

A Proposed Novel Approach to the Study of the Dual-Mode Mechanism of Dyeing Nylon with Acid Dyes

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ABSTRACT: Study of the dual mode mechanism of dyeing nylon with acid dyes, consisting of Langmuir-type sorption on charged terminal amino groups, accompanied by Nernst-type uptake, known as "overdyeing," is subject to complications primarily (but not exclusively) because of structural nonhomogeneity of the polymeric substrate. We present here a system that combines structural simplicity with ease of manipulation of amine content; wherein the nylon substrate is replaced by a liquid phase consisting of a specially selected amine dissolved

in a suitable organic solvent. This system displays the characteristic features of the aforementioned dual mode dyeing mechanism, as shown by experimental data of the uptake of C.I. Orange 7 as a function of aqueous dye concentration and amine concentration in the organic phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1055–1057, 2007

Key words: adsorption; dyes/pigments; polyamides; ion exchangers; modeling

INTRODUCTION

Dyeing of nylon with acid dyes is traditionally¹ described in terms of a mechanism of sorption of the dye anion on charged terminal aminogroups, acting as Langmuir adsorption sites (designated here as "amine dyeing"), coupled with simple Nernst partition (as is commonly seen in dyeing with disperse dyes), which is observable as amine dyeing approaches saturation and is known as "overdyeing." Accordingly, the uptake of a monobasic dye (which is of specific interest to us here), at constant pH, may be described by

$$C_D = C_{D1} + C_{D2} = K_1 C_{DW} + C_F K_2 C_{DW} / (1 + K_2 C_{DW})$$

where C_D and C_{DW} represent concentration of sorbed dye and of dye in aqueous solution respectively; C_F denotes the concentration of adsorption sites and is subject to an upper limit set by the concentration of terminal aminogroups in the fiber C_{F0} ; and K_1 and K_2 are the Nernst partition and Langmuir affinity constants respectively. This formula was verified, at pH low enough to ensure $C_F \approx C_{F0}$, principally by Atherton et al.,¹ who studied C_D versus C_{DW} isotherms in fibers of a given C_{F0} , and by Palmer,² who measured C_D as a function of C_{F0} (using fibers of different C_{F0}) at a given C_{DW} .

It was recognized,¹ however, that the formulation of amine dyeing in terms of Langmuir adsorption was physically unsatisfactory, because it predicts diminution of C_F (for steric reasons) well below C_{F0} with rising acid dye basicity, whereas the polybasic dye data were consistent with C_F values not deviating markedly from C_{F0} . This problem was later resolved by showing^{3,4} that a physically realistic ion exchange mechanism of amine dyeing does reduce to the form of a Langmuir isotherm (with apparent C_F and K_2 values related to the ion exchange equilibrium constant), in the case of a monobasic dye. (The isotherm for polybasic dyes turns out to be less simple, thus leaving the polybasic dye affinities calculated by Atherton et al.¹ open to, at least minor, revision.) On the other hand, Palmer's results² also showed unexpectedly marked dependence of dye uptake on C_{F0} at a high pH, where $C_F \rightarrow 0$ (hence amine dyeing should be largely suppressed), thus raising interesting questions about the nature of the overdyeing mechanism.

In addition to the above-mentioned mechanistic groundwork, the physicochemical properties of the dual mode sorption parameters (such as dependence of K_1 and K_2 on temperature, on systematic changes in dye molecular structure or on the nature of the polymeric substrate) have been studied extensively^{5–10} and the information gained has contributed materially to our understanding of the corresponding dye diffusion behavior.^{5–8,11}

On the other hand, evidence has been accumulating of complications, attributable to the lack of structural homogeneity of the nylon matrix, which tend

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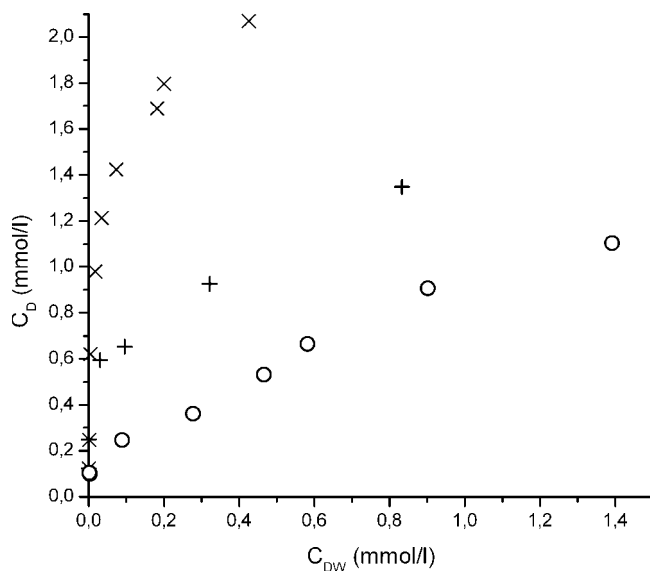


Figure 1 Measured equilibrium dye concentration in the organic solution phase (C_D) versus dye concentration in aqueous solution (C_{DW}), with MDOA concentration in the former phase $C_{F0} = 0.025$ mol/L (\circ), 0.050 mol/L ($+$), and 0.100 mol/L (\times).

to obscure the basic dyeing mechanisms of interest and are difficult to allow for in any reasonably tractable theoretical approach. For example, attention had already been drawn in an early work² to such effects as variable (pH-dependent) accessibility of the nylon spherulitic regions to acid dyes. More recently, the work of Shibusawa and Nakamura¹² has shown that even in the case of disperse dyes simple Nernst partition may be complicated by the presence of (sometimes more than one) Langmuir components.

