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Dye aggregation in solution: study of C.I. direct red I

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Abstract

The variation of the average number of molecular aggregation for C.I. Direct Red I has been studied in aqueous solutions as a function of the dye concentration, temperature and solution pH. The objective of this paper is to evaluate the optimal conditions and dye structure in the dyeing process. Electrochemical and VIS spectrophotometrical methods have been used to calculate molecular aggregation. The electrochemical calculation uses the reduction process of the dye, and previous calculations by other authors have been reported at a given pH and varying the solution concentration. Molecular aggregation also depends on pH, and an understanding of the reduction mechanism at several pH values is therefore necessary. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Azo dyes; Dye aggregation; Reduction mechanism

1. Introduction

Dye molecules with phenyl groups can adopt a planar structure and readily tend to form intermolecular interactions that facilitate permanent aggregation under some experimental conditions It is important to understand dye aggregation in aqueous solution and distribution of n-mers, in order that the dyeing processing will be successful. One factor to be optimized in the dyeing process is the fast diffusion of dye molecules into the fiber, a process which requires maximum disaggregation of the dye molecules. Disaggregation of the dye molecules has been achieved by adding to the solution a surfactant, and the action of this surfactant depends strongly on the chemical structure of both the dye and surfactant.

A complex is formed by the dye and the surfactant integrated by a reduced number of dye molecules and a similar number of surfactant molecules. This complex is stable at ambient temperature, but becomes unstable as the temperature increases during the dyeing process. The dye is liberated at a certain temperature in a minimum state of aggregation. C.I. Direct Red I was chosen as a model dye because we were interested in the action of the carboxylic functional group as a function of solution pH when the dye was a derivative of benzidine. Decrease of dye solubility as a function of pH directly affected the molecular aggregation.

This paper studies the different aggregation states of C.I. Direct Red I in solution in the pH range used in industrial dyeing applications in order to understand the complexes formed when the dye interacts with the surfactant.

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Dye aggregation in aqueous solutions has been the object of several reports [1–12]. These studies were all dedicated to quantify the variation of the average number of molecular aggregation as a function of the dye concentration. In this investigation, the analysis is extended to variations of solution pH and temperature. Electrochemical and VIS spectrophotometrical methods have been used to calculate the molecular aggregation. The electrochemical calculation uses the reduction process of the dye, and thus previous awareness of the reduction mechanism at several pH values is necessary.

2. Experimental

C.I. Direct Red I (C.I. 22310) was a commercial product which was purified by precipitation; (molecular mass of 627 r.m.m) [13] (see Fig. 5). The dye solutions were prepared from (0.02M) sodium acetate, adding either NaOH or acetic acid (0.02M) to obtain the desired pH value. All measurements were made at controlled temperature using a COLORA NB-3 ultrathermostat. The VIS spectra were obtained using a UV-Vis Pye Unicam SP-1750 with a thermostated cell system at pathway 1 cm.

The polarographic curves were registered on a Polarecord E-506 with a Stand E-505 (Metrohm-Herisau); voltammetric curves were obtained using either an Electrochemolab (Amel) or a Chemtrix system (Tektronik Oscilloscope). In the latter a hanging mercury drop electrode was used. The counter electrode consisted of a platinum wire and the reference electrode was a saturated calomel electrode (SCE), potentials always being referenced to this electrode. The electrochemical cell was always under thermostat conditions and the water used was double distilled.

