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THERMODYNAMIC STUDY OF A SYMMETRICAL DISAZO DIRECT DYE DERIVED FROM 4,4'-DIAMINO-BENZANILIDE ON MERCERIZED COTTON

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ABSTRACT:
The sorption isotherms of a symmetrical disazo direct dye with symmetrical structure on a mercerized cotton were determined at 60°, 86° and 96°C. In order to find out the best sorption model of the considered dyes, a theoretical study was also performed. The experimental data obtained from the dyeing process was fitted by non-linear and linear regression analysis to the classical Freundlich, Langmuir and Nernst isotherms. Better statistical results were obtained in the case of the Freundlich sorption model.

KEY WORDS:
Direct dyes, dyeing theory, adsorption isotherms, Nernst model, Freundlich model, Langmuir model

1. INTRODUCTION

The textile dyeing equilibrium of the direct dyes on cellulose fibres presents a great interest, but a general model which could offer complete explanations of the dye–cellulose fibre sorption was not reported yet [1-4].

The dye adsorption at equilibrium represents the maximum possible sorption from the dyebath, under certain conditions. From the final dye equilibrium concentrations, sorption isotherms are obtained, most of them corresponding to the Freundlich and Langmuir equations [1].

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

$$[C]_f = K_F \cdot [C]_s^x \tag{1}$$

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 Nernst adsorption isotherms (equation 2) are considered as a limit case of Freundlich and Langmuir adsorption isotherms [5].

$$[C]_f = K_P \cdot [C]_s \tag{2}$$

The Langmuir isotherm (equation 3) has been obtained from kinetics considerations [4]. The basic assumption is related to the idea that the dye adsorption takes place on independent fixed sites, in monomolecular layer and all the adsorption positions are equivalent energetically.

$$\frac{1}{[C]_f} = \frac{1}{S_f \cdot [C]_s} \cdot K_L + \frac{1}{S_f} \tag{3}$$

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

Some authors reported that the Langmuir model offers a better interpretation of the direct dye cellulose sorption than the Freundlich one [2-3, 6-9]. In this present work, an experimental and theoretical study of the sorption of one disazo direct dye with symmetrical structure on a cellulosic substrate was performed. The aim of this study was to establish the best sorption model of the considered dye. For this purpose, the equilibrium sorption data of the studied dye were fitted by non-linear regression analysis to the Nernst, Freundlich and Langmuir sorption models.

2. THE STUDY

General

All the chemicals were purchased from Merck Co, Aldrich Chemical Co and Reactivul Bucureşti.

The dye used in this study was a disazo direct dye derived from 4,4'-diaminobenzanilide. The coupling component was resorcinol. The dye was synthesized, purified by several recrystallizations from distilled water and characterized by means of electronic spectra (VIS) and mass spectroscopy (MS-FAB) and its homogeneity was determined by thin layer chromatography (TLC).

Electronic spectra were recorded on a Cecil CE 7200 spectrophotometer. Mass spectra were recorded on a Nermag R 10-10 spectrometer, from nitrobenzylalcool and glycerol as matrix. The TLC data were taken from silica gel plates (Merck 60F-25) and *i*-propanol/methylethylketone/NH_4OH 25%=4:3:3 (v:v:v) as eluting system.

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.

Procedures

Synthesis of resorcinol ←4, 4'-diaminobenzanilide→ resorcinol

A suspension of 11.5 g 4,4'-diaminobenzanilide (0.05 mol), 70 ml water, 26 ml (0.27 mol) 35% HCl and 50 g ice was bis-diazotised by the direct method [10].

11.4 g (0.1 mol) of resorcinol were dissolved in a solution containing 0.5 g sodium acetate in 90 mL water. The solution was cooled to 5°C and was added dropwise to the solution of bis-diazonium salt obtained above, in a 45 minutes period. The temperature of the reaction mixture was kept around 5°C and the pH of the reaction was maintained around 8.5 by addition of 0.5 mol/L Na_2CO_3 aqueous solution. The mixture was stirred for three hours at 5-10°C. The dye was precipitated by salting out with natrium chloride and was separated by vacuum filtration. The yellow disazo dye was obtained in 88% yield.

