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Dyes and Pigments 69 (2006) 40–44

DYES and PIGMENTS

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Influence of oxyethylenated alkylamines in the dyeing of polyamide 66 fibres

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Received 27 October 2004; received in revised form 30 January 2005; accepted 25 February 2005
Available online 26 April 2005

Abstract

This paper analyzes the influence of the chemical structure of a series of oxyethylenated laurylamines (LA-EO) on the formation of complexes with the dye C.I. Direct Red 1, as well as on the dyeing kinetics of the polyamide 66 fibres. The spectrophotometric analysis of the dyebath in the absence and in the presence of different LA-EO has been carried out. The variables studied were the molar ratio (MR) between the dye and the LA-EO (1:0–1:16), the chemical structure of the LA-EO (15, 20, 25, 40 and 60 mol of ethylene oxide) and the temperature (25 °C and 60 °C). The results reveal the stoichiometry of the complex formation (D_nS_m) between the dye and the LA-EO. There are two different types of complexes formed. The first-one is insoluble, formed at lower molar ratios (MR). The second-one is soluble, formed at higher MR, being able to control the dyebath exhaustion. The stoichiometry of the dye–auxiliary complex depends on the temperature and the chemical structure of the LA-EO. The dyeing behaviour of PA66 fibres is in correlation with the type of complex formed. It was shown that the presence of LA-EO slows down the dyeing rate and improves levelling.

Keywords: Anionic dye; Oxyethylenated laurylamine; Dye/auxiliary interaction; Polyamide 66; Spectrophotometry

1. Introduction

Hughes et al. [1] have shown that the combined use of non-ionic, weak cationic and anionic auxiliary products in the dyeing of polyamide allows more even dyeing and diminishes the dyeing speed and exhaustion. In the same study, the solution behaviour of acid dyes in the presence of strong and weak cationic auxiliary products has been assessed. Strong cationic auxiliary product gave rise to precipitation of the dye/auxiliary complex and subsequent redissolving. In the presence of the weak cationic product the precipitation of dye/auxiliary complex did not occur. All these phenomena occurred at a certain molar ratio between the dye and auxiliary (MR). Brooks [2], who studied the use of auxiliaries in wool dyeing, observed that the presence of Matexil LC-CWL (ICI) influences both the kinetics and the equilibrium of the acid dye absorption. Anyway, as pointed out by Valko [3], these studies lacked the exact chemical identification of auxiliaries used. Only their commercial names were indicated, thus making it impossible to relate their dyeing behaviour to the chemical structure. The only available data was that they belong to the oxyethylenated alkylamine type.

The complexes formed between dyes and auxiliaries have been the objective of numerous studies. Several techniques have been used to determine the stoichiometry of the complex formation, such as spectrophotometry [4–15], surface tension measurement [5,15,16], and electrochemical techniques enabling to make difference

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0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.02.015

between the behaviour of the free dye and the dye/auxiliary complex [17].

The purpose of this study was to assess the influence of the chemical constitution of the auxiliary products (LA-OE) in the dyeing of polyamide 66 with an anionic dye. To this end, the influence of the ethylene oxide (EO) content on the formation of complexes in the dyebath and on the dyeing kinetics was analyzed.

2. Experimental

Dyeing experiments were carried out using 5.6 dtex flat polyamide 66 filament yarns. Before dyeing, the fibres were washed with Sandozin NIA (2 g/L) and Na_2CO_3 (2 g/L) at dyebath ratio 1/40, for 30 min at 85 °C. The samples were rinsed and dried at room temperature. The moisture content of the fibre was 3.62%.

The dye used was C.I. Direct Red 1 (C.I. 22310) (Fig. 1), purified by precipitation method (sodium acetate) to 79.4%. The same dye was used in a previous study [4]. As auxiliary products, a series of laurylamines with different ethylene oxide (EO) contents were synthesized by Tensia-Surfac (Barcelona, Spain) (Fig. 1). Laurylamines with an average of 15, 20, 25, 40 and 60 mol of ethylene oxide (LA-15, LA-20, LA-25, LA-40 and LA-60) were used. The purity of these products was more than 99.5%, evaluated by the amine group assessment method.

The spectrophotometric measurements were done by using SP 1750 (Pye-Unicam) spectrophotometer with a thermostatically controlled cell at 25 °C and 60 °C, using the 10 mm cuvettes.