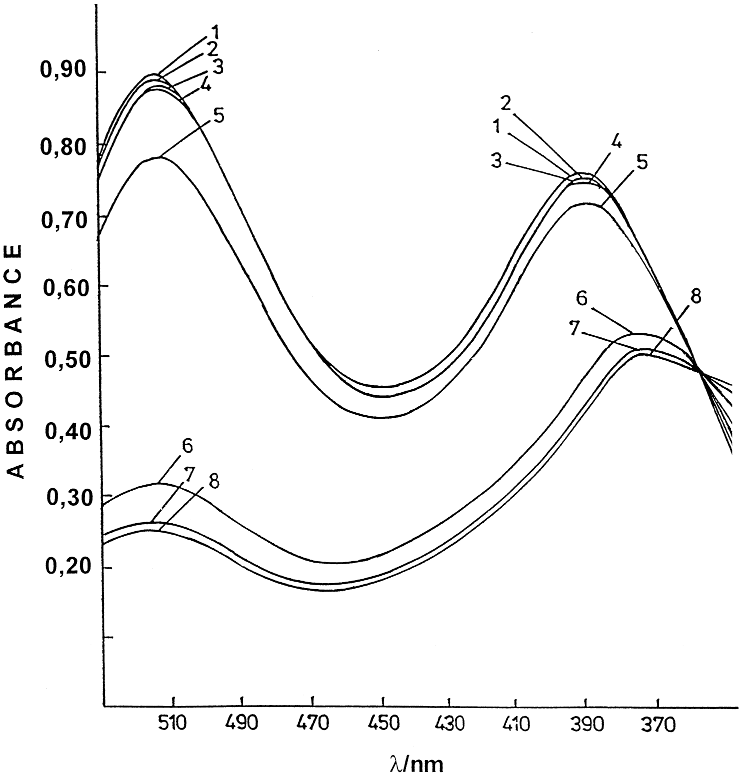

Fig. 1. Absorbance spectra of C.I. Direct Red I Dye concentration = 3,16.10^{-5} mol dm^{-3}; t = 25°C; pH = 9,9 (1); 6,94 (2); 6,6 (3); 5,9 (4); 5,5(5); 5,0(6); 4,58 (7) and 4,0 (8).

3. Results

3.1. Spectrophotometric measurements

Fig. 1 shows the absorption spectra of C.I. Direct Red I at 25°C as a function of pH, and shows that the maximum at 370 nm undergoes a bathochromic shift as the pH increases, while the maximum at 505 nm remains constant. The presence of an isobestic point indicates the existence of an acid-base equilibrium between two stable forms of the dye molecule. In the case of the maximum at 505 nm, the absorbance varies more with the pH than in the former case, and it therefore seems more appropriate to study the change of the chemical state of the dye in aqueous solution at this wavelength. Fig. 2 shows the value of the absorbance at 505 nm against pH. An S-shaped curve is obtained, which allows the spectrophotometric pK value of the dye molecule to be calculated. At 25°C, the value is 5.25 [10]. At pH values lower than this pK value, the carboxylic group will be protonated, its solubility decreases and the average number of molecular aggregation will therefore increase:

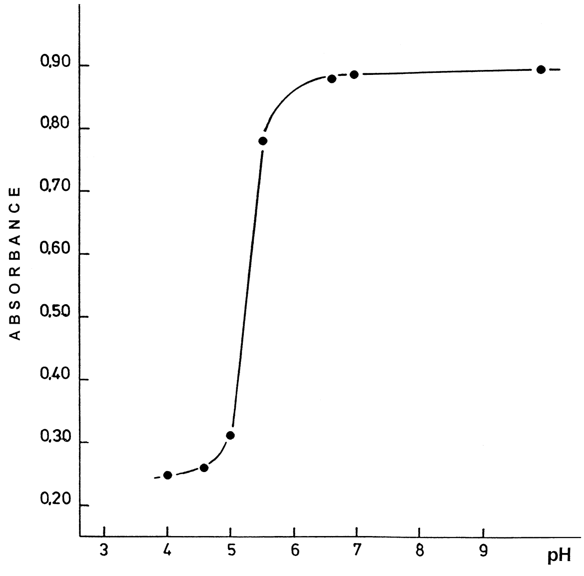

Fig. 2. Plot of absorbance as a function of solution pH. Dye concentration = 3,16.10^{-5} mol dm^{-3}; t = 25°C and λ = 505 nm.

$$D - COOH + H_2O \rightleftharpoons D - COO^- + H_3O^+ \quad (1)$$

The spectrophotometric technique used enables an analysis to be made as to how the system parameters (pH, dye concentration, temperature) may influence the aggregation state of the dye in solution. However, variation of the spectrophotometric response does not distinguish the simultaneous change of structure in the acid-base equilibrium and the molecular aggregation of the dye. A complementary technique is then required to separate these two effects. In this investigation, the electrochemical technique was used.

