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Improvement in Acrylic Fibres Dyeing

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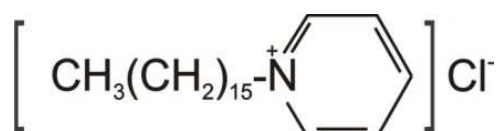
1. Introduction

At the interface of an electrically charged textile fabric and an aqueous solution containing an electrolyte, a surface-active agent, or a dye, an electrical double layer is set up. An electrokinetic potential or zeta potential, ζ , is developed when one of these two charged surfaces moves with respect to the other. This potential plays an important role in the electrical characterization of textile materials and in dyeing and, more generally, in many important wet processes to which textile fibers are subjected (Dai, 1994; Jacobash, 1985; Lokhande, 1970; Teli, 1993). In our opinion, the most appropriate electrokinetic technique to study the zeta potential of fibrous systems is the streaming potential method (Espinosa & Gonzalez, 1991, Gonzalez & Espinosa, 1988). Studies of the sorption of ionic and reactive dyestuff on textile fabrics shows that the electrokinetic potential and surface charge density of fibers can be influenced to a great extent by surfactant and dyes (Anders, 1965). Analysis of the solid surface free energy, together with electrokinetic measurements of the system and an investigation of the adsorption of surfactants and dyes on textiles, provides extensive information about dyeing and finishing mechanisms of fabrics (Peters, 1975). The determination of the surface free energy of a solid surface is important in a wide range of problems in pure and applied science. The surface free energy concept can be used for investigating physicochemical surface properties of textile fabrics and the results of these investigations can be correlated with important technical properties of textile applications (Grundke et al., 1991, Chibowski & Gonzalez, 1993; Holys & Chibowski, 1992; Espinosa et al., 1997; Chibowski et al. 1998). Because of the importance of acrylic fibers in textile industry, investigations in improving their dyeing properties are very interesting. In the present study, we have used as acrylic fibres samples of 100% pure Leacril fibers, of 1.3 dtex, from Montefibre S.A., Barcelona (Spain). Leacril fibers practically do not swell in water (Shukla et al., 1991). The retention of water vapor on the fibers is of the order of ca. 0.8% (Frushour & Knorr, 1985). These fibers are hydrophobic in nature, and they are not easily penetrated by the dyes ((Lokhande, 1970). The use of the surfactants to assist wetting of textile fabrics and, more particularly, for the level of dyeing has become widespread (Cegarra et al. 1984). In the present study, we have used various cationic and reactive dyes in the dyeing process of Leacril fibers. For improvement in Leacril fibers dyeing, we have used various surfactants in the pretreatment of the fibers, in order to obtain the conditions that increase the amount of dye uptaken by the mentioned acrylic fibers. On the other hand, also our purpose is to know the different physico-chemical mechanisms that govern the adsorption of different dyes onto the textile materials when these materials have been pretreated with different ionic surfactants.

2. Effect of n-cetylpyridinium chloride on the zeta potential and surface free energy of the leacril fibers

Acrylic fibers consist of ca. 90% acrylonitrile and ca. 9% vinyl acetate, (Frushour & Knorr, 1985). Sulfur dioxide and potassium persulfate were used as initiating agents for the copolymerization reaction. These compounds produce a large number of both sulphonate and sulfate end-groups on the fiber (Adamson, 1982). These end-groups are ionized in aqueous medium and hence these groups produce negative charge on the fiber surface. The fibrous samples were rinsed repeatedly with deionized water until the conductivity of the washing water remained constant. Finally, they were dried in an oven at 313 °K.

In this work we have used N-Cetylpyridinium chloride (N-CPCI) surfactant, as the agent which we have tested for the pretreatment of Leacril to improve the posterior adsorption of different dyes onto Leacril fibers. This surfactant is A.R. grade from Merck, and was used without further purification. Chemical structure is shown in scheme 1.



Scheme 1.

Water with a conductivity of ca. 10^{-6} S cm^{-1} was used to prepare the different solutions. For the determination of the zeta potential of Leacril fibers, we have used porous plugs with constant Leacril content (1 g) and densities of packing in the plug of 75.7, 86.6, 101, 121.2, 151.5 and 202 kg m^{-3} , in the streaming potential experiments. An Anton Paar EKA, Electrokinetic Analyzer, from Graz (Austria) was used for the determination of the zeta potential of the Leacril samples in the pretreatment of the fibers with the surfactant and also in the posterior dyeing, with different dyes, of the above pretreated samples. The samples of untreated Leacril fibers were conditioned before the electrokinetic and sorption experiments with solutions of N-Cetylpyridinium chloride at temperatures of 283°K., 293°K., 303°K. and 313°K. for 72 h, this time being sufficient to attain equilibrium.

For the determination of the zeta potential of the system, the models of bundle of capillaries, Goring and Mason, Biefer and Mason, and Chang and Robertson (Goring & Mason, 1950; Biefer & Mason, 1950; Chang & Robertson, 1967) were applied to evaluate the zeta potentials of the Leacril plugs. However we have verified that the Goring and Mason model is, in our case, the model which presents a superior correlation coefficient both over the whole tested range of concentration of N-Cetylpyridinium chloride in solution and for all the investigated packing densities of Leacril in the plug (Espinosa & Giménez, 1996).

