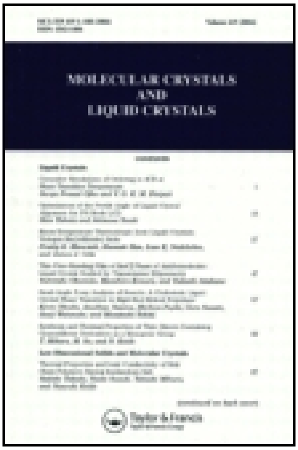

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Experimental And Theoretical Study Of The Adsorption Of A Trisazo Direct Dye Derived From 4,4'-Diaminobenzanilide On A Cellulose Substrate

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EXPERIMENTAL AND THEORETICAL STUDY OF THE ADSORPTION OF A TRISAZO DIRECT DYE DERIVED FROM 4,4′-DIAMINOBENZANILIDE ON A CELLULOSE SUBSTRATE

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An experimental and theoretical study of the adsorption of a trisazo direct dye on mercerized cotton fibre was performed at three different temperatures: 60°, 86° and 96°C and one salt concentration. The experimental data obtained from the dyeing process was fitted by linear regression analysis to the standard Nernst isotherm and by non-linear regression analysis to the Freundlich and Langmuir isotherms. In order to find out the best sorption model, the multimodal sorption model performed by non-linear regression analysis was considered too. Better statistical results were obtained in the case of the dual mode sorption model.

Keywords: cellulose fibres; dual mode sorption model; dyeing theory; Freundlich and Langmuir isotherms; Nernst

INTRODUCTION

Cellulose is one of the most important natural structural materials. The successful application of cellulose in the purification of dyes, in desalting of water, as well as the fact that many water-soluble reagents used in the finishing processes of cellulose fibres are anionic, give us reasons to study the adsorption of a trisazo direct dye on a cellulosic substrate (e.g. mercerized cotton).

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The adsorption behaviour of direct dyes on cellulose has never been satisfactorily explained. The models most widely used for describing the equilibrium sorption of direct dyes on cellulosic substrates have been proposed by Nernst (Eq. (1)), Freundlich (Eq. (2)) and Langmuir (Eq. (3)) [1].

$$[C]_f = K_p \cdot [C]_s \tag{1}$$

where $[C]_f$ and $[C]_s$, represent the equilibrium concentrations of the dye in the fibre and in solution, in mol/kg fibre and in mol/L, respectively. K_P is the equilibrium constant.

$$[C]_f = K_F \cdot [C]_s^x \tag{2}$$

where K_F is the equilibrium constant and the exponent x has a value less than unity.

$$[C]_f = \frac{S_f \cdot K_{L1} \cdot [C]_s}{(1 + K_{L1} \cdot [C]_s)} \tag{3}$$

where S_f is the saturation value, in mol/kg fibre, and K_L is the equilibrium constant.

According to some authors [2,3], Langmuir isotherms offer a better interpretation of the direct dye cellulose sorption in comparison to the Freundlich ones. Our previous studies led to the same conclusion [4,5].

A more recent approach has been proposed by Shibushawa *et al.* in the case of disperse dye adsorption on Nylon 6 fibres [7,8]. They used a multimodal sorption model, expressed by Eq. (4), which is a Nernst type partitioning and a multimodal Langmuir sorption, with "n" saturables binding sites.

In this model, the values of K_P, K_{Lj} and S_j can be evaluated by means of non-linear least squares fit of the experimental data to Eq. (4):

$$[C]_f = [C]_p + \sum_{j=1}^{n} [C]_{Lj} = K_p \cdot [C]_s + \sum_{j=1}^{n} \frac{S_j \cdot K_{Lj} \cdot [C]_s}{1 + K_{Lj} \cdot [C]_s} \tag{4}$$

where $[C]_P$ and $[C]_{Lj}$ are the equilibrium dye concentration sorbed on fibre by Henry's law and by the multimodal Langmuir sorption, respectively. K_P is the partition constant, K_{Lj} represents the multimodal Langmuir constant.