3.2. Electrochemical measurements

The aqueous solutions of C.I. Direct Red I were studied electrochemically in the pH range 2–12, with temperature variation between 25°C and 70°C 25%v. Dimethylformamide (25%v) was added to disaggregate the dye, to enable measurements to be made of the current generated by ionisation of all the dye molecules. In this case, the dye was fully disaggregated. The reduction mechanism of C.I. Direct Red I depends on pH [14,15], as deduced from the voltammetric study and the variation of the electrochemical parameters, i_p, E_p (Fig. 5). At pH 7, the voltammetric response, [Fig. 3(a)], shows that reduction of the azo-group **1** (peak **A**) is reversible (oxidation peak **C**) by exchange of 2 electrons, [Fig. 3(b)], while the reduction of azo-group **2** directly produces two amines irreversibly (peak **B**) exchanging 4 electrons [Fig. 3(a)]. At pH 4, the voltammograms show that the reduction of both azo-groups is irreversible, [Fig. 4(a)], and when the potential scan is sufficiently negative, three reduction peaks (**A**, **B** and **D**) are observed. The reversibility of azo-group **1** still is evident if the potential scan is reversed immediately after peak **A** appears, [Fig. 4(b)]; Ep = 30 mV.

3.3. Dye aggregation

From analysis of the diffusion currents in polarography, the average number of dye aggregation was calculated at several concentrations, and at temperatures 25°C and 60°C and pH values

