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Adsorption Study of Cationic Surfactants in Presence of Dyes on the Cotton/Water Interface

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Abstract

The adsorption study of surfactant/dye mixed systems on natural fibres is important because these bioactive systems used in dyeing processes may reach surface waters and have a consistent impact upon health. The contamination of soil and surface water with the strongly active organic compounds (surfactants and dyes) was recognized as an important problem in the last years.

By UV-VIS spectrophotometry and surface tension measurements the formation of colloidal associates between cationic surfactants and dyes used for dyeing of fibres was put in evidence. A clear difference between the adsorbent system in the case of monomer surfactant and the adsorbent system in the presence of the dye in solution was found by calculating the surface occupied by surfactant molecules on the cotton/water interface. The type of interaction and the organization mode of surfactant-dye complexes on the cotton/water interface were established by treating the original data using classical and recent equations of adsorption isotherms (Fowler-Guggenheim, Langmuir)

Keywords: Adsorption, cotton, dye, complex surfactant-dye, cationic surfactant

1. Introduction

The adsorption of surfactants is a process with considerable application in detergence, flotation, pharmaceutical industry, cosmetics, dyes industry, for stabilization of colloidal solutions and dispersions [1].

In general, the adsorption isotherms of ionic surfactants at a solid/liquid interface are characterized by several regions. The morphology of adsorbed structures associated with every region was described for the first time in [2]. Systems with more regions on the adsorption isotherms are: anionic surfactants on alumina [3], cationic surfactants on silica [4], and cationic surfactants on metallic oxides [5].

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Although there are many studies on the adsorption of surfactants on solids from solution, the interest for such studies still persists.

The aim of this article is to determine the shape of adsorption isotherms for some cationic surfactants of alkylpyridinium chloride type in aqueous solution and in presence of dyes at the cotton/water interface, as well as the interaction type and the organization mode of molecules in the different adsorption steps.

For quantitative modeling of the surfactant adsorption process in aqueous solution and in the presence of a dye at the cotton/water interface, specific models of surfactant adsorption on solids were verified (Fowler-Guggenheim and Langmuir). Cationic surfactants used were chosen because of their bacteriostatic and bactericide properties.

2. Experimental

2.1. Materials and methods

The used cationic surfactants are alkylpyridinium chlorides denoted as C_mP_yCl, where m = 10, 12, 16; these compounds are obtained for the first time by Williamson synthesis [6].

Critical micellar concentration values at the liquid/gas interface for a cationic surfactant series of alkylpyridinium chloride type are presented in Table 1.

Table 1. Critical micellar concentration values (CMC) for cationic surfactants studied in aqueous solution at 25^0C

Surfactant	Abbreviation	CMC·10^3 (mol/L)
$C_{10}H_{21}NC_5H_5Cl$	$C_{10}PyCl$	65.00
$C_{12}H_{25}NC_5H_5Cl$	$C_{12}PyCl$	15.60
$C_{16}H_{33}NC_5H_5Cl$	$C_{16}PyCl$	0.90

Cationic dye (RT), newly synthesized [7], derivative of the compact condensed system 2-aminothiazoloOK[4,5-b]quinoxaline-6-carboxylic acid. The dye was purified by recrystallization from solvents; its purity was checked by thin layer chromatography and HPLC. The structure of this cationic dye is presented in Fig. 1.

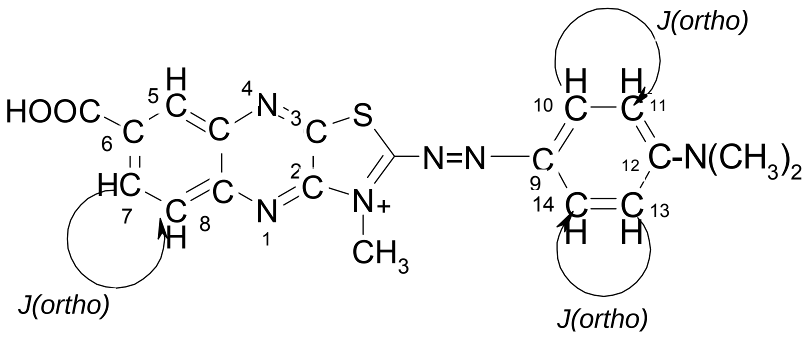

Fig.1. The structure of cationic dye RT

The selection of this dye for adsorption study on cotton in the presence of cationic surfactants was based on its affinity to natural fibres [7] and its stability in time.