In the Figure 1, are shown the zeta potentials obtained for Leacril, as a function of the molar concentration of N-CPCI at 293°K. It can be observed that the values of zeta potential are not high. The zeta potential of the system is negative at low concentrations of the surfactant in solution. Zeta potential sign changes at concentrations higher than ca. 2×10^{-5} M of surfactant in solution, its value being zero at this concentration. It increases for values up to 10^{-4} M of N-CPCI, where ζ is maximum, and then decreases as the concentration of the surfactant in solution increases. Further, zeta potential is very low at concentrations between 5×10^{-3} M and 10^{-2} M of surfactant.

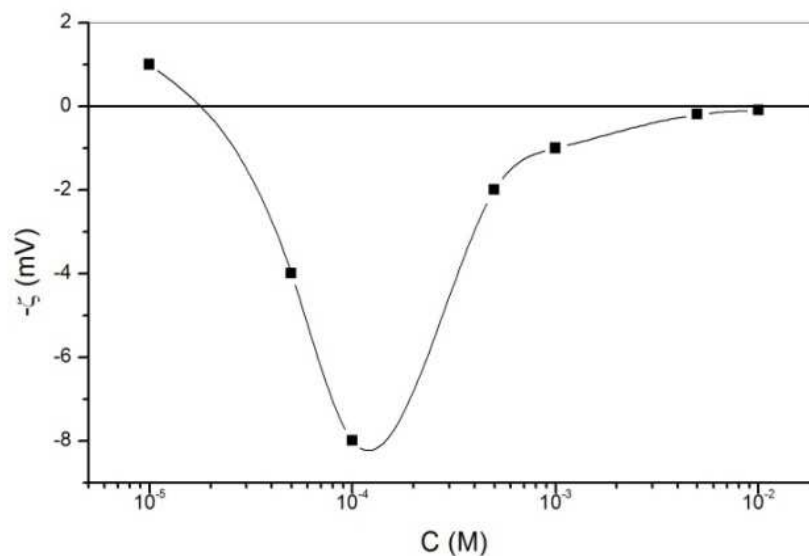


Fig. 1. Zeta potential of Leacril, as a function of NCPCl concentration 293°K..

Sorption experiments at different temperatures have been done to explain the electrokinetic behavior. Figure 2 shows the amount of N-CPCl in the Leacril, M_{eq} , at different temperatures, as a function of the final (equilibrium) concentration of the surfactant in solution.

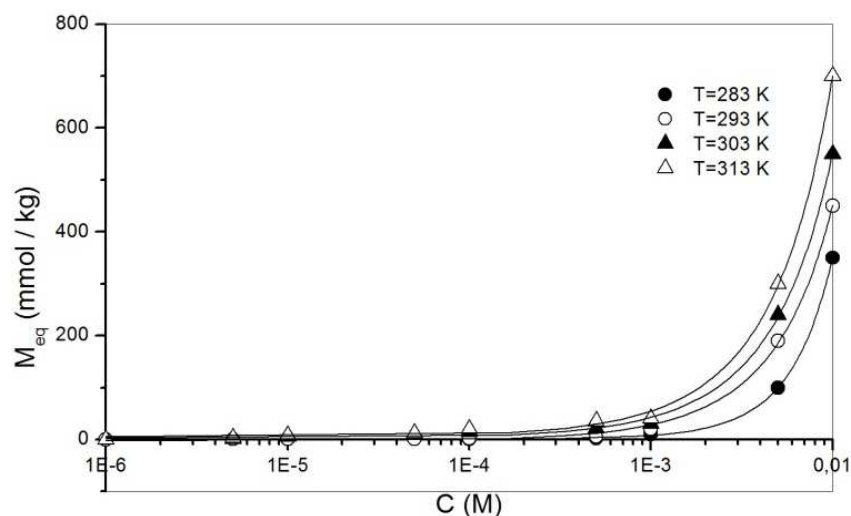


Fig. 2. Amount of NCPCl adsorbed, M_{eq} , at different temperatures.

It can be seen that M_{eq} increases with both increasing concentration of N-CPCl in solution and increasing temperature of sorption. The amount of surfactant taken up by the fiber is low when the equilibrium concentration is lower than 10^{-4} M, and increases abruptly above this value, attaining a value of 730 mmol/kg at 10^{-2} M of surfactant in solution and 313°K. The results shown in Figures 1 and 2, suggest a mode of binding that can be interpreted, probably, on the basis of electrostatic attraction between both the sulphonate and sulfate end-groups of the Leacril fibers and the cation of the surfactant. The increase of the amount of surfactant taken up by the fiber at increasing temperature of the sorption is due, probably, to the increasing ionization of the sulphonate and sulfate end-group of the Leacril at pH=5.8, and the electrostatic attraction between the mentioned end-groups of the fiber

