

# Influence of Temperature and of the Electrolyte Concentration in the Dyeing Process of a Cellulosic Fibre with a Disazo Direct Dye

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**Abstract:** Direct or substantive dyes are widely used in the dyeing process of cellulosic fibres because of their easy handling. In contrast to natural dyes which must be mordanted in order to be applied on the same kind of substrates, direct dyes can be used directly. These dyes contain solubilizing sulfonic acid groups that are ionized in aqueous solution, and therefore the dye molecule is present in the dyebath as the anion. As result, an electrolyte must be added to the dye liquor because cellulose fibers have a negative surface charge in water, which would repel the dye anion. The cations of the electrolyte neutralize the negative charge and favor the adsorption of the dye ions on the fiber. The dye sorption can be described with the help of Nernst, Freundlich or Langmuir adsorption isotherms. The aim of the present work was to establish the influence of two important parameters (temperature and electrolyte concentration) on the dyeing of a cellulosic substrate - mercerized cotton- with one disazo direct dyes, through the study of the equilibrium isotherms. The dyeings were carried out at three different temperatures: 60°, 86° and 96°C and at two sodium chloride concentrations: 4 g/L and 10 g/L. The study of the dyeing process was performed by comparing the experimental isotherms of the studied dyes with the classical sorption isotherms: Nernst, Freundlich and Langmuir. The most appropriate sorption model was established by linear regression analysis. Better statistical results were obtained in the case of Langmuir adsorption model. For this sorption model, the saturation values, the dyes affinity, the enthalpy and the entropy of the dyeing process have been evaluated, at the three dyeing temperatures and two salt concentrations.

**Keywords:** azo dyes, dyeing theory, sorption isotherms, Nernst model, Freundlich model, Langmuir model

## 1. Introduction

The textile dyeing equilibrium of the direct dyes on cellulose fibres presents a great interest, and several studies on this subject have been reported in literature [1-7]. However a general model which could offer complete explanations of the dye-cellulose fibre sorption was not reported yet.

The dye adsorption at equilibrium represents the maximum possible sorption from the dyebath, under certain conditions. From the final dye equilibrium concentrations, adsorption isotherms such as the Freundlich, Langmuir and Nernst isotherms are obtained. Most adsorption isotherms correspond to the Freundlich and Langmuir equations [1].

In the case of the Freundlich model (1) the dye is considered as being contained in an internal phase of volume V of the fibre [1].

$$\ln[C]_f = \ln K_F + x \cdot \ln[C]_s \quad (1)$$

where:  $[C]_f$  represents the dye concentration in the fibre at equilibrium, in mol/kg dry fibre, and  $[C]_s$  represents the dye concentration in solution at equilibrium, in mol/L;  $K_F$  is the equilibrium constant, and  $x$  is a sub-unitary power.

The Langmuir isotherm (2) has been obtained from kinetics considerations [1-3]. The basic assumption is related to the idea that the dye adsorption takes place on independent fixed sites, in a monomolecular layer and all the adsorption positions are equivalent energetically.

$$\frac{1}{[C]_f} = \frac{1}{S_f \cdot [C]_s} \cdot K_L + \frac{1}{S_f} \quad (2)$$

where  $S_f$  is the saturation value in mols/kg fibre and  $K_L$  is the equilibrium constant.

The Nernst adsorption isotherms (3) are considered as a limit case of Freundlich and Langmuir adsorption isotherms [5].

$$[C]_f = K_P \cdot [C]_s \quad (3)$$

Some authors reported that the Langmuir model offers a better interpretation of the direct dye cellulose sorption than the Freundlich one [4-6]. Our previous studies led to the same conclusion [8-11].

In this present work, an experimental and theoretical study of the sorption of a disazo direct dye on a cellulosic substrate was performed in order to establish the best sorption model of the considered dye. For this purpose, the equilibrium sorption data of the studied dye were fitted by linear regression analysis to the classical Nernst, Freundlich, and Langmuir sorption models.

## 2. Experimental

### Materials

The chemicals used in this study were purchased from Merck Co, Aldrich Chemical Co and Reactivul București.

The structure of the dye used in this study is shown in Fig. 1.

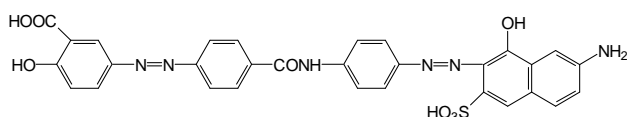


Figure 1. Chemical structure of the studied dye

The dye was synthesized starting from 4,4'-diaminobenzanilide (as diazo component) and salicylic acid and 6-amino-4-hydroxynaphthalene-2-sulfonic acid (as coupling components) [12]. The dye was purified by several recrystallizations from distilled water and characterized by means of electronic spectra (VIS) and mass spectroscopy (MS-FAB). Its homogeneity was determined by thin layer chromatography (TLC).