Methylene Blue (AM) was used in this study owing to its strong adsorption on natural fibres and its bacteriostatic and disinfecting properties; it has M = 373.9 g/mol, which corresponds to methylene blue dichloride with three water molecules.

Hydrophilic cotton fibre of type BC for medicinal use, produced by Rompel Surgical Products, S.T. 01/1999, SREN ISO 9002; this cotton has specific surface S_{sp}=31.71 m^2/g, determined by the methylene blue adsorption method [8], which corresponds to cotton type B_{26}, in accordance with International Standards of Cotton.

The adsorption data were obtained by UV-VIS spectrophotometry. The measurements were performed using the SECOMAM S750 spectrophotometer and the UNICAM-HELIOS-α spectrophotometer, coupled on-line to PC systems;

The surface tension was determined by the Du Nouy method by measuring the F force necessary to detach a Pt-Ir ring from a liquid surface.

3. Results and discussions

3.1. Part I: Adsorption study of alkylpyridinium chlorides from aqueous solution on cotton

For the adsorption study of alkylpyridinium chlorides on cotton, solutions of the cationic surfactant at different concentrations ($0.5 \cdot 10^{-4}$ –$1.00 \cdot 10^{-3}$ mol/L) were prepared and put in contact with cotton fibres for 24 h at 20^0C. The adsorbed quantity was evaluated by the equation:

$$a = [(c_i - c)\cdot V]/m \quad (\text{mol/g}) \qquad (1)$$

where: a – adsorbed quantity on cotton; c_i – initial surfactant concentration; c – equilibrium concentration; V – volume of solution; m – solid mass.

The equilibrium concentration was determined from a calibration curve of the surfactant. The adsorption isotherms for the cationic surfactants studied at the cotton/water interface are presented in Fig. 2.

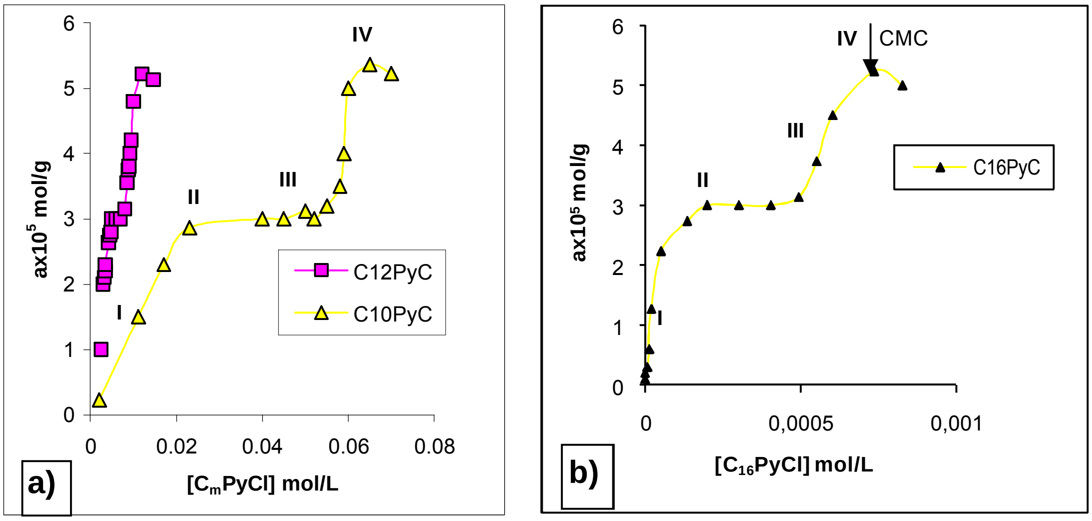

Fig. 2. a) Adsorption isotherms of $C_{10}P_yCl$ and $C_{12}P_yCl$ surfactants on cotton at 20^0C;
b) Adsorption isotherm of $C_{16}P_yCl$ surfactant on cotton at 20^0C.