and the cation of the surfactant is favored by the increasing temperature of sorption of the system under these conditions. The fact that the positive value of the zeta potential decreases in the concentration range where the highest amount of the surfactant in the fiber, M_{eq} , appears (Figures 1 and 2), shows that the electrostatic interactions cannot be the only interaction responsible for the uptake of the surfactant by the fibers, some sort of specific interactions between Leacril and N-CPCI must exist. Given the hydrophobic character of the Leacril and the amphiphilic nature of the surfactant molecules, hydrophobic attractions between the fiber and the hydrophobic part of the surfactant might account for the interaction, explaining the sorption of N-CPCI on the Leacril even when it is hindered by electrostatic repulsion. The low zeta potential values for $5 \times 10^{-3}M$ and $10^{-2}M$ surfactant concentration must be consequence of double layer compression.

On the other hand, analysis of the solid surface free energy together with investigation of both, the adsorption and electrokinetic behavior of the system, in the process of adsorption of surfactants and dyes onto textile fabrics, provide extensive information concerning the dyeing, wetting, and finishing mechanisms of the textile materials (Mittal, 1993). Such an investigation has not been reported previously for Leacril fabric, and studies of the surface free energy of Leacril in the processes of dyeing are very scarce.

According to the van Oss et al. approach (Van Oss, 1987,1988a, 1988b, 1989, 1992a,1992b,1994), the interaction between a liquid and a solid surface can be determined from the relationship between the work of adhesion of the liquid to the solid surface, W_a , and the work of cohesion between the liquid molecules, W_c , which is called work of spreading W_s and it is defined by the equation:

$$W_a - W_c = W_s = 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + 2\sqrt{\gamma_S^+ \cdot \gamma_L^-} + 2\sqrt{\gamma_S^- \cdot \gamma_L^+} - 2\gamma_L \quad (1)$$

Where γ_S^{LW} , γ_S^+ , γ_S^- and γ_L^{LW} , γ_L^+ , γ_L^- were the components, Lifshitz-van der Waals, and acid-base, electron-acceptor and electron-donor, of solid surface and liquid, respectively. The thermodynamic characterization of the fabric surface was determined, using the thin-layer wicking method (Chibowski, 1992; Chibowski & Gonzalez, 1993; Chibowski & Holysz, 1992; Duran et al., 1994). According to the Washburn equation, eq.[2], a linear relationship must be obtained between the time (t) that a liquid takes to penetrate a distance (x) through a thin porous layer of a solid, in our experiments, through a piece of Leacril fabric of $25 \times 4 \text{ cm}^2$:

$$x^2 = \frac{Rt}{2\eta} \Delta G \quad (2)$$

where ΔG is the surface free energy change that takes place when the initial solid-air interface is substituted by the solid-liquid interface in the wicking process. R is the average pore radius of the solid, and η the viscosity of the liquid. In order to determine four unknown parameters of the solid surface, R effective radius porous, and the surface free energy components, γ_S^{LW} , Lifshitz-van der Waals component, γ_S^- , electron-donor and γ_S^+ , electron-acceptor components, four wicking systems can be considered in which different values of ΔG in eq. [2] appear. This systems result from the combination of two kind of liquid, non-polar and polar liquid, and two different situations of the solid sample, precontacted strip, if the sample has been previously exposed to saturated vapor of the liquid, and bare strip, when the sample is clean and dry. The situations studied were:

1. When the liquid used wets the solid completely, we used a non-polar liquid such as n-decane, and the solid has been previously saturated with its vapor in such a way that a

duplex film is formed onto the solid surface (precontacted plate), then ΔG_p in the wicking process is: $\Delta G_p = \gamma_L$, (the surface tension of the liquid) and then R can be estimated.

- The same liquid (n-decane) is used as above, but the strip has not been exposed to the saturated vapor (bare strip) the specific free energy changes, ΔG_b , in the penetration process, is determined from the difference between work of adhesion, W_a and work of cohesion W_c . This allows determination of γ_S^{LW} and eq. [2] is given by:

$$\Delta G_b = W_a - W_c = 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} - 2\gamma_L \quad (3)$$

- The solid surface is precontacted with a polar liquid vapor but the penetrating liquid (water or formamide) does not completely spread onto the solid surface. A dynamic contact angle, θ , appears and ΔG_p is now:

$$\Delta G_p = \gamma_L \cos\theta \quad (4)$$

- The same liquid as in case (iii) is used. The solid surface is bare and the liquid forms a dynamic contact angle, θ . In this situation free energy changes involved are:

$$\Delta G_b = \gamma_L \cos\theta + W_a - W_c = \gamma_L \cos\theta + 2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}} + 2\sqrt{\gamma_S^+ \cdot \gamma_L^-} + 2\sqrt{\gamma_S^- \cdot \gamma_L^+} - 2\gamma_L \quad (5)$$

From the combination between eq.[4] and eq. [5], and using two different polar liquids as water and formamide, we can obtained the values of the acid-base components, γ_S^+ , γ_S^- of the solid surface (Chibowski et al., 1998).