In this case, the existence of a multimolecular partitioning process of the dye between solution and fibre (Nernst) and "n" other monomolecular processes with other types of saturables sites could be considered.

The standard deviation of the experimental values of dye concentrations on the substrate (C_f) obtained from that calculated by Eq. (4) is given by Eq. (5) and is expressed in [%]:

$$SS = \left[\frac{1}{N}\cdot\sum_{i=1}^{N}\left(\frac{C_{fi\,exp} - C_{ficalc}}{C_{ficalc}}\cdot 100\right)^2\right]^{\frac{1}{2}} \tag{5}$$

where the indices "exp" and "calc" refer to experimental and calculated values by Eq. (4), respectively; index "i" refers to the number of sorption data.

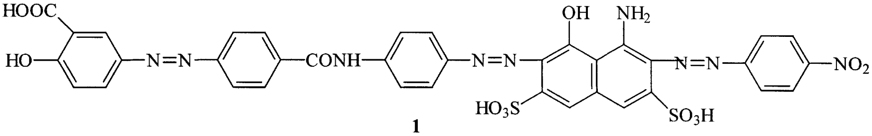
The purpose of this research was to study experimentally and theoretically the adsorption of a trisazo direct dye derived from 4, 4′-diaminobenzanilide on a cellulose substrate, i.e. mercerized cotton. Experimental equilibrium sorption data of this direct dye on mercerized cotton has been fitted by linear regression to the Nernst standard adsorption isotherm. Furthermore non-linear regression analysis was also applied to the multimodal sorption model which has not been studied before for direct dye adsorption on cellulose fibres, and also to the classical Freundlich and Langmuir adsorption isotherms.

EXPERIMENTAL

1. Materials

Samples of fabric made with mercerized cotton (100%) were used. To eliminate all the products added to the fibres in post-spinning treatments, the samples were soaked in a bath with a liquor ratio of 20:1 at 80°C for 60 minutes. After repeated rinsing with distilled water, the samples were air-dried.

The dye used in this study was a trisazo direct dye with the chemical structure **1**.



1

Chemical structure of dye **1**

This dye is a homologue of the benzidinic C. I. Direct Green 8. A three steps process was developed in order to synthesize this dye. The procedure involved the direct bis-diazotisation of 4, 4′-diaminobenzanilide and two coupling reactions of the resultant bis-diazonium salt with salicylic acid and, respectively, with a monoazo compound; this last compound was prepared by the coupling reaction of the diazonium salt of p-nitroaniline with 1-amino-8-hydroxy-3, 6-naphtalindisulfonic acid (H acid).

The bis-diazotisation occurred with the best yield when temperature was maintained in a range of 0°–3°C and the pH of the mixture was around 1. The amount of the bis-diazonium salt of 4, 4′ -diaminobenzanilide was calculated from the amount of sodium nitride consumed, and was used to determine the amount of couplers employed in subsequent steps.

In the first coupling step, 3% excess of coupling component (salicylic acid) was used. The coupling reaction was carried out in a range of temperature of 0–2°C, in two hours and a final pH of 7.5–8. The second coupling reaction was performed at 4–5°C, a pH around 9 and required 3 hours.

According to this procedure, synthesis of **1** proceeds with good reproducibility and a high overall yield, namely 92.4% for the three steps involved.

Compound **1** was purified by several recrystallizations from distilled water and characterized by thin layer chromatography, electronic spectra and mass spectroscopy. The TLC data were taken from silica gel plates (Merck 60 F-25), using CAMAG 20 × 20 and 10 × 10 cuves and *i*-propanole : methyl-ethyl-ketone : ammonium 25% = 4:3:3 as eluting system. Electronic spectra were recorded on a Specord M-40 Karl Zeiss Jena spectrophotometer from dye solutions in 1% ammonium acetate and 0.1 mol/L natrium hydroxide aqueous solution. Mass spectra were recorded on a Nermag R 10-10 spectrometer using Fast Atomic Bombardment technique.