Adsorption isotherms of cationic surfactants of C_mPyCl type on cotton belong to the L class, 4 under-classes according to the isotherms classification [9]. The surfactant is adsorbed by electrostatic interaction with the cotton substrate loaded with negative charges.

An increase in the adsorbed quantities on the substrate is observed at surfactant concentrations close to CMC, where a maximum is observed. The latter points to the fact that the formation of micelles in the solution prevails over the formation of a bi-layer at the cotton/water interface; moreover, the maximum gives an evidence for the equilibrated behavior of cationic surfactants on a certain class of substrates.

On the basis of the adsorption results, we calculated the molecular specific surfaces ($\overset{*}{A}$) by equation:

$$\overset{*}{A} = \frac{1}{N_A \cdot \Gamma_{\max}} \qquad (\text{nm}^2/\text{molecule}) \qquad (2)$$

where: N_A- Avogadro's number, Γ_{max} – maximum adsorbed quantity at the solid/liquid interface.

Table 2. Occupied surfaces of cationic surfactant molecules on cotton fibre at 20^0C.

Studied system	$a \cdot 10^5$ mol /g	$N_A \cdot a \cdot 10^5$ molecules/g	$\overset{*}{A}$ nm^2/molecule	$\Gamma \cdot 10^6$ mol/m^2
C_{10}PyCl	5.30	$30.89 \cdot 10^{28}$	1.02	1.617
C_{12}PyCl	5.25	$31.62 \cdot 10^{28}$	1.00	1.655
C_{16}PyCl	5.44	$32.76 \cdot 10^{28}$	0.96	1.715

The molecular specific surface decreases with the increase in hydrocarbon chain length of the surfactant.

3.1.2. Part II: Adsorption study of alkylpyridinium chlorides in the presence of dyes at the cotton/water interface

For the adsorption study of mixed aqueous solutions of cationic surfactant $C_{16}P_yCl$ – dye on cotton, samples with different concentrations of the dye RT [$0.5 \cdot 10^{-4}$ – $1 \cdot 10^{-3}$ mol/l] and the surfactant $C_{16}P_yCl$, as well as of the monomeric dye AM [$0.5 \cdot 10^{-5}$ – $10 \cdot 10^{-5}$mol/l] and the surfactant $C_{16}P_yCl$ were prepared. The samples were put in contact with cotton fibres for 24 h at 20^0C. The volume of the mixture was 30 mL and the solid mass was 0.3 g cotton.

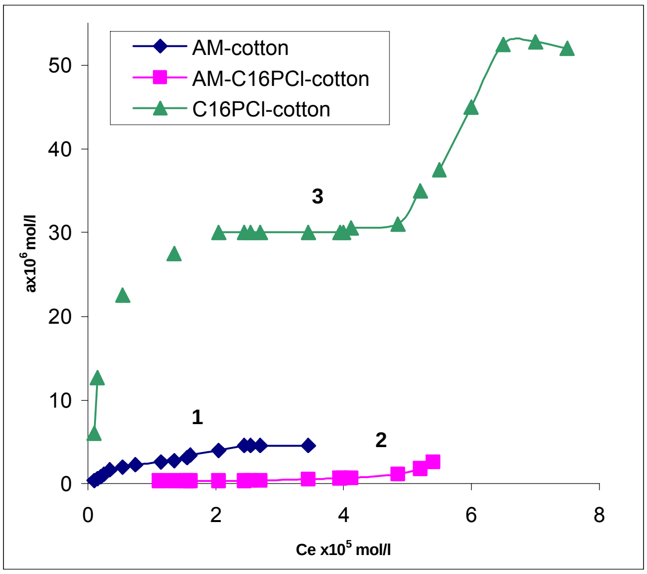

Fig. 3. Adsorption isotherms: 1 - aqueous solutions of methylene blue on cotton; 2 - mixed system $C_{16}P_yCl$ – methylene blue on cotton; 3 - aqueous solutions of surfactant $C_{16}P_yCl$ at 20^0C.