Our experiments were performed with water, n-decane, and formamide (Table 1). Straight lines are obtained in the plots of the penetrated distance, x, vs. the time of penetration, t. From the slope of the straight lines, ΔG is obtained, and from this data, the surface free energy components of the fabric are estimated.

Liquid	γ^{TOT} (mJ/m ²)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
n-Decane	23.9	23.9	0	0
Diiodomethane	50.8	50.8	0.0	0.0
Water	72.8	21.8	25.5	25.5
Formamide	58	39.0	2.28	39.6

Table 1. Surface tension parameters of liquids used for thin-layer wicking and contact angle measurements.

The results are shown in Table 2.

N-CPCI C(M)	γ_S^{LW} (mJ/m ²)	γ_S^+ (mJ/m ²)	γ_S^- (mJ/m ²)
0	43.35	0	60.50
10 ⁻⁴	44.4	0.14	57.81
5 · 10 ⁻⁴	45.7	0.16	55.71
10 ⁻³	46.96	0.19	53.59
10 ⁻²	47.9	1.40	35.80

Table 2. Lifshitz-van der Waals, and acid-base components of surface free energy of Leacril as function of the concentration N-CPCI of the treatment.

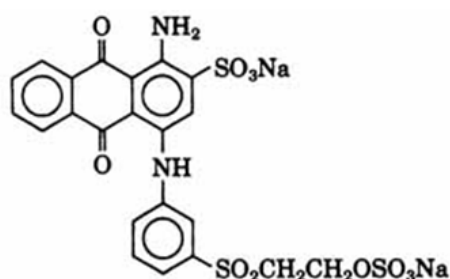
In Table 2, we observe that there are no appreciable differences between the obtained values of γ_s^{LW} in the different processes investigated. The high value for γ_s^- 60.5 mJ/m², obtained in the case of untreated Leacril, is probably due to the presence of sulphonate and sulfate end-groups in the Leacril fabrics (Espinosa et al. 1997a, 1997b; 1998). These groups are donors of electrons and produce a high value in the component γ_s^- for untreated Leacril. This above value is similar to that obtained by van Oss et al. with water-soluble polyethyleneoxide (PEO) (van Oss, 1994). A value of $\gamma_s^- = 60.5$ mJ/m² consistent with these authors' findings suggests that the Leacril surface is a stronger electron donor and hence hydrophilic in nature. Also consistent with van Oss et al., values of γ_s^- higher than 28.3 mJ/m² indicate that the solid surfaces that present this behavior have a hydrophilic character. In our case, for Leacril fabrics, the hydrophilicity of the surface could be attributed to the presence of the sulphonate and sulfate end-groups on the surface of the fabric due to their strong electron-donor character (Espinosa et al., 1998).

In previous studies (Espinosa & Giménez, 1996; Espinosa et al., 1997), it was discussed that the adsorption of N-CPCI on Leacril fabrics probably occurs by electrostatic attraction between the cation of the surfactant and the sulphonate and sulfate end-groups of the Leacril. These processes produce a decrease in the negative charge of the Leacril, and, the γ_s^- decreases with the increasing treatment of Leacril. This may be observed in Table 2. In contrast, γ_s^+ is almost constant for both untreated Leacril and treated Leacril with increasing concentrations of N-CPCI in solution. The small variation of the values of γ_s^+ shown in Table 2 is not sufficiently significant to allow conclusions to be reached about this question.

The value of γ_s^- 35.8 mJ/m², at 10⁻² M of N-CPCI in the treatment of the fabric (Table 2) is probably due to the presence of N⁺ - pyridinium groups in the N-CPCI adsorbed on the fabrics, which is very evident at the highest concentrations of the surfactant on the fabric (see Fig. 1 and Table 1). In this process, there is probably a notable acid-base neutralization due to the interaction between the cation of the surfactant and the sulphonate and sulfate end-groups on the surface of the Leacril.

3. Effect of n-cetylpyridinium chloride on the adsorption of a reactive dye onto leacril fabrics

In this study, we have used the samples of Leacril fibers above mentioned in the paragraph no. 1 of this work. Also we have used the above surfactant N-Cetylpyridinium chloride in the pretreatment of Leacril, before of posterior dyeing of Leacril with the reactive dye. The reactive dye used has been Remazol Brilliant Blue R (RBB-R), C.I. 61200, reactive blue 19, and this dye is an amineantraquinone vinylsulphonated. This dye is referred by Hagen et al. (Hagen et al., 1966). On the other hand, this dye is of AR grade from Sigma Chemical Co. (USA) and was used without further purification. The chemical structure of the RBB-R dye is shown in scheme 2:



Scheme 2.