The chromatographic mobility of **1** was found to be $R_f = 0.77$. The VIS spectrum was examined in the region of 350 and 800 nm. The spectra contains two maxima at about $\lambda^1_{max} = 650\,nm$ ($E^{1g/L}_{1cm} = 29.7$) and $\lambda^2_{max} = 705\,nm$ ($E^{1g/L}_{1cm} = 28.9$) in 1% aqueous solution of CH_3COONH_4 and $\lambda^1{}_{max} = 640\,nm$ ($E^{1g/L}_{1cm} = 35.1$) in 0.1 mol/L aqueous NaOH solution. The molecular peak [MS (FAB^-)] was found at 854.34 m/z.

2. Dyeing System and Measurements

All dyeing processes were carried out in round flasks, equipped with a stirrer, a condenser and a thermometer. The dyeings were made at three different temperatures, namely 60°, 86° and 96°C (±1°C). The cotton samples weight in every case was near 70 mg and was known to the nearest 0.1 mg. The liquor to goods ratio was 150/1. Initial dyebath concentrations of the studied dye were from 0.15 g/L to 5 g/L. Sodium chloride concentrations in the dyebath were in every case $6.84.10^{-2}$ mol/L.

The time necessary for reaching equilibrium for each dyeing temperature was evaluated in a series of preliminary experiments. Other details on the dyeing system can be found in references [4,5]. It was found that 3 hours were required to establish equilibrium at 96°C, while 4 hours and 6 hours were needed at 86°C and 60°C, respectively.

The dyed cotton samples were removed from the hot dyebath and rinsed for about 30 seconds in ice water to remove the adhering dye liquor. The dye was extracted from the samples with several portions of 25% aqueous pyridine at about 80°C. The molar extinction coefficients were determined at one wavelength from the Lambert–Beer law.

The dye concentrations in the dyebath as well as of the extracted dye from the substrate were recorded spectrophotometrically, using a Specord M40 UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Dye **1** was used to study experimentally and theoretically the dye adsorption on mercerized cotton. Dyeings were carried out until equilibrium was reached, at three different temperatures and in presence of sodium chloride. Since approximately 99% of the dye originally present in the system was accounted for after dyeing, the assumption was made that no significant amount of dye was lost or decomposed under the dyeing conditions employed.

The experimental equilibrium dye concentrations in fibre $[C]_f$ and in solution $[C]_s$ were fitted to Eq. (1) by linear regression analysis. Calculations were performed by the STATISTICA package [8]. The statistical criterions used in the regression analysis were the multiple regression coefficient (r) and the standard deviation (SS) calculated according to Eq. (5).

The values of the thermodynamic parameter K_P and the statistical results thus obtained are presented in Table 1.

Furthermore, the experimental equilibrium dye concentrations in fibre $[C]_f$ and in solution $[C]_s$ were fitted to Eqs. (2), (3) and (4) by non-linear regression analysis. Calculations were performed by a program developed by the authors. The values of the thermodynamic parameters K_F, K_P, K_L and S_j have been evaluated by means of non-linear least squares fit of

TABLE 1 Thermodynamic Data and Statistical Results of the Adsorption of Dye **1** on Mercerized Cotton according to Eq. (1) (Nernst model)*

T [°C]	K_P	r	SS
96	33.49 ± 4.65	0.838	825.03
86	34.13 ± 4.72	0.828	1292.99
60	44.71 ± 6.20	0.833	1702.37

*K_P represents the equilibrium constant, r represents the multiple regression coefficient, SS the standard deviation calculated according to Eq. (5).

TABLE 2 Thermodynamic Data and Statistical Results of the Adsorption on Mercerized Cotton of Dye **1** according to Eq. (2) (Freundlich model)*

T [°C]	K_F	x	r	SS
96	0.545 ± 0.052	0.273 ± 0.01	0.966	6.93
86	0.584 ± 0.059	0.265 ± 0.013	0.966	8.73
60	0.494 ± 0.047	0.214 ± 0.012	0.987	9.79

*K_F represents the partition constant, x-the exponent less than unity, r represents multiple regression coefficient and SS the standard deviation calculated according to Eq. (5).

