticipated form for dyes of lower “affinity.” For dyes of higher “affinity” the dye anion sorption can be greater than the basic endgroup content. There is no need

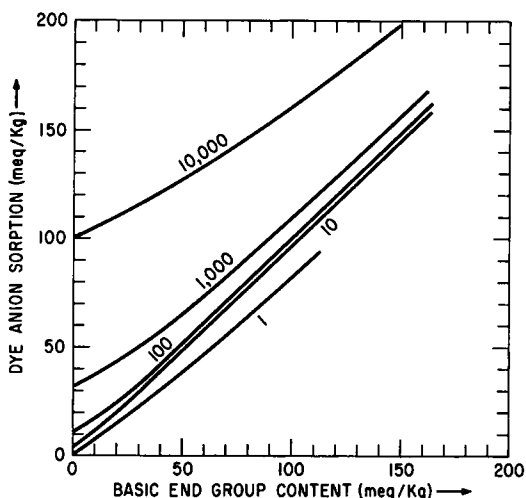


Fig. 4. Dye anion sorption at pH 3 as a function of basic endgroup content and dye anion affinity. Numbers on curves are K values for the dye anion.

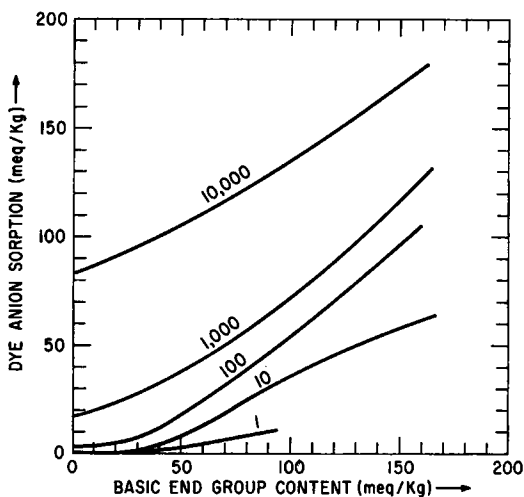


Fig. 5. Dye anion sorption at pH 9 as a function of basic endgroup content and dye anion affinity. Numbers on curves are K values for the dye anion.

to invoke a dual sorption mechanism to explain this effect—it arises quite naturally from the present analysis as an inevitable consequence of the much greater tendency of the dye anions to be sorbed by the polymer matrix. This appears to clarify the misconceptions on this point which abound in the literature on dyeing.

The dye sorbed in excess of the amine endgroup content at pH 3.5, for example, is accompanied by sodium ions and hydrogen ions to preserve electrical neutrality. This effect will be examined in more detail in a later

discussion of the sorption isotherms in these systems. The present model is able to reproduce the principal features of the sorption isotherms reported in the literature.

The unexpected increase in dye sorption at very high pH values may be attributed to the high ionic concentrations in the solution, and has been experimentally verified by us for a dye of high stability to sodium hydroxide such as C.I. Direct Yellow 12.

Similar calculations have been made for a range of polymers with different basic endgroup contents but with the same acidic group contents. The results in Figures 2 to 5 show the type of behavior to be expected at different pH values for dye anions of different "affinities" and offer a plausible explanation of the experimental behavior first noted by Palmer,¹⁵ but never subsequently clarified in theoretical terms.

CONCLUSIONS

Even in its most simple form, the theoretical model presented here can reproduce most of the features of acid dyeing of polyamides. The model is applicable to other types of dyeing systems and can in principle be made to take account of some of the more complex factors that may influence dyeing behavior.

The initial simple model is closely related to existing treatments of the sorption of acids by polyamides.¹⁶ It differs from most analyses of polyamide dyeing in that no specific interactions are assumed between the dye anion and the charged amino groups in the fiber.

Additional computations, to be discussed in detail in later papers, suggest that the carboxyl endgroups of polyamides may have a far from negligible effect on the sorption of acid dye anions, especially at higher pH values. Some measurements by Zollinger¹⁷ appear to confirm this conclusion.

Numerical computations based on this model should help to increase our understanding of the sorption of ionic dyes by fibers containing ionizable groups. For the sorption of nonionic components it is necessary only to set the appropriate $z_i = 0$.

The formal introduction of the structure factors χ_i is necessary to draw attention to the role played by the prehistory and fine structure of the polymer. If a polymer is macroscopically inhomogeneous in structure, it may not be possible to treat it as a single homogeneous phase.¹⁸

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