The isotherm of monomeric methylene blue on cotton is of L class according to Giles classification and it shows an increase in the quantity adsorbed on cotton with the increase in dye concentration in solution. The affinity of AM for cotton fibres is due to van der Waals forces; the adsorption increases with the increase in dye concentration, and when the sites on the surface are occupied, the further increase in dye concentration suppresses adsorption.

The isotherm of mixed aqueous solutions of AM-$C_{16}P_yCl$ points to a competitive adsorption, the dye being dissolved in the micelles of the cationic surfactant. The surfactant stops the adsorption of dye at the cotton/water interface. The minimum surface occupied by a molecule at the cotton/water interface for AM-$C_{16}P_yCl$ systems is 2.59 nm^2/molecule whereas with aqueous solutions of surfactant the surface occupied by a molecule is 1.5 nm^2/ molecule.

The adsorption isotherm of the cationic dye RT on cotton reveals the increased adsorption on cotton with the increase in dye concentration in the mixture. The adsorption isotherm is of Langmuir type and it is associated with mono-stratum formation [10]. This is an indication for the affinity of the cationic dye to the cotton fibre loaded with negative charges, the adsorption taking place by electrostatic interactions. For concentrated solutions of dye the adsorption maximum on cotton is reached at $\Gamma = 3.689 \cdot 10^{-7}$ mol/m^2, where $a_{max}=11.7 \cdot 10^{-5}$ mol/g; in this way an increase in concentration will not lead to an increase in adsorption because the saturation point is reached.

This behavior is specific for fibres with a limited number of active sites. The accessible active sites lead to increased adsorption accompanied by increased dye concentration. If these sites are occupied, the increase in dye concentration does not lead to increased adsorption.

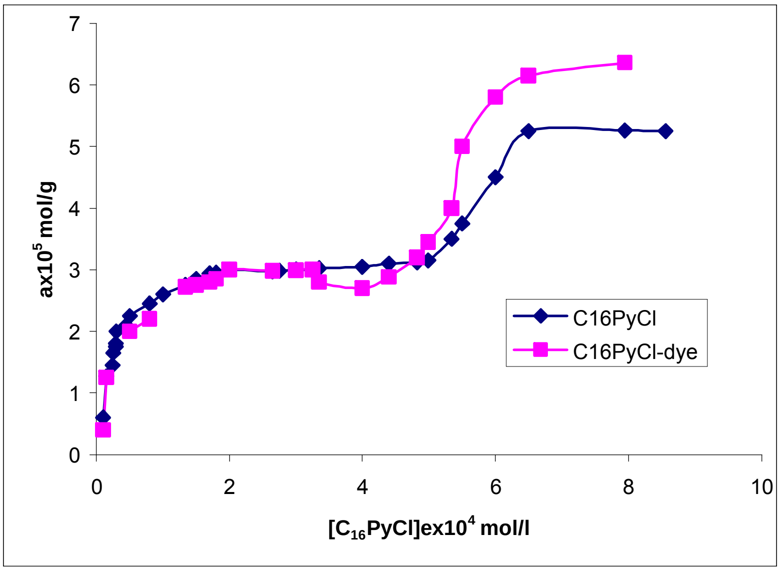

Fig 4. Adsorption isotherms for aqueous solutions of cationic surfactant and mixed solutions of surfactant $C_{16}P_yCl$–cationic dye RT at 20^0C.

The adsorption isotherms of $C_{16}PyCl$ micelle-cationic dye RT mixed systems point to a preferential adsorption of the cationic surfactant at the cotton/water interface. By using a cationic dye the cationic change capacity of the substrate can be measured.