Electronic spectra were recorded on a Specord M-40 Karl Zeiss Jena spectrophotometer from dye solution in 1 mol/L sodium hydroxide. The dye presents one maximum of absorption at  $\lambda_{\max} = 482 \text{ nm}$  ( $\epsilon_{1\text{cm}}^{1\text{g/L}} = 75$ ).

Mass spectra were recorded on a Nermag R 10-10 spectrometer using Fast Atomic Bombardment technique in negative mode [MS(FAB)], from nitrobenzylalcohol and glycerol as matrix. The mass spectra was dominated by the molecular ion peak [M-H], which corresponds to the dye as free acid. The molecular peak of the dye was found at 625.39 m/z.

The TLC data were taken from silica gel plates (Merck 60F-25), using iso-propanol:methyl-ethyl-ketone:ammonia 25% = 4:3:3 (v:v:v) as eluent. The chromatographic mobility,  $R_F$ , was 0.67.

In the experimental study of the dye sorption on a cellulosic substrate, samples of mercerized cotton (100 %) were used. The samples were soaked in a bath with a liquor ratio of 20:1 at 80°C for 60 minutes, rinsed with distilled water and air - dried.

### Dyeing System and Measurements

The dyeing processes were carried out in round flasks, equipped with a stirrer, a condenser and a thermometer at three temperatures, namely 60°, 86° and 96°C ( $\pm 1^\circ\text{C}$ ). The cotton samples weight in every case was near 70 mg ( $\pm 0.1 \text{ mg}$ ) and the liquor ratio was 150:1. The initial dyebath concentrations of the studied dye varied from 0.15 g/L to 5 g/L. Sodium chloride concentrations in the dyebath were  $6.84 \cdot 10^{-2} \text{ mol/L}$  and  $13.7 \cdot 10^{-2} \text{ mol/L}$ .

In order to evaluate the time necessary for reaching equilibrium for each dyeing temperature and each sodium chloride concentration, a series of preliminary experiments were carried out.

The dyed cotton samples were removed from the hot dyebath, rinsed for about 30 seconds in ice water, and then the dye was extracted with 25% aqueous pyridine at 80°C.

The quantitative evaluation of the dyeing process was performed spectrophotometrically, using a Specord M40 UV-VIS spectrophotometer. Other details on the dyeing system can be found in [8-11].

In order to find out the model which describes best the sorption of the studied dyes on mercerized cotton, the experimental data thus obtained were fitted to the classical (Nernst, Freundlich and Langmuir) sorption models by linear regression analysis. Calculations were performed by the STATISTICA package [13].

## 3. Results and discussion

The dyeings were carried out under equilibrium conditions and the experimental equilibrium dye concentrations in fibre  $[C]_f$  respectively in solution  $[C]_s$  were fitted to (1), (2) and (3) by linear regression analysis. The statistical tests implied in the regression analysis were the squared regression coefficient ( $r^2$ ), the standard deviation (SE) and the Fisher test (F).

The values of the thermodynamic parameters  $K_F$ ,  $K_P$ ,  $K_L$  respectively  $S_f$  and the statistical results are presented in Tables 1-6.

TABLE 1. Freundlich Model. Thermodynamic data and statistical results according to (1).\*

T [°C]	$\ln K_F$	x	$r^2$	SE	F
96	1.43±0.15	0.28±0.02	0.941	0.004	302.84
86	1.55±0.10	0.25±0.02	0.724	0.019	60.31
60	1.57±0.11	0.23±0.02	0.945	0.003	327.71

\* NaCl concentration  $6.84 \cdot 10^{-2} \text{ mol/L}$

TABLE 2. Freundlich Model. Thermodynamic data and statistical results according to (1).\*

T [°C]	$\ln K_F$	x	$r^2$	SE	F
96	1.58±0.12	0.22±0.02	0.948	0.002	340.89
86	1.63±0.14	0.20±0.02	0.741	0.012	62.76
60	1.76±0.15	0.19±0.02	0.944	0.003	336.29

\* NaCl concentration  $13.7 \cdot 10^{-2} \text{ mol/L}$

TABLE 3. Langmuir Model. Thermodynamic data and statistical results according to (2).\*

T [°C]	$S_f^{-1}$	$(K_L \cdot S_f)^{-1} \cdot 10^3$	$r^2$	SE	F
96	19.93±0.38	5±0.38	0.979	0.002	898.13
86	19.93±0.56	2.8±0.37	0.920	0.004	219.70
60	17.84±0.37	2±0.02	0.946	0.003	332.29

\* NaCl concentration  $6.84 \cdot 10^{-2} \text{ mol/L}$

TABLE 4. Langmuir Model. Thermodynamic data and statistical results according to (3).\*