Accordingly, it seemed to us that studies of simpler systems exhibiting amine dyeing and over dyeing mechanisms should contribute materially to our better understanding of these fundamental mechanisms and their interrelation. Here, we present a liquid ion exchange system,¹³ which on the basis of the preliminary results reported later, appears to be promising in this respect.

EXPERIMENTAL

The system chosen consists of *N*-methyl-di-*n*-octylamine (MDOA) dissolved in chloroform (representing the fiber phase) in contact with an aqueous solution of pure C.I. Orange 7 (a monobasic acid dye). No MDOA was detectable in the aqueous phase after equilibration. Also no dye uptake by the pure organic solvent was observed.

The equilibration experiments were performed at $(25.0 \pm 0.1)^\circ\text{C}$ by shaking mechanically equal amounts (20.0 cm^3) of aqueous and organic solutions for 24 h, in stoppered tubes immersed in a thermo-

stat. The equilibrium dye concentration in the liquid organic phase (C_D) was determined from the difference between the initial and final equilibrium (C_{DW}) aqueous dye concentrations measured spectrophotometrically.

RESULTS AND DISCUSSION

The sorption isotherms obtained for three different concentrations of MDOA (C_{F0}) are shown in Figure 1. They depend markedly on C_{F0} and exhibit reasonably distinct initial steep curved portions, followed by less steep quasi-linear regions, which may plausibly be considered to represent amine dyeing and over dyeing (i.e., C_{D2} and C_{D1} in the above-mentioned equation) respectively.

Replotting the data in the form of C_D/C_{F0} (see Fig. 2) makes this picture clearer, on one hand, and on the other, reveals an obvious tendency of the resulting reduced isotherms to coincide, which is particularly pronounced at higher C_{F0} values. The latter result implies that both C_{D1} and C_{D2} tend to vary in line with C_{F0} .

Such dependence of C_{D2} on C_{F0} was demonstrated experimentally² for amine dyeing of nylon, under conditions of low pH yielding $C_F \approx C_{F0}$ (see introductory section), but the same result is expected, on the basis of the above-mentioned equation, for $C_F < C_{F0}$, as long as $C_F/C_{F0} \approx \text{constant}$ when C_{F0} is varied. The latter condition appears to apply here reasonably well at higher C_{F0} values but less so at the lowest one (presumably because of a change in the environment of the aminogroups in the organic solution phase). In the former case, a degree of ionization of

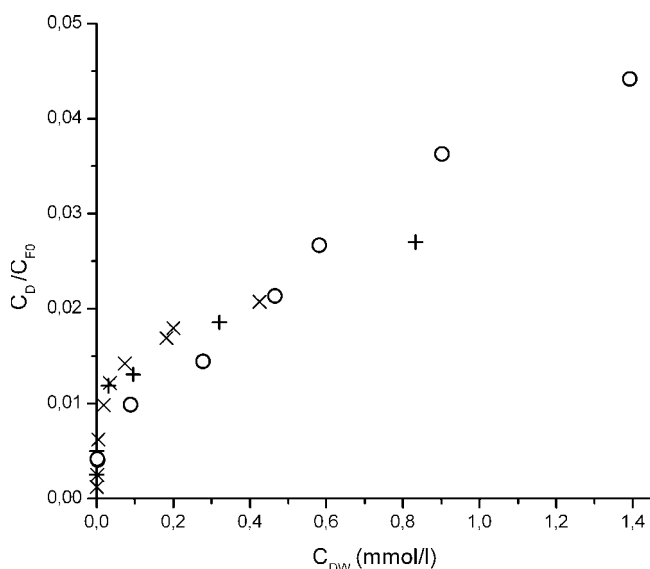


Figure 2 Data of Figure 1 replotted on a C_D/C_{F0} basis using the same symbols.

MDOA not much above 1% is indicated by the height of the steep part of the isotherms, which characterizes the amine dyeing mechanism. This does not seem unreasonable, in view of the prevailing nearly neutral pH (normally pH = 6.0) and the organic environment of the amine groups.

The analogous dependence of C_{D1} on C_{F0} , implied by the present results, seems to us to run parallel to Palmer's findings² (referred to in the introductory section) that acid dye uptake by nylon, under conditions of high pH (leading to $C_F \rightarrow 0$ and hence $C_{D2} \rightarrow 0$), is nevertheless markedly dependent on C_{F0} . The present study casts more light on this point by showing unequivocally that the amine *is* involved in the over dyeing mechanism (since no dye uptake by the pure organic solvent can be observed, as stated in the experimental section), thus enhancing the plausibility of Palmer's suggestion that sorbed dye tends to facilitate ionization of uncharged aminogroups in the fiber phase.

CONCLUSIONS

In the system presented here, the use of a tertiary amine with suitably large nonpolar substituents serves the dual purpose of (i) preventing extraction by the aqueous phase of the amine dissolved in the organic phase and (ii) providing a simple homogeneous substrate, which can, as we have shown, reproduce basic characteristic features of both amine dyeing and over dyeing. Moreover, the liquid nature of this "fiber phase" allows fast and uncomplicated

experimentation along both of the lines pioneered by Atherton et al.¹ (C_D versus C_{DW} at constant C_F and pH) and by Palmer² (C_D versus C_{F0} at constant C_{DW} and pH) respectively. The only presently foreseeable complications in this respect may be expected when variation of dye or amine concentration leads to material changes in the organization of the amine molecules dissolved in the organic phase. However, such "microstructural effects" can easily be followed and characterized by appropriate techniques.

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