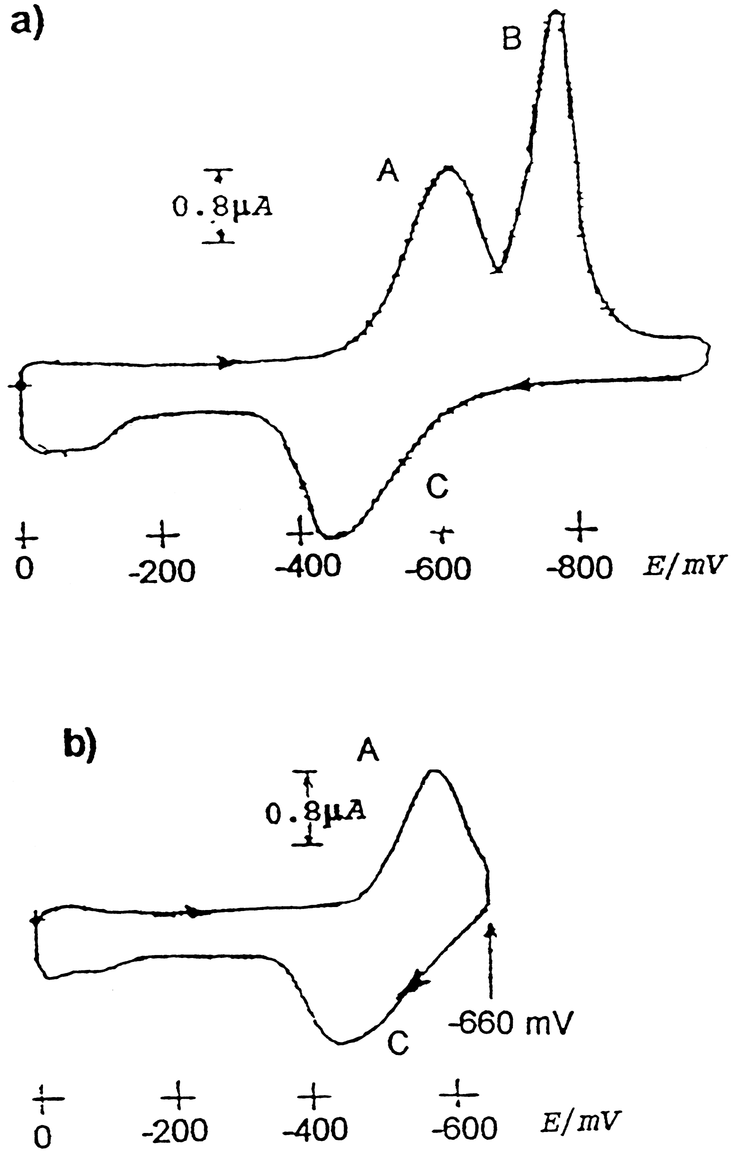

Fig. 3. Cyclic voltammograms of C.I. Direct Red I. Dye concentration = 12,66.10^{-5} mol dm^{-3}; pH = 7,8; t = 25°C; Scan rate = 0,5 Vs^{-1}; initial potential = 0V; reversing potential: (a)−900 mV and (b)−660 mV.

4 and 7, which are the typical conditions in the dyeing process. As the limiting step in the dye reduction on the mercury electrode is the diffusion of the aggregated molecule to the surface, the diffusion coefficient (D) of these species can be determined using the Ilkovik equation ($i = k.n.C.D^{1/2}$) [14]. Once the diffusion coefficient is known, the apparent molecular weight (M') can be calculated from the Hillson and MacKay empirical equation [1]:

$$\log M' = -11,64 - 2,65 \log D \qquad (2)$$

The average number of dye aggregations can be obtained from the ratio of M' with respect to the mass of a dye molecule (M). This methology has