T [°C]	$S_f^{-1}$	$(K_L \cdot S_f)^{-1} \cdot 10^3$	$r^2$	SE	F
96	18.26±0.25	4.43±0.25	0.980	0.002	925.43
86	17.94±0.35	2.14±0.15	0.934	0.004	284.52
60	15.43±0.45	1.02±0.15	0.942	0.003	329.48

\* NaCl concentration  $13.7 \cdot 10^{-2} \text{ mol/L}$

TABLE 5. Nernst Model. Thermodynamic data and statistical results according to (3).\*

T [°C]	Kp	r <sup>2</sup>	SE	F
96	14.27±1.16	0.773	0.017	68.18
86	15.77±2.08	0.741	0.019	57.34
60	17.79±2.32	0.747	0.023	58.11

\* NaCl concentration 6.84 x 10<sup>-2</sup> mol/L

TABLE 6. Nernst Model. Thermodynamic data and statistical results according to (3).\*

T [°C]	Kp	r <sup>2</sup>	SE	F
96	17.15±2.05	0.778	0.016	70.02
86	18.43±2.15	0.775	0.016	69.45
60	19.84±2.29	0.752	0.021	57.86

\* NaCl concentration 13.7 x 10<sup>-2</sup> mol/L

In agreement with theory [1], for all the sorption models, it was noticed that the increase in NaCl concentration, led to the raise of the dye adsorption on the textile substrate, due to the diminishing of the electronegative potential that the cellulosic fibres acquire when they are immersed in aqueous solutions. On the other hand, the increase of temperature led to the reduction of the dye concentration adsorbed by the fibre.

The inspection of the statistical data presented in Tables 1-6, indicated a more significant fitting of the experimental data in the case of the Langmuir model in comparison to the Nernst, respectively Freundlich models.

Thus, the standard affinities,  $\Delta\mu^0$ , have been calculated for the Langmuir model, using (4). The results are shown in Table 7.

$$-\Delta\mu^0 = RT \cdot \ln K \quad (4)$$

TABLE 7. Saturation values and standard affinities of the disazo dye on cotton

T [°C]	96 °C	86 °C	60 °C	
NaCl [mol/L]				S <sub>f</sub> [mol/kg]
6.84 x 10 <sup>-2</sup>	0.050	0.050	0.056	S <sub>f</sub> [mol/kg]
13.7x10 <sup>-2</sup>	0.055	0.056	0.065	- $\Delta\mu^0 \times 10^{-3}$ [kcal/mol]
6.84 x 10 <sup>-2</sup>	6.079	6.317	7.529	- $\Delta\mu^0 \times 10^{-3}$ [kcal/mol]
13.7x10 <sup>-2</sup>	7.502	7.528	8.634	

Using the affinities calculated by equation (4), the standard enthalpy of dyeing,  $\Delta H^0$ , of the studied dye was evaluated by a graphical method [1], from the plot of  $\Delta\mu^0/T$  versus  $1/T$  and the following values were found:

$\Delta H^0 = -22.35$  kcal/mol (for 6.84 x 10<sup>-2</sup> mol/L NaCl) and  $\Delta H^0 = -13.46$  kcal/mol (for 13.7x10<sup>-2</sup> mol/L NaCl). The enthalpy of dyeing may be considered as the sum of the heats of formation of the various bonds holding dyes and fibres together.

The standard entropy of dyeing,  $\Delta S^0$ , was calculated from the Gibbs equation (5):

$$\Delta\mu^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (5)$$

The values of  $\Delta S^0$  thus evaluated are:  $\Delta S^0 = -13.50$  cal/mol.K (for 6.84 x 10<sup>-2</sup> mol/L NaCl) and  $\Delta S^0 = -9.23$  cal/mol.K (for 13.7 x 10<sup>-2</sup> mol/L NaCl).

The values of the enthalpies and entropies of dyeing were found negatives and this is in agreement with the theory which states that the distribution of the dye between the fibre and the bath moves in favour of the aqueous phase as the temperature increases [1].

According to Boltzman's conception, the entropy is proportional to the probability of the system. From the dyeing point of view the entropy change is of practical importance especially in two cases, in which either two dyes are compared on a common fibre or one dye is compared on two fibres. Therefore, dyeing entropy can almost be identified with dye/fibre orientation [1].

## 4. Conclusions

The equilibrium sorption isotherms of a disazo direct dye on cotton were determined at three temperatures and two sodium chloride concentrations.

Experimental data were fitted to the standard known adsorption isotherms of Nernst, Freundlich, and Langmuir sorption models by linear regression. The results indicated best statistical values in the case of Langmuir sorption model. For this model, the dye affinity for cotton, the enthalpy and entropy of dyeing, have been evaluated.

The augment of temperature diminishes the affinity and the increase of NaCl concentration in the dyeing system leads to greater values of  $\Delta\mu^0$ .

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