Samples of the synthesized dye, free of sodium chloride were obtained by dyeing cotton fabric in boiling solutions containing 5 g of dye in 250 mL water. After rinsing the dyed fabrics, the dye was extracted using solutions of 50-60% aqueous pyridine. The extracts were then evaporated, giving a dye free of salts.

Dyeing system and measurements

The dyeing processes were carried out in round flasks, equipped with a stirrer, a condenser and a thermometer. The dyeings were made at three temperatures, namely 60°, 86° and 96°C (± 1°C). The cotton samples weight in every case was near 70 mg (±0.1 mg). 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 in every case $6.84.10^{-2}$ mol/L.

The time necessary for reaching equilibrium for each dye and each dyeing temperature was evaluated in a series of preliminary experiments.

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 dyed samples with 25% aqueous pyridine at 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 the extracted dye from the substrate were recorded spectrophotometrically, using a Specord M40 UV-VIS spectrophotometer. Other details on the dyeing system can be found in references [6-9].

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 nonlinear regression analysis. For this purpose, the STATISTICA software [11] was used.

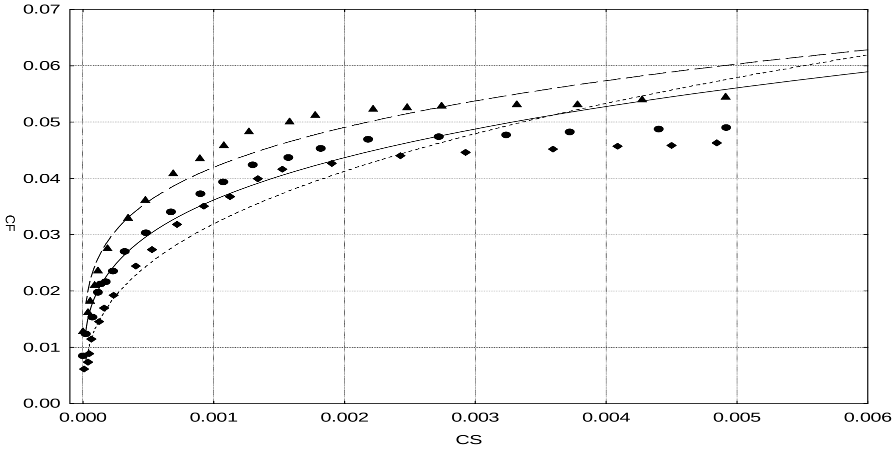


Figure 1. Freundlich adsorption isotherm at 60° (▲points and large interrupted fitting line), 86° (● points and continuous fitting line) and 96° (◆ points and small interrupted fitting line)

The standard deviation (expressed in [%]) of the experimental values obtained for the concentration of the dye on the substrate (C_f) from the calculated ones) was calculated according to equation (4).

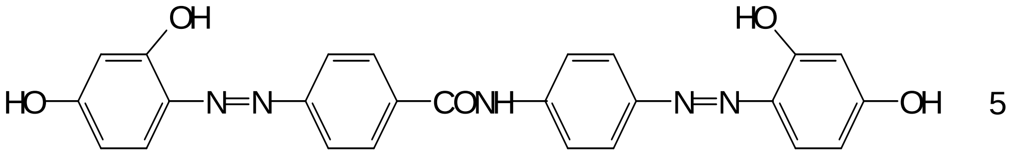
$$SS = \left[\frac{1}{N} \sum_{i=1}^{N} \left(\frac{C_{fi\,exp} - C_{ficalc}}{C_{ficalc}} \times 100 \right)^2 \right]^{\frac{1}{2}} \tag{4}$$

where the suffixes "exp" and "calc" refer to experimental and calculated values, respectively; suffix "i" refers to the number of sorption data.

Figure 1 presents the Freundlich dye adsorption isotherm at 60°, 86° and 96°.