Experiments were done as we have described in part 1. In Figure 3 are shown the zeta potential of the system untreated Leacril/RBB-R, as a function of the concentration of RBB-R in the liquid phase. We have used the Goring and Mason model for the determination of the zeta potential of the above system. All the values of the zeta potential of the system (Fig. 3) are negative. The increase in the zeta potential for concentrations of dye between 10^{-6} M up to 10^{-5} M of dye in solution can be attributed at the hydrophobic interactions between the fiber and the hydrophobic part of the dye molecule. In this process, the electric charge of the interface increase due to the presence of sulphonate groups in the dye onto the surface of fibers, in the adsorption process of the dye onto the Leacril in these conditions. On the other hand, by concentrations of dye higher than 10^{-5} M the chemical reactions between the $-NH_2$ and $-NH$ groups of the reactive dye and the sulphonate and sulfate end-groups of Leacril could be the responsible of the decrease in the zeta potential of the system shown in Figure 3 in this range of dye concentration. In this process the negative charge of the fiber and hence the zeta potential of the system, decrease in this range of concentration of reactive dye.

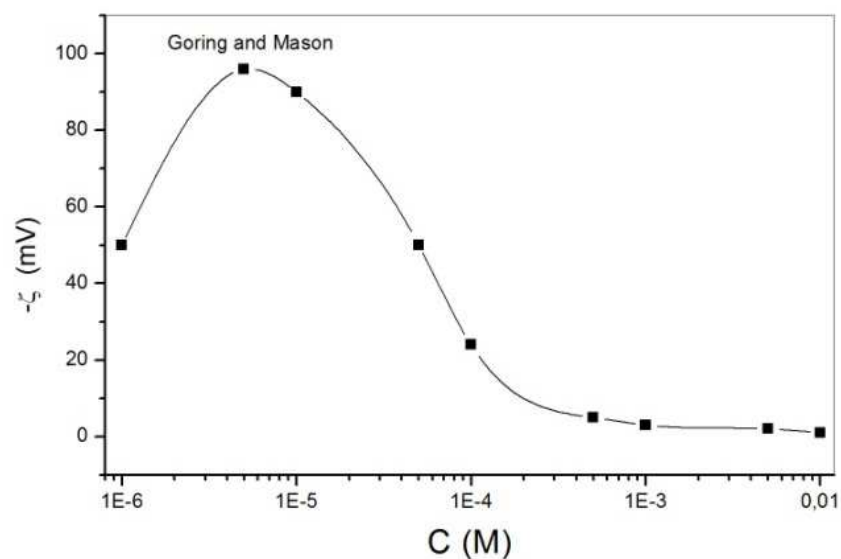


Fig. 3. Zeta potential of the system untreated Leacril/RBB-R, as a function of RBB-R concentration.

In Fig. 4 are shown the amount of RBB-R uptaken by untreated Leacril at equilibrium, M_{eq} as function of the equilibrium concentration of dye in solution, at different temperatures of adsorption. This adsorption is scarce at concentrations of dye lower than 10^{-4} M and increases abruptly for the highest concentrations of dye in the liquid phase. Also it can be observed that this adsorption is favored by an increase in the temperature of adsorption process of the RBB-R onto the fiber. This behavior can be explained for the above chemical reactions between the above mentioned groups of the fiber and the reactive dye. This fact confirms the behavior of the zeta potential of the system shown in Figure 3.

With the aim of to improve the dyeing conditions of the Leacril fibers with RBB-R, we have used 10^{-3} M of N-CPCI in the pretreatment of the Leacril. Subsequently, the treated Leacril with 10^{-3} M of the surfactant, have been dyed with different concentrations of RBB-R at the same temperatures used in the Figure 4. Also we have determined the zeta potential of the system in these conditions. In Figure 5 can be observed the behavior of the zeta potential of the system as a function of the equilibrium concentration of the reactive dye in the liquid

phase for untreated Leacril and for Leacril treated previously with 10^{-3} M of the above surfactant. Also we have used the Goring and Mason model for the determination of the zeta potential in these conditions.

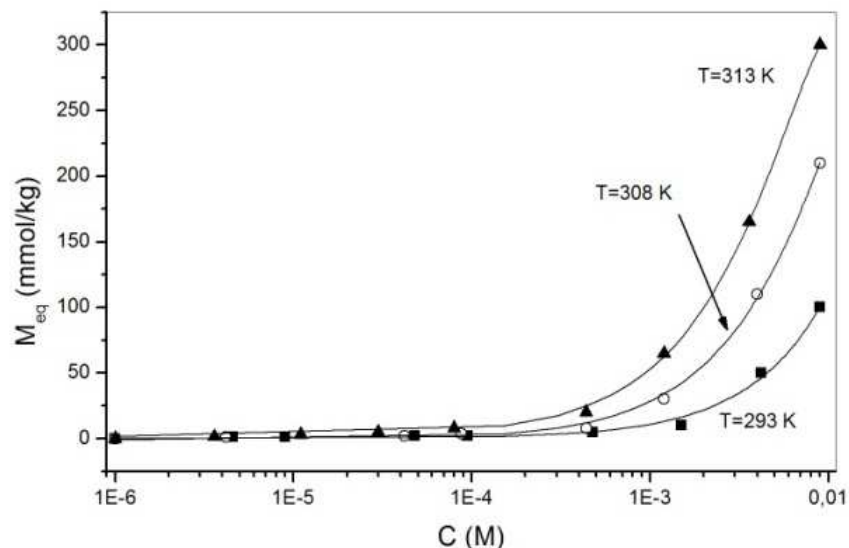


Fig. 4. RBB-R uptaken by untreated Leacril at equilibrium, M_{eq} , at different temperatures, as function of the equilibrium concentration of dye in solution.