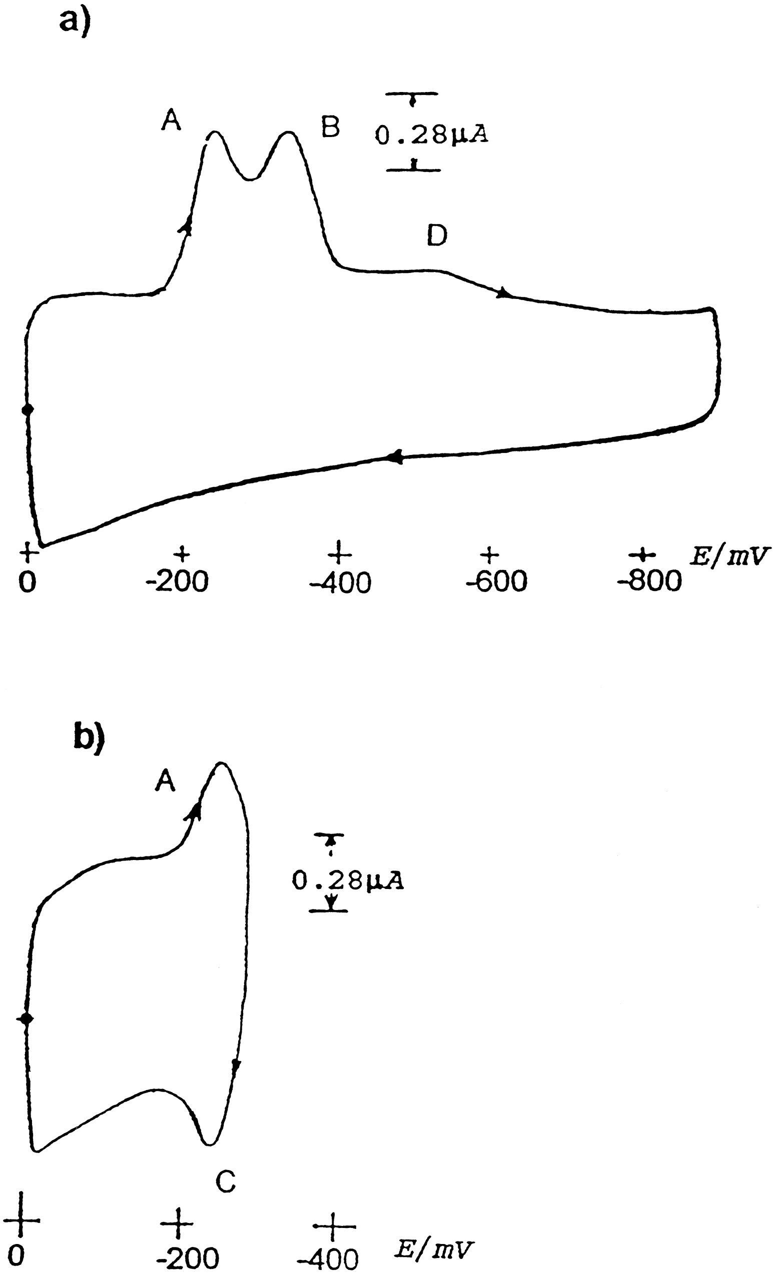

Fig. 4. Cyclic voltammograms of C.I. Direct Red I. Dye concentration = $3.01.10^{-5}$ mol dm^{-3}; pH = 4; t = 25°C; scan rate = 0,5 V.s^{-1}; initial potential = 0V; reversing potential: (a)−900 mV and (b)−300 mV.

been applied by several authors [2,3,6–8]. Correct use of the Ilkovic equation requires knowledge of the number of exchanged electrons per dye molecule. From Fig. 6, the number of electrons is 8 at pH 4 and 6 at pH 7. Fig. 7 gives the results of the dye aggregation number as a function of the dye concentration at pH 7 and at two temperature values.