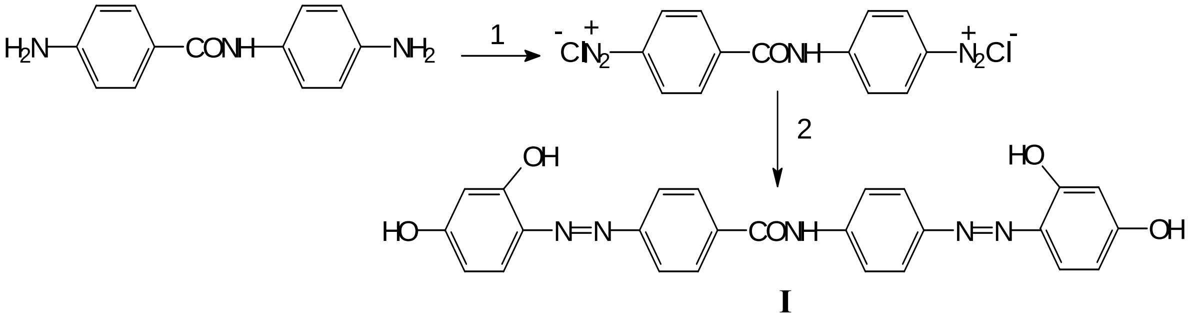
3. DISCUSSIONS

In the present study, the sorption isotherms of a symmetrical disazo direct dye on mercerized cotton were determined at 60°, 86° and 96°C. The studied dye (I) contains 4,4'-diaminobenzanilide as diazo component and resorcinol as coupling component.



Dye **I**

The dye was prepared in a two steps procedure, as shown in Scheme 1.



Scheme 1

1. NaNO$_2$, HCl, 0°C, 1 hour, 2. Resorcinol, 1:2 molar ratio, pH = 8.5-9, 5-12°C, 3 hours.

The bis-diazotization of 4, 4'-diaminobenzanilide was carried out by the direct method, in aqueous HCl solutions.

The coupling step was conducted at a pH value of 8.5-9, and with a 2-3% excess of coupling component. The progress of the coupling reaction was monitored by the usual way (drop reaction) and by thin layer chromatography (TLC), when the formation of dye **I** was examined. Dye **I** was obtained with overall high yields and was characterized by means of VIS spectra and negative (-) FAB – MS spectroscopy. Dye homogeneity was examined by TLC. The chromatographic mobility (R_f) of dye I was found equal to 0.76. The VIS spectrum was examined in the region of 350 to 800 nm. The spectra contain one maxim of absorption at about λ_{max}= 435 nm ($\varepsilon_{1cm}^{1g/L}$ = 52) in 0.1 mol/L aqueous NaOH solution. The molecular peak [MS(FAB-1)] was found at 468.45 m/z.

The disazo dye **I** was further used in the experimental study of the dye sorption on mercerized cotton, as shown in Experimental section. Dyeings were carried out until equilibrium was reached, at three different temperatures and in presence of sodium chloride. The experimental equilibrium dye concentrations in fibre $[C]_f$ and in solution $[C]_s$ were fitted to equations (1) and (2) by nonlinear regression analysis and to equation (3) by linear regression analysis, in order to provide the best model of sorption of the studied dye on cotton.

The values of the thermodynamic parameters K_F, K_L respectively S_f have been evaluated by means of nonlinear least squares fit of experimental sorption data to respective equations (1, 2), respectively by linear regression fit of experimental sorption data to equation (3) for K_P. The multiple regression coefficient (R) and the standard deviation (SS) calculated by equation (4) were used as statistical criterions in the regression analysis.

The thermodynamic data and the statistical results obtained for the studied dyes are presented in tables 1, 2 and 3.

TABLE 1
Thermodynamic data and statistical results of the sorption on mercerized cotton of dye I according to equation $[C]_f = K_F \cdot [C]_S^x$ (Freundlich model)*

T [°C]	K_F [L/lg]	x	R	SS [%]
96	0.411	0.37	0.949	11.59
86	0.238	0.27	0.979	6.6
60	0.199	0.23	0.977	9.3

*K_F represents the Freundlich partition constant; x- the subunitary power;
R- the multiple regression coefficient and SS-the standard deviation.