In Figure 5, it can be observed a similar behavior of the zeta potential of the system in both cases. However, in this Figure can be observed that the zeta potential values of the system are higher for Leacril treated with 10^{-3} M of N-CPCI that in the case of untreated Leacril, in all range of concentration of RBB-R in the liquid phase. In Figure 5 the increase in the zeta potential for treated fiber in the range of 10^{-6} M up to 10^{-5} M of RBB-R in solution could be explained by the increase of the hydrophobic interactions between the hydrophobic part of the reactive dye and the hydrophobic parts of the Leacril/N-CPCI in the pretreatment of the Leacril.

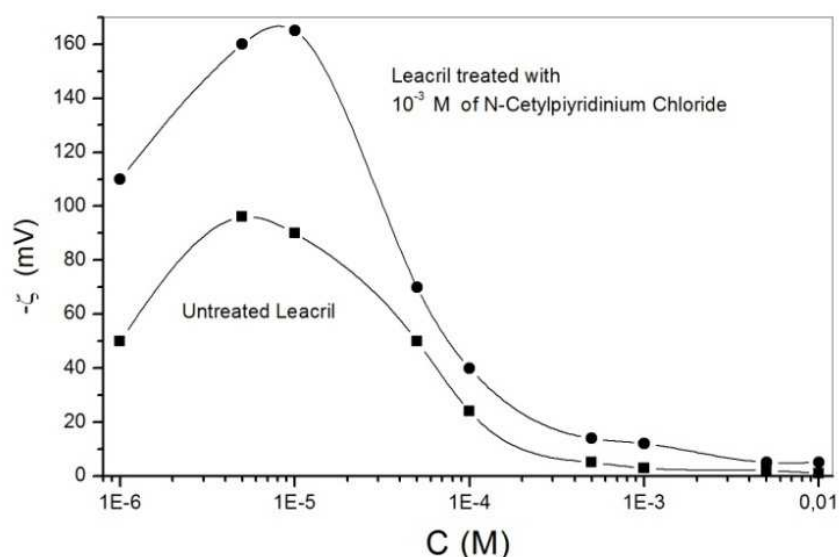


Fig. 5. Zeta potential of untreated Leacril and for Leacril treated previously with 10^{-3} M of N-CPCI as a function of RBB-R concentration.

In these processes the negative charge of the Leacril increases due to the presence of sulphonate groups in the molecules of the reactive dye adsorbed onto the pretreated fiber. When the concentration of the reactive dye in solution is between 10^{-5}M up to 10^{-2}M , the electrostatic interactions between both the cationic group of the pyridinium ring of the surfactant previously adsorbed and the sulphonate groups of the RBB-R could be responsible of the strong decreased in the negative value of zeta potential of the system in the concentration range mentioned. On the other hand, the chemical reactions between the groups $-\text{NH}_2$ and $-\text{NH}$ of the RBB-R and the sulphonate and sulfate end-groups of the Leacril also contributes in a great measure at the strong decrease in the zeta potential of the system treated Leacril/RBB-R at the highest concentrations range of the reactive dye in the liquid phase. Hence, due to the above adsorption mechanisms the negative zeta potentials of the system treated Leacril/RBB-R attain higher values in the case of pretreated Leacril with 10^{-3}M of N-CPCI that in the case of untreated Leacril, in all concentration range of RBB-R in the liquid phase. It is evident in Figure 5 that the reactive dye is adsorbed in a superior amount for treated Leacril with the surfactant than in the case of untreated Leacril.

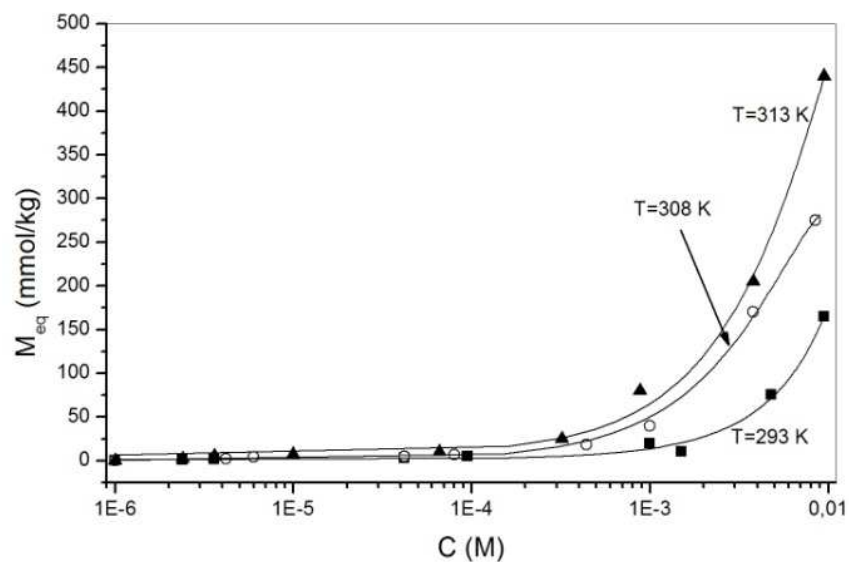
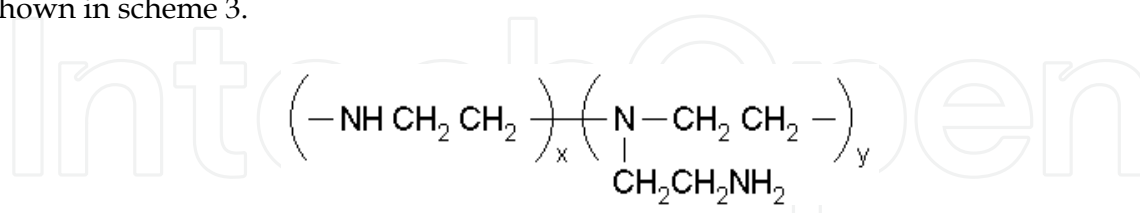