The dyeing was performed in an apparatus described in a previous study [18], which enables the extraction of small portions of the dyebath in order to evaluate the exhaustion [19]. Before the spectrophotometric evaluation, pyridine (20% vol.) was added to each dyebath sample extracted, as described in a previous publication [4]. The dyeing was performed at a dyebath ratio of 1/100, for 60 min at 60 °C. The acetic–acetate pH regulating system was chosen to allow comparison of the results of this study with those obtained at lower pH values [20]. It has been shown that the type of pH regulating system considerably influences the adsorption of acid dyes (and other anionic dyes) in polyamide [20]. The following conditions have been used for the dyeing kinetics study:

- Dye: 0.25% owf (dye concentration: 3.16×10^{-5} mol/L);
- anhydrous sodium acetate: 0.02 mol/L, acetic acid or sodium hydroxide to give pH = 7;
- auxiliary product (LA-EO) to give the required MR (1:0; 1:0.5; 1:1; 1:2; 1:4; 1:8 and 1:16).

Since one of the objectives of the study was to relate the dyeing behaviour to the formation of complexes between the dye and the auxiliary products in solution, the dyeing kinetics was determined under the conditions that correspond to those chosen for the spectrophotometric analysis. In all cases the spectrophotometric measurements were done at the wavelength of maximum absorbance of the dye C.I. Direct Red 1 (λ_{max} = 498 nm).

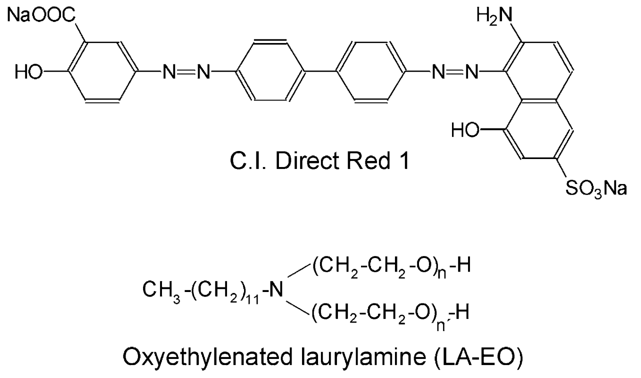

Fig. 1. The structure of the dye and oxyethylenated laurylamines used in the study.

3. Results and discussion

3.1. Spectrophotometric measurements

Fig. 2 shows the absorption spectra of the C.I. Direct Red 1 in the presence of LA-15 at different MR at pH = 7 and 25 °C. The other dye/LA-EO solutions show similar behaviour of absorption spectra.

The presence of several isosbestic points indicates the existence of several species at equilibrium, the fact that has been detected before by other researchers [1,4–6].

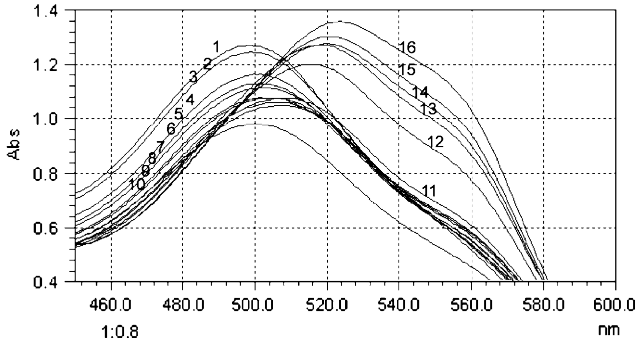

Fig. 2. Absorption spectra of C.I. Direct Red 1 and LA-15, at pH = 7 and 25 °C. MR: (1) 1:0; (2) 1:0.1; (3) 1:0.2; (4) 1:0.3; (5) 1:0.4; (6) 1:0.5; (7) 1:0.6; (8) 1:0.7; (9) 1:0.8; (10) 1:0.9; (11) 1:1; (12) 1:2; (13) 1:3; (14) 1:4; (15) 1:8; and (16) 1:16.

Spectra 1–10 show that the common trend of the absorbance maxima decreases with increasing auxiliary concentration, showing an isosbestic point ($\lambda = 528$ nm) with bathochromic shift. This indicates the existence of an equilibrium between the free dye (D), auxiliary (S) and dye/auxiliary complex (D_nS_m) (according to Eq. (1)). The spectra with the lowest absorbance maximum value correspond to the formation of a complex with well defined stoichiometry, named *insoluble complex*. Spectra 11–16 also show bathochromic shift, but with an absorbance increase with increasing auxiliary concentration. These spectra show another isosbestic point ($\lambda = 496$ nm) indicating the formation of other type of complex (D_nS_m) that contains several molecules of auxiliary (m) per molecule of dye (n), which is denominated as *soluble complex*. This pattern of absorbance spectra implies the existence of different equilibria between the dye, auxiliary and dye/auxiliary complex, according to Eq. (1):