TABLE 2
Thermodynamic data and statistical results of the sorption on mercerized cotton of dye I according to equation $\frac{1}{[C]_f} = \frac{1}{S_f \cdot [C]_s} \cdot K_L + \frac{1}{S_f}$ (Langmuir model)*

T [°C]	S_1 [mol/kg]	K_L [L/mol]	R	SS
96	0.041	10050.96	0.920	24.63
86	0.041	50252.52	0.703	27.62
60	0.046	125002.3	0.579	27.39

*S_1 represents the saturation value; K_L - Langmuir partition constant;
R –the multiple regression coefficient and SS-the standard deviation

TABLE 3
Thermodynamic data and statistical results of the sorption on mercerized cotton of dye I according to equation $[C]_f = K_P \cdot [C]_S$ (Nernst sorption model)*

T [°C]	$K_P x10^{-2}$ [L/mol]	R	SS
96	13.63	0.883	10.49
86	15.09	0.864	32.09
60	17.19	0.866	62.84

* K_P - Nernst partition constant;
R- the multiple regression coefficient and SS-the standard deviation.

Comparing the obtained data presented in Tables 1, 2 and 3 it could be seen that for the studied dye, overall high values of R respectively low standard deviation (SS) values were obtained for the Freundlich sorption model as compared to the classical Nernst and Langmuir models.

4. CONCLUSIONS

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

Experimental data were fitted to the standard known adsorption isotherms of Nernst, Freundlich, and Langmuir by nonlinear regression. The results indicated best statistical values in the case of the Freundlich sorption model.

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REFERENCES

[1] Vickerstaff T., The Physical Chemistry of Dyeing, Imperial Chemical Industries Limited: London, **1954**.
[2] Porter J. J., Perkins W. S., A Study Of The Thermodynamics Of Sorption Of Three Direct Dyes On Cellophane Film, *Textile Res J*, *40*, 81-87, **1970**.

[3] Bairathi A., Dyeing Sorption Isotherms Of Three Direct Dyes And Their Mixtures On Purified Cotton, *Textile Chem. Color.*, *25*, 41-46, **1993**.

[4] Peters R.H., Textile Chemistry. The Physical Chemistry of Dyeing, Elsevier Amsterdam, Vol. III, **1975**.

[5] Rys P., Zollinger H., Fundamentals of the Chemistry and Application of Dyes, Wiley-Interscience: London-New York-Sydney and Toronto, **1972**.

[6] Simu G., Funar-Timofei S., Hora S., Schmidt W. E., Kurunczi L., Şişu E., Morin N., Coloranti Directi Derivati ai 4,4'-Diaminobenzanilidei. I. Sinteza si Studiul Izotermelor de Adsorbtie pe Bumbac ale unui Colorant Disazoic Direct cu Structura Asimetrici, *Rev Chim (Bucharest)*, *53*, 826-829, **2002**.

[7] Simu G., Funar-Timofei S., Hora S., Kurunczi L., Experimental and Theoretical Study of the Adsorption of a Trisazo Direct Dye Derived from 4,4'-Diaminobenzanilide on a Cellulose Substrate, *Molec Cryst Liq Cryst*, *416*, 97-104, **2004**.

[8] Simu G., Funar-Timofei S., Kurunczi L., Schmidt W., A Thermodynamic Study of the Sorption of an Asymmetric Disazo Direct Dye on Mercerized Cotton, *Rev Roum Chim*, *49(3-4)*, 345-349, **2004**.

[9] Simu G., Funar-Timofei S., Kurunczi L., Hora S., Schmidt W., Grad M., Synthesis and Study of Adsorption Isotherms of a Trisazo Direct Dye on Cotton Fibre, *Cellulose Chem Technol*, *38 (5-6)*, 409-416, **2004**.

[10] Simu G. M., Chicu S. A., Morin N., Schmidt W., Sisu E., Direct Dyes Derived from 4,4'-Diaminobenzanilide. Synthesis, Characterization and Toxicity Evaluation of a disazo symmetric direct dye, *Turk J Chem*, *28*, 579-585, **2004**.

[11] STATISTICA 7.1, StatSoft Inc, Tulsa, OK, USA