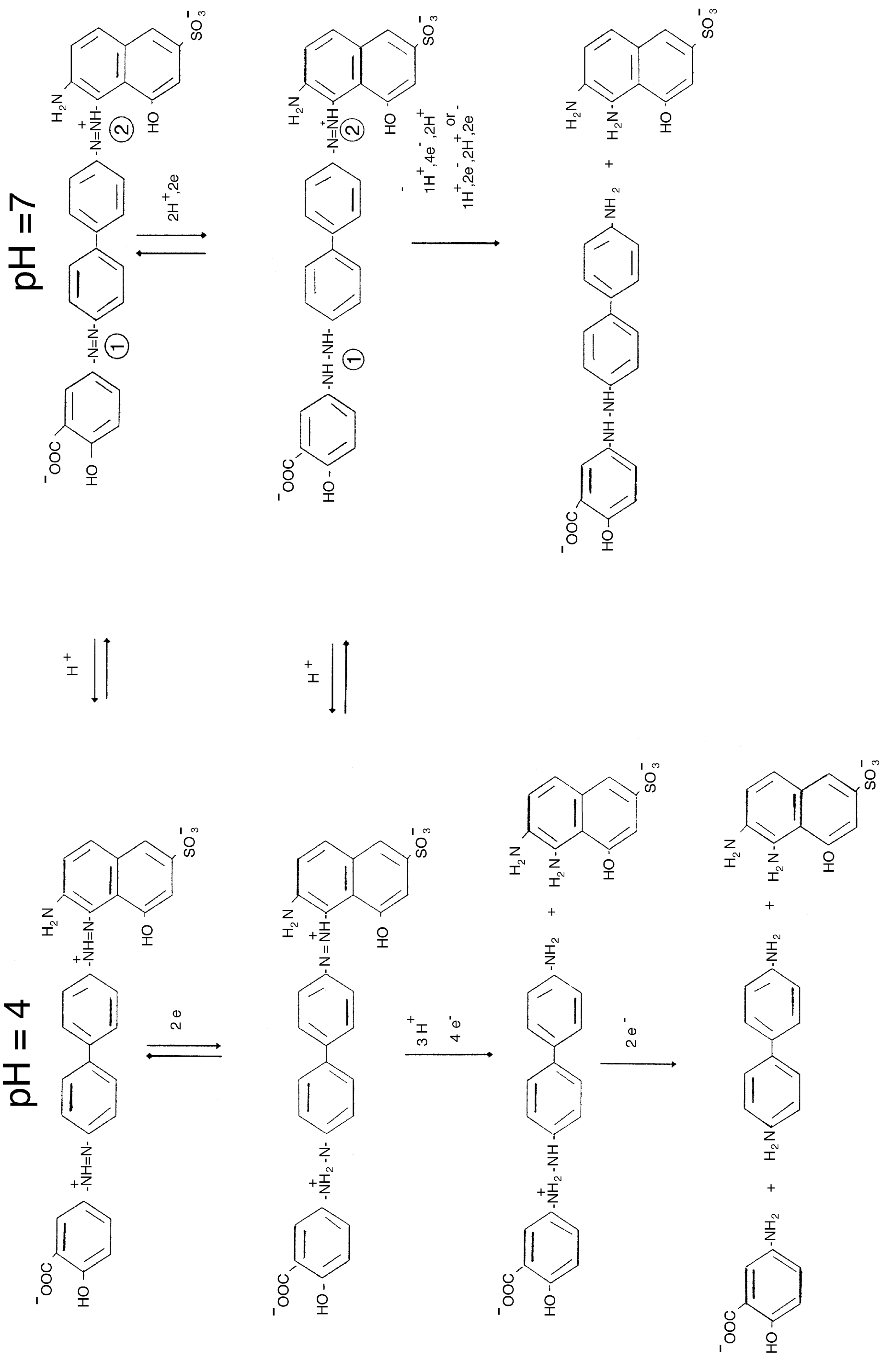

Fig. 5. Reduction mechanism of C.I. Direct Red I.

4. Discussion

From the spectrophotometric results, we conclude that when the pH of the dye solutions changes from 4 to 7, two different phenomena simultaneously occur, viz., the acid-base structural change and dye aggregation. The change in absorbance on increasing temperature is low compared to the

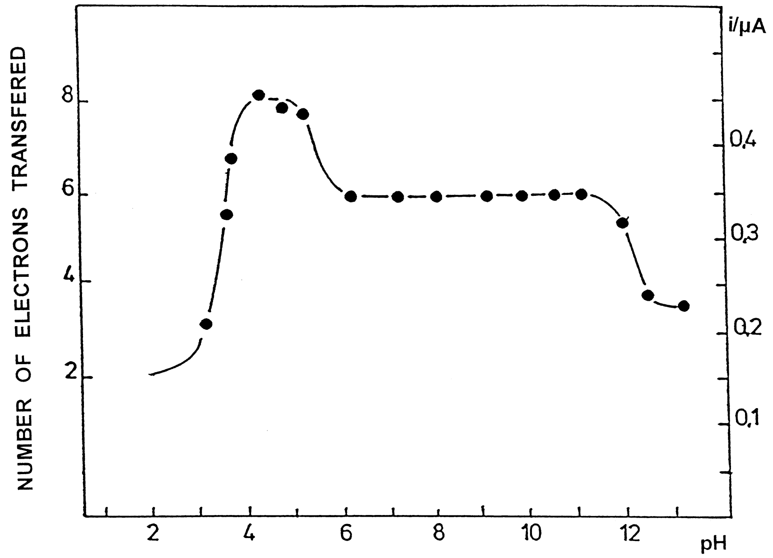

Fig. 6. Number of exchanged electrons per molecule of C.I. Direct Red I as a function of solution pH.