$$nD + mS \leftrightarrow D_nS_m \tag{1}$$

Fig. 3 shows the absorbance (measured at $\lambda = 498$ nm) of dye/auxiliary solutions vs. molar ratio (MR) at 25 °C (Fig. 3a) and 60 °C (Fig. 3b). The point of slope change reveals the stoichiometry (n/m) of the complexes (D_nS_m) formed, according to Eq. (1). This method has been previously used by other researchers [4,5,21]. At 25 °C the stoichiometry of the complex formation (n/m) is 1:0.5 for LA-20 and LA-60, and 1:1 for LA-15, LA-25 and LA-40. At 60 °C the stoichiometry is 1:3 for LA-15 and LA-40, 1:2 for LA-25 and 1:1 for all other auxiliaries (Table 1). Other stoichiometries are also possible.

Fig. 4 compares the absorbance change of the dye/LA-15 at pH = 7 and at two different temperatures (25 °C and 60 °C). At 25 °C the dye/LA-15 solutions contain mostly D_1S_1 complex for MR ≤ 1:1 (*insoluble complex*). For MR > 1:1 the complexes D_1S_m with $m > 1$ (*soluble complex*) are predominant. At 60 °C, the predominant complex up to MR ≤ 1:3 is the complex D_1S_3 (*insoluble complex*) and at MR > 1:3 the complex D_1S_{3+m} becomes predominant [4,9].

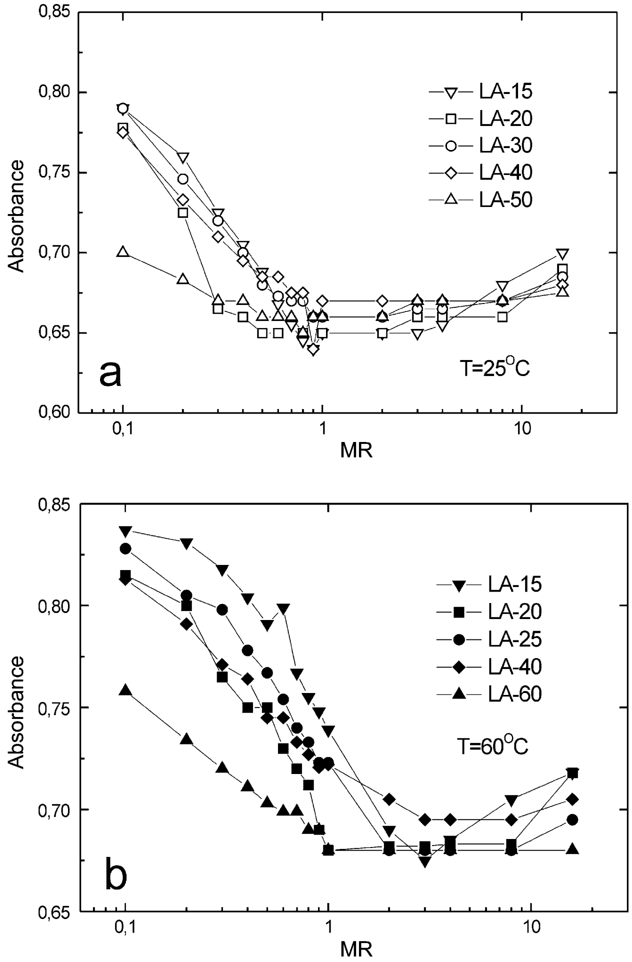

Fig. 3. Absorbance change of C.I. Direct Red 1/LA-EO solutions, at pH 7, vs. molar ratio (MR) in the presence of different LA-EO (15, 20, 25, 40 and 60 mol of ethylene oxide) at 25 °C (a) and 60 °C (b).

Among the different kinds of possible interactions between dye and auxiliary, the electrostatic interactions between anionic group of the dye and cationic group of the auxiliary occur mostly when an *insoluble complex* is formed. As *soluble complex* is formed from *insoluble complex*, the hydrophobic interactions must be involved [4,9,22–26]. As shown in Table 1 and Fig. 4, at 25 °C the D_1S_1 complex is formed and at 60 °C the formation of the D_1S_3 complex is observed. The formation of the soluble complex D_1S_3 is the consequence of the lowering of the solubility of auxiliary by increasing the temperature (from 25 °C to 60 °C), because of the loss of hydration of the ethylene oxide groups of the auxiliary (Eq. (2)) [17,20].

$$D_1S_1 + 2S \xrightarrow{\Delta t>0} D_1S_3 \tag{2}$$

3.2. Dyeing kinetics

Fig. 5 shows the dyeing kinetics of the polyamide 66 fibre with the C.I. Red Direct 1, in the presence of the