Fig. 6. Amount of RBB-R uptaken by Leacril pretreated with 10^{-3}M N-CPCI at equilibrium, M_{eq} , as function of the equilibrium concentration of dye in solution, at different temperatures.

In Figure 6 are shown the amount of the RBB-R adsorbed at equilibrium, M_{eq} , onto pretreated Leacril with 10^{-3}M of the surfactant as a function of the equilibrium concentration of the reactive dye in solution. These experiments have been done at the same temperatures shown in the above Figure 4. It can be seen in Figure 6, that all the values of M_{eq} of pretreated Leacril with the surfactant are higher than they are in the case of untreated Leacril shown in Figure 4. Also it can be seen, that an increase in the temperature of adsorption favors the adsorption of RBB-R onto pretreated Leacril. These facts show that, probably, the above mentioned chemical reactions between the treated fibers and the RBB-R dye are responsible for the strong adsorption of the reactive dye onto the treated Leacril (Gonzalez et al., 1987; Espinosa et al., 1997c). It is evident that the pretreatment of the Leacril with the surfactant improve the adsorption of the RBB-R onto Leacril.

4. Influence of polyethyleneimine ion on the adsorption of rbb-r onto leacril fibers

In other works, we have also observed the positive effect of the pretreatment of Leacril with a polycationic surfactant, polyethyleneimine ion PEI, in the posterior adsorption of this reactive dye (Giménez et al., 2007; Ramos et al., 2006). Chemical structure of this compound is shown in scheme 3.



Scheme 3.

In Fig. 7 it is shown the amount of RBB-R adsorbed onto Leacril fiber previously treated with different concentrations of PEI as function of the equilibrium concentration of dye in solution, in the range between 10⁻⁶M to 10⁻³M, and at 293°K. As mentioned before, the amount of reactive dye adsorbed onto Leacril untreated at room temperature is scarce; we think that the attractive interactions are very weak and do not overcome the mutual electrostatic repulsion anionic functional groups. However, when the fibers are pretreated with increasing concentrations of the polyelectrolyte in solution, the amount of reactive dye adsorbed increases, reaching values of 90 mmol/kg of dried fiber, at 10⁻³M RBB-R in liquid phase, for a concentration of 5 g/l of PEI in the pretreatment, and at room temperature. These data could be very interesting for textile industry because the process takes place at low temperature.