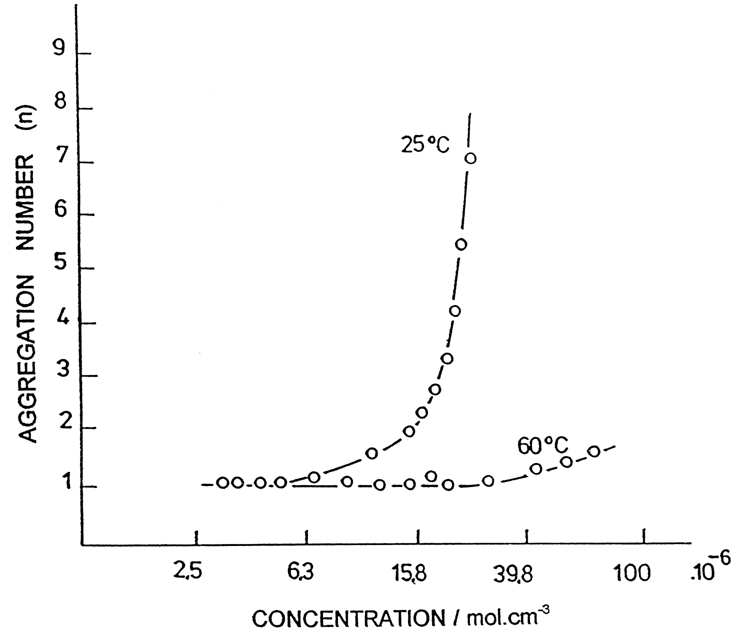

Fig. 7. Average number of dye aggregation against its concentration in solution. pH = 7. (Temperatures are shown in the plot.)

change caused by varying the pH value. For all pH values and temperature range, variation in the dye concentration does not produce a bathochromic shift in the absorption maxima, nor isobestic points, making it difficult to detect dye aggregation.

Based on the polarographic results, a plausible equilibria model between aggregated species is shown in Fig. 8. Thus, limitations found in spectrophotometric measurements to calculate dye aggregation can be overcome by the electrochemical techniques, these allowing us to know the ionic state of the dye at the corresponding pH value, and also to evaluate the average number of dye aggregation.

At low temperature 25°C, the equilibria in Fig. 8 depend strongly on the dye concentration. At pH 7 and 60°C, the dye is in a monomeric state, tending to dimerization at higher dye concentrations. In order to show a general behavior against the three parameters (pH, temperature and concentration), Figs. 9 and 10 show a 3D representation of the average number of aggregation as a function of, first, concentration and temperature, and second, concentration and pH.

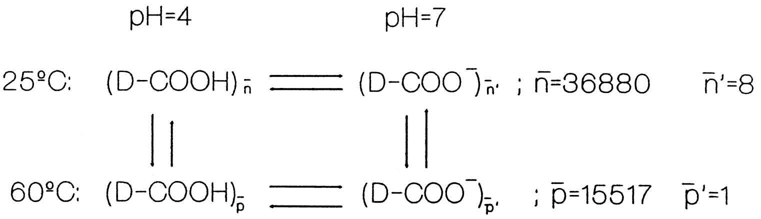

Fig. 8. Dye aggregation equilibria at two pH values and two temperatures. Dye concentration: 3,01.10^{-5} mol dm^{-3}.