Table 1
Stoichiometry of the complexes D_nS_m at pH 7

LA-EO	Stoichiometry of the complex formation (n/m)	
	25 °C	60 °C
LA-15	1:1	1:3
LA-20	1:0.5	1:1
LA-25	1:1	1:2
LA-40	1:1	1:3
LA-60	1:0.5	1:1

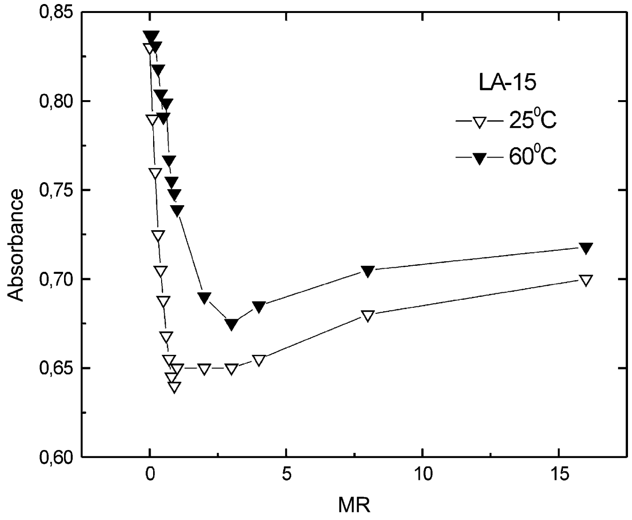

Fig. 4. Absorbance variation of C.I. Direct Red 1 with MR, for LA-15, pH 7, 25 °C and 60 °C. (λ = 498 nm).

auxiliary product (LA-60) at different MR. It can be observed that by increasing MR in the initial dyebath, the amount of the dye that remains in the dyebath after dyeing (not being adsorbed by the fibre) increases. This behaviour has been observed for all LA-EO, at identical dyeing conditions.

Fig. 6 shows the variation of dye exhaustion as the function of MR for each of auxiliaries studied, after 60 min of dyeing (i.e. final exhaustion). The final exhaustion always decreases with increase of MR. The common characteristic (except for LA-20) is that the dye exhaustion until MR = 1:1 is practically identical with the exhaustion obtained in the dyebath without auxiliary being present (MR = 1:0). By increasing the auxiliary concentration above MR = 1:1, the dye exhaustion decreases in correlation with MR increase.

The final exhaustion values are similar for each LA-EO used, except for LA-20 which shows lower values than expected. The different behaviour of LA-20 could be attributed to a better stability of dye/LA-20 complex compared to the complexes formed between the dye and other LA-EO used. This fact has been confirmed by measuring the stability constants at 60 °C and pH 7 of the corresponding complexes of the same series of LA-EO [17].

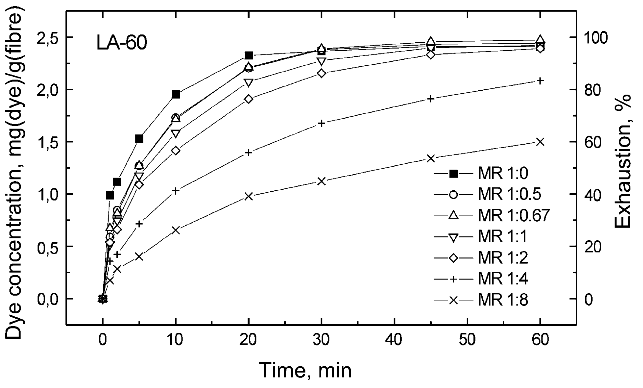

Fig. 5. Rate of dyeing of polyamide 66 with C.I. Direct Red 1 in the presence of LA-60, at pH = 7 and 60 °C.

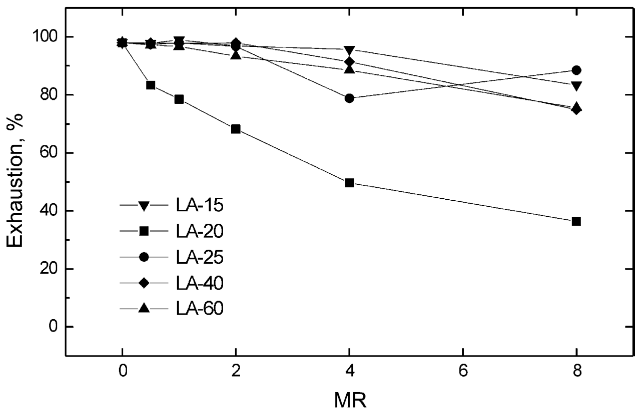

Fig. 6. Dye exhaustion (%) after 60 min at 60 °C as the function of MR.