The most complex behavior was observed in the case of non-ionic dyes. Many of these dyes are dissolved at concentrations above CMC [11]. The studies show that if the surfactant is cationic, the dissolved dye can be easily adsorbed on the fibres, and the depth of coloring is proportional to the cationic change capacity or to the increased ion pair adsorption.

If the surfactant is anionic, less dye is transferred to the substrate. However, if a substrate is dyed with a cationic dye solution, then the anionic surfactant solution is colored at room temperature (the dye is transferred again in solution). On the basis of the obtained results, we can affirm that ion pair adsorption ensures dye transfer on fibre or in solution.

For demonstrating the type of interaction and the mode of orientation of cationic surfactants of alkylpyridinium chloride type from aqueous solution on cotton, classical methods were used, developed for ionic surfactants adsorption on solid surfaces.

MODEL Fowler-Guggenheim [12]: a model which explains the lateral interactions between adsorbed molecules on solid surface.

In this model the equation of adsorption is:

$$-\log\left(c\cdot\frac{\Gamma_{m}}{\Gamma}-1\right)=\log K-\frac{2\cdot\omega}{2.303}\cdot\frac{\Gamma}{\Gamma_{m}} \qquad (3)$$

where Γ - the adsorption coefficient at the equilibrium concentration of the surfactant in solution c; Γ_m - the maximum adsorption coefficient; K - the characteristic constant of the interaction between the adsorbed molecules and the solid surface sites, ω - a parameter due to interaction between adsorbed molecules.

The equation (3) is a linear equation; the slope is denoted with alpha (α) which is equal to 2α/2.303.

From the Fowler-Guggenheim equation we can obtain the free energy of adsorption ΔG_{ads} and the free energy of interaction ΔG_{int} (Table 3).

Table 3. Adsorption and interaction energy values between adsorbed molecules at cotton/water interface at 25^0C (Fowler-Guggenheim Model).

Surfactant	**Ln K**	**Kx10^3**	**alpha**	**ω**	ΔG_{ads} **kj/mol**	ΔG_{int} **kj/mol**	**R^2**
$C_{16}P_yCl$	-5.20	5.5	-2.01	-2.31	-12.99	-5.81	0.984
AM-$C_{16}P_yCl$	-8.33	0.23	-1.32	-1.52	-20.9	-3.80	0.987
RT- $C_{16}P_yCl$	-3.30	36.7	-3.40	-3.91	-8.27	-9.82	0.965
[RT]	-6.65	1.28	-1.19	-1.37	-16.67	-3.47	0.931

$\Delta G_{ads}=-RT\ln K$ (kj/mol), $\Delta G_{int}=RT\omega$ (kj/mol), α = 2α/2.303.

The model reveals the existence of electrostatic interactions in region I. For the system AM - $C_{16}P_yCl$, a higher value of ΔG_{ads} was registered than in the case of a single surfactant, which shows the higher adsorption power of the dye. In the case of the mixed systems RT - $C_{16}P_yCl$, a decrease in the adsorption energy and an increase in the interaction energy in comparison with aqueous cationic surfactant solutions is observed.

MODEL *Langmuir:* a model which explains the electrostatic interactions between surfactant, dye molecules and cotton surface.

For determination of the maximum superficial excess Γ_{max}, defined as the maximum mol number of the substance that can be adsorbed on the interface and the minimum surface occupied by an adsorbed molecule on liquid-gas and liquid-liquid interface, the Langmuir isotherm is used:

$$\Gamma_2^{(1)} = \frac{B}{RT}\frac{Kc_2}{1+Kc_2} \qquad (4)$$

where K is the adsorption constant.