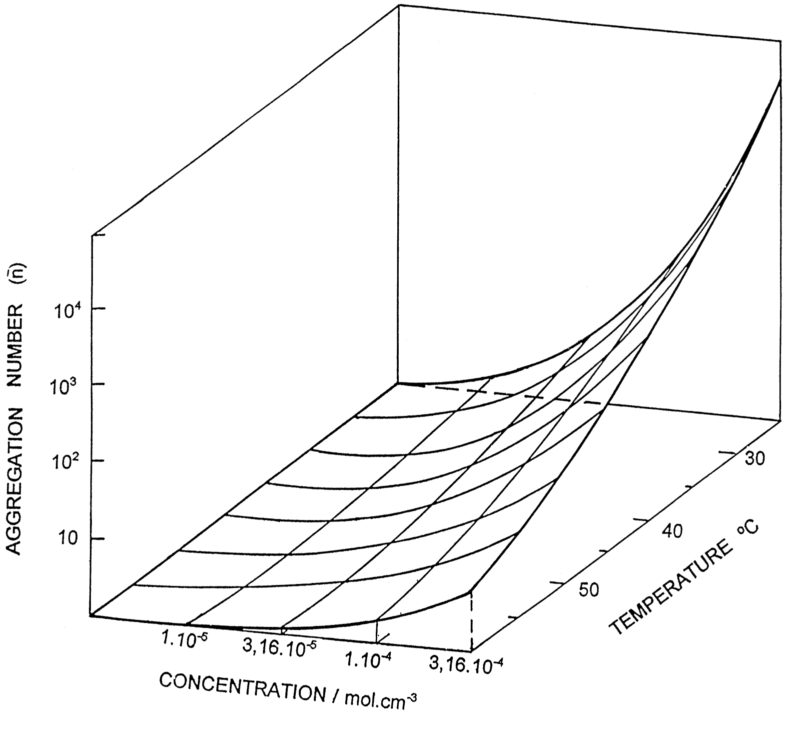

Fig. 9. 3D-representation of the average number of dye aggregation as a function of dye concentration and temperature. pH = 7.

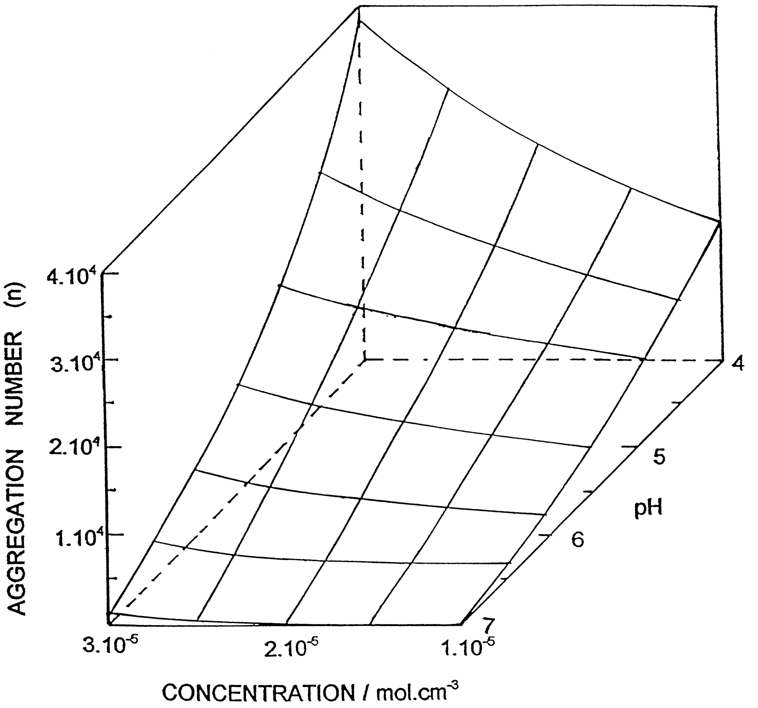

Fig. 10. 3D-representation of the average number of dye aggregation as a function of dye concentration and pH. t = 25°C.

5. Conclusions

DC Polarography allows calculation to be made of the average number of dye aggregation in aqueous solutions, but the reduction mechanism of the dye molecule must be known previously within the pH range useful in the dyeing process.

The high average numbers obtained at pH 4 are in agreement with the ionic state of the dye molecule, only the sulphonate functional group being ionized. At higher pH values, the carboxylic functional group is dissociated, increasing the solubility and then lowering the aggregation number.

An increase of the bath temperature from 25°C to 60°C also lowers the aggregation number, indicating that the interaction forces between the dye molecules are secondary.

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