TABLE 3 Thermodynamic Data and Statistical Results of the Adsorption on Mercerized Cotton of Dye **1** according to Eq. (3) Langmuir Model*

T [°C]	S_1	K_{L1}	r	SS
96	0.107 ± 0.0023	6865.424 ± 374.337	0.985	6.73
86	0.120 ± 0.0025	8180.640 ± 389.735	0.988	6.61
60	0.136 ± 0.0042	14116.57 ± 1130.03	0.966	10.43

*S_1 represents the saturation value, K_{L1} the partition constant, r the multiple regression coefficient and SS the standard deviation calculated according to Eq. (5).

experimental sorption data. The statistical criterions used in the regression analysis were the multiple regression coefficient (r) and the standard deviation (SS) calculated according to Eq. (5).

The calculated thermodynamic data and the statistical results are presented in Tables 2–5.

In the case of the studied dye the inspection of the statistical data presented in Tables 2–5, indicated a more significant fitting of experimental data in the case of the dual-mode sorption models (Nernst–Langmuir and

TABLE 4 Thermodynamic Data and Statistical Results of the Adsorption on Mercerized Cotton of Dye **1** according to the General Eq. (4) in the Case of Dual-Mode Sorption Model (Nernst–Langmuir)*

T [°C]	K_P	S_1	K_{L1}	r	SS
96	4.967 ± 1.309	0.093 ± 0.0037	8681.052 ± 686.881	0.991	5.22
86	5.219 ± 1.264	0.105 ± 0.0039	10290.72 ± 719.73	0.993	5.08
60	10.008 ± 2.222	0.110 ± 0.0056	20782.76 ± 2377.34	0.991	7.57

*S_1 represents the saturation value, K_P and K_{L1} the partition constants, r the multiple regression coefficient, SS the standard deviation calculated according to Eq. (5).

TABLE 5 Thermodynamic Data and Statistical Results of the Adsorption on Mercerized Cotton of Dye **1** According to the General Eq. (4) in the Case of Dual - Mode Sorption Model (Bimodal Langmuir)*

T [°C]	S_1	K_{L1}	S_2	K_{L2}	r	SS
96	0.071 ± 0.008	1422.96 ± 413.28	0.0498 ± 0.0096	22312.86 ± 7297.83	0.998	3.14
86	0.073 ± 0.010	1694.71 ± 577.62	0.0595 ± 0.0121	22470.13 ± 6483.05	0.998	3.18
60	0.084 ± 0.025	382.854 ± 343.57	0.0966 ± 0.0107	26497.08 ± 5975.57	0.995	7.28

*S_1 and S_2 represent the saturation values, K_{L1} and K_{L2} the partition constants, r the multiple regression coefficient, SS the standard deviation calculated according to Eq. (5).

bimodal Langmuir, respectively) in comparison to the classical Freundlich, and Langmuir ones. Better statistical results were obtained by decreasing the dyeing temperature.

Even if the statistical results derived from the non-linear model for the bimodal Langmuir model (sorption by higher affinity sites with a small saturation value and by lower affinity sites with a large saturation value) were slightly better, the thermodynamic calculated data were not reliable at low temperatures in comparison to those obtained by the dual Nernst–Langmuir sorption model.

CONCLUSIONS

The equilibrium isotherms of the trisazo direct dye **1** on mercerized cotton were determined at three different temperatures and one sodium chloride concentration.

Experimental data thus obtained were fitted to the standard adsorption isotherm of Nernst by linear regression and to the Freundlich as well as the Langmuir ones, by non-linear regression analysis.

The multimodal sorption model was also applied, as a new concept in the theoretical treatment of the direct dyes adsorption on cellulosic substrates.

Best results were obtained for the dual mode sorption model, which is a Nernst type partitioning plus a Langmuir sorption.

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