Fig. 7 shows the variation of the rate constant (k), calculated using Cegarra–Puente equation (Eq. (3)) [27], as the function of MR for different laurylamines (LA-EO) after 60 min.

$$\ln\left(\frac{1-C_t^2}{C_\infty^2}\right)=kt \qquad (3)$$

Comparison of Figs. 6 and 7 shows that an exceptional decrease in exhaustion in the presence of LA-20 at different MR corresponds to the decrease in the rate of dyeing. For other LA-EO the decrease in the rate of dyeing is not so well pronounced, and increased exhaustion values (over 80%) are mostly maintained. At MR = 1:8 it could be observed that dyeing in the presence of LA-20 occurs at very low rate, this being the main reason for low exhaustion. For LA-15, LA-25,

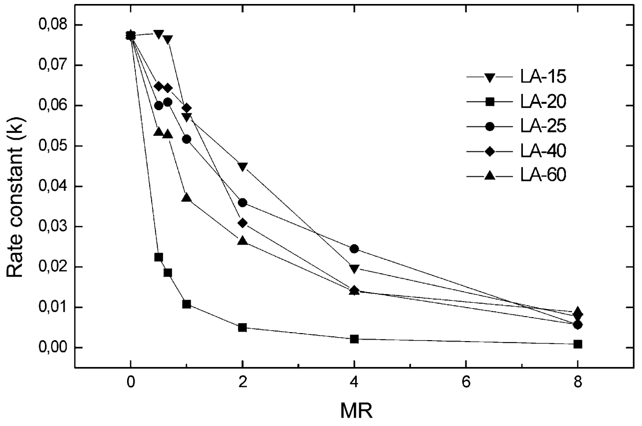

Fig. 7. Rate constant (k) after 60 min of dyeing vs. MR for different laurylamines (LA-EO).

LA-40 and LA-60 the dyeing rates are very similar to each other, this being responsible for small differences in exhaustion values. When the number of moles of auxiliary in the dyebath is less than the number of moles of the dye (MR $\leq$ 1:1), the exhaustion is over 90% for all LA-EO, except for LA-20 (Fig. 6). This could be attributed to the fact that low stability of the complex promotes the immediate and complete dye release from the complex, and released (free) dye is being then adsorbed by the fibre (F) (Eq. (4)) (Fig. 5).

$$nD+DS_m+F\rightarrow D{-}F+mS \tag{4}$$

When the number of moles of auxiliary is bigger than the number of moles of the dye (MR > 1:1), the complex that is initially formed is more stable because of several moles of auxiliary present per each mole of the dye. During dyeing, the dye is being released slowly from the complex and adsorbed gradually by the fibre. At increased auxiliary concentrations, free auxiliary is able to interact with the complex in the dyebath, thus making the complex more stable because of the increased number of molecules of auxiliary within it. This process continues until the complex attains the maximum stability, without releasing the dye anymore. These facts confirm the hypothesis that the dye/auxiliary complex, which is in equilibrium with the free dye and auxiliary, is the main factor controlling the dye adsorption by the fibre (Eq. (5)). Therefore, low dye exhaustion is the consequence of the increased stability of the dye/auxiliary complex.

$$nD+DS_m+F\rightarrow D{-}F+DS_{m'}, \quad m'>m \tag{5}$$

According to the results obtained and from the point of view of application, for the dyeing conditions shown in Fig. 5, at MR < 1:1 it is possible to reduce considerably the initial dyeing rate, which consequently gives better levelling and increased final dye exhaustion after 60 min.

4. Conclusions

The conclusions of this study are as follows:

- Several dye/auxiliary complexes were detected, depending on the temperature. At 25 °C, the complexes formed are D_1S_1 and D_2S_1, while at 60 °C D_1S_1, D_1S_2 and D_1S_3 are formed.
- At 60 °C, for any LA-EO, free dye always exists in the dyebath, regardless of the MR. As the MR increases, the quantity of free dye (and exhaustion) diminishes.
- The presence of the auxiliary product influences the exhaustion after 60 min only when the MR is higher than 1:1, except in the case of LA-20.
- It was shown that the dye/auxiliary complex controls the dye exhaustion in dyeing.
- During dyeing, for MR $\leq$ 1:1, the exhaustion of almost 100% is obtained as a consequence of the instability of the complexes. For MR > 1:1, the exhaustion is always lower than 100% due to the increasing complex stability during dyeing.
- The presence of this type of auxiliary products improves levelling and gives good final dye exhaustion values.

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