This equation can be deduced from the integral equation of surface tension isotherm combined with Gibbs equation. The linear form of the adsorption equation permits graphic determination (Fig. 5) of the maximum adsorption coefficient and the constant k:

$$\frac{c_2}{\Gamma_2} = \frac{c_2}{\Gamma_{max}} + \frac{1}{\Gamma_{max} \cdot K}$$

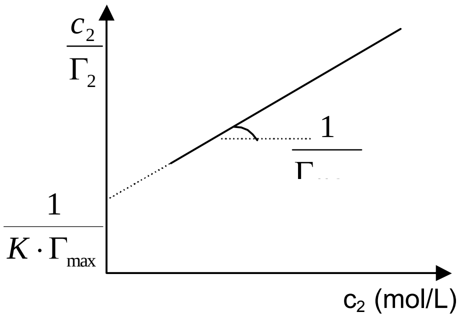

Fig. 5. Langmuir adsorption isotherm

Having in view the definition of superficial excess, the inverse of this value is equal to the surface occupied by a molecule in the superficial layer. Γ_{max} being known, we have calculated the minimum surface occupied by a molecule at the interface, $\overset{*}{A}$ by equation (2).

Table 4. Evaluated values by Langmuir equation

Studied system	$a_{max}\cdot10^5$ mol/g	$\Gamma_{max}\cdot10^6$ mol/m^2	kx10^5	nm^2/ molec	Ln K	F_{ads}=-RTlnK kj/mol	R^2
$C_{16}P_yCl$	3.35	1.056	2.58	1.57	-10.56	-26.45	0.998
AM	0.684	0.215	1.580	0.775	-11.05	-27.71	0.923
AM-$C_{16}P_yCl$	0.203	0.640	4.63	2.59	-9.97	-24.99	0.995
RT	5.708	1.800	37.40	0.926	-7.88	19.78	0.920
RT - $C_{16}P_yCl$	3.340	1.053	3.32	1.57	-10.31	-25.86	0.996

In the case of mixed aqueous solutions of AM - $C_{16}P_yCl$, the specific molecular surface was 2.5 nm^2/molecule at the cotton/water interface, while for the aqueous surfactant solutions the occupied surface is 1.57 nm^2/ molecule.

For the cationic dye system RT - $C_{16}P_yCl$, the minimum surface occupied by a molecule at the interface is equal to the surface occupied by surfactant molecules, which confirms the preferential adsorption of surfactant molecules at the cotton/water interface (Fig. 4).

4. Conclusions

The adsorption isotherms of cationic surfactants of alkylpyridinium chloride type at the cotton/water interface belong to the L class, 4 under-classes of preferential adsorption isotherms. In the first stage of adsorption, the cationic surfactant is adsorbed on the cotton surface by electrostatic interaction. At surfactant concentrations close to CMC an increase in the adsorbed quantity on the substrate is observed due to hydrophobic interactions between the hydrocarbon chains of molecules adsorbed at the interface and those in solution; close to CMC a maximum is observed which points to the fact that the formation of micelles in solution prevails over the formation of a bi-layer at the interface.

It was found that the cationic change capacity of cotton fibres can be measured using the cationic dyes AM and RT. The adsorption isotherms of aqueous mixed solutions of alkylpyridinium chloride - methylene blue ($C_{16}P_yCl$-AM) were obtained. These isotherms pointed to a competitive adsorption between surfactant and dye. The studies revealed that the dye is dissolved in the micelles of the cationic surfactant, which hampers its adsorption on the fibres; the depth of dyeing is proportional to the cationic change capacity or to the increase in ion pair adsorption.

The type of interactions and the orientation mode of cationic surfactant molecules in each stage of adsorption at the cotton/water interface are studied by verification of original data on classic models (Fowler-Guggenheim, Langmuir) concerning the adsorption of ionic surfactants on solids. For dye – surfactant aqueous solutions AM - $C_{16}P_yCl$, high values of the adsorption energy were obtained in comparison with the values obtained for surfactant aqueous solutions. This points to a high extent of dye adsorption on the cotton/water interface. For the dye – surfactant RT - $C_{16}P_yCl$ system, the adsorption energy is lower, but the interaction energy is higher, which confirms the preferential adsorption of surfactant molecules at the cotton/water interface.

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