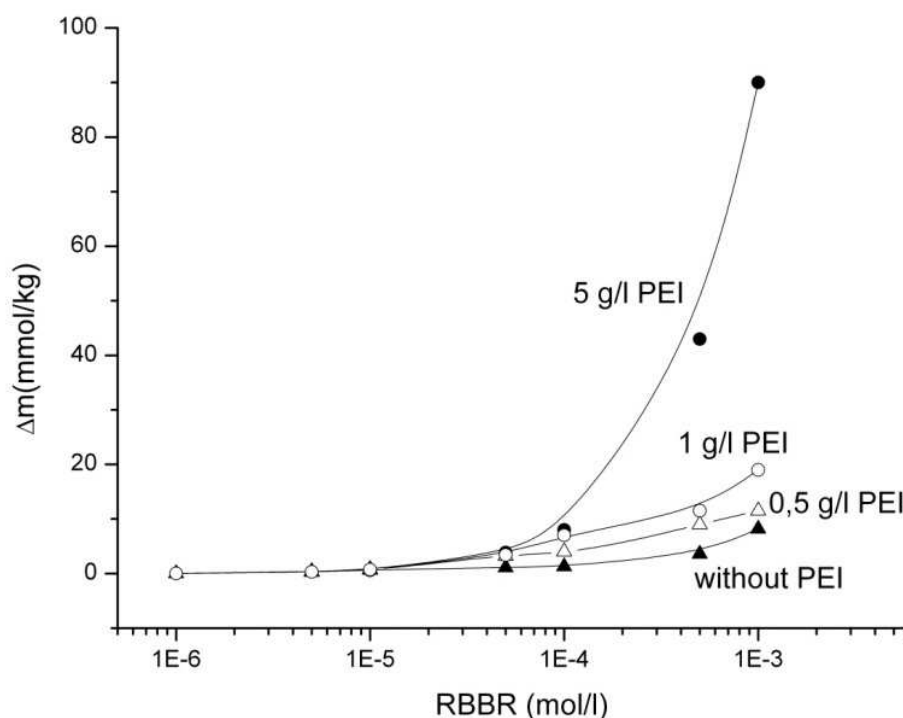


Fig. 7. Amount of RBB-R uptaken by Leacril pretreated with different concentration of PEI in solution as function of RBBR concentration at 293°K .

The evolution of zeta potential of the Leacril pretreated with different concentration of PEI as function of dye aqueous solution of RBB-R concentration is represented in Fig. 8. It can be observed that the zeta potential of the system increases to reach positive values when Leacril has been pretreated with PEI, in the range of low concentrations of dye in solution. This fact could be due to the presence of amine groups from the PEI molecules adsorbed onto Leacril, possibly ionized, providing the cationic charge density to the fiber as we have observed in previous works (Ramos et al. 2006). This effect becomes more significant as the PEI concentration of the pretreatment gets higher. On the other hand, we have found that at the highest RBB-R concentrations in the liquid phase, zeta potential decreases. In our opinion, probably this is caused by the presence of the RBB-R molecules in the fiber surface, which could be taken up by chemical reaction between the amine groups of PEI previously adsorbed and the reactive β -sulphato-ethylsulfanyl group of dye molecule. Finally, the negative charge of sulfonate groups of dye molecules adsorbed onto Leacril surface would justify the decrease in zeta potential values at the highest concentration tested.

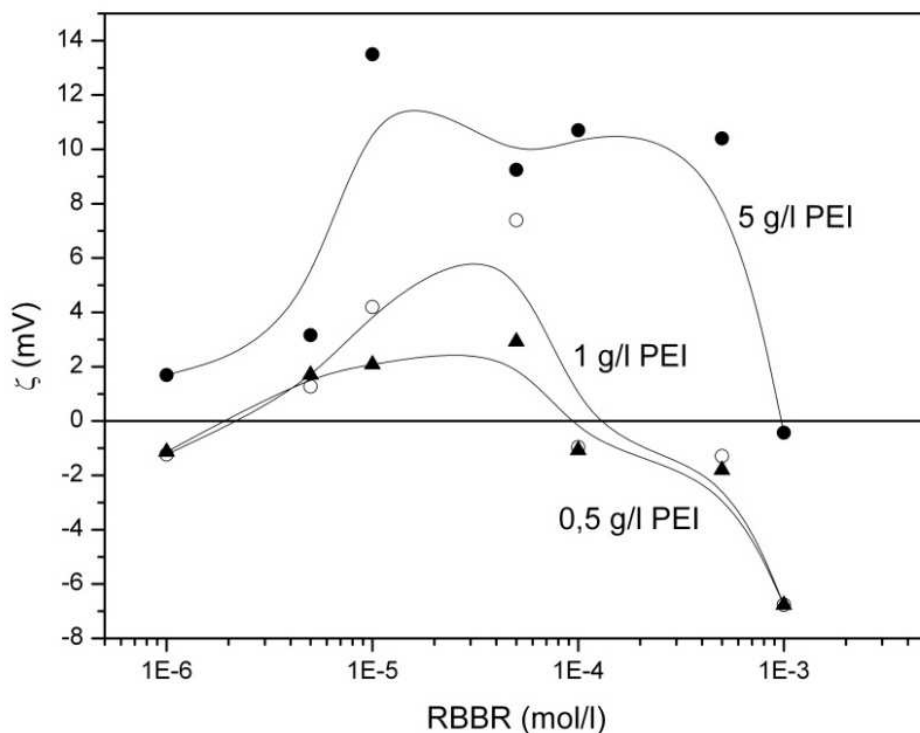


Fig. 8. Zeta potential of Leacril pretreated with different concentration of PEI as function of RBB-R concentration at 293°K .

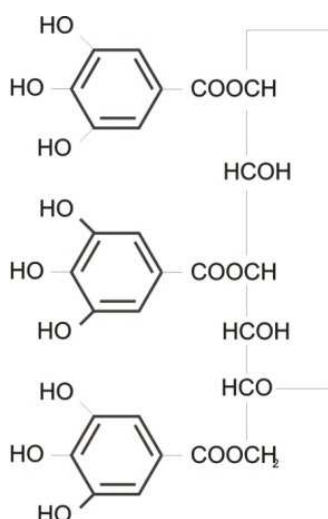
In table 3 are shown the evolution of the Surface free Energy components of Leacril pretreated with 5g/l PEI as function of two concentrations of RBB-R, and also it is presented the components of dye molecule, determined with contact angle measurements and using van Oss method. The most significant result exposed in this table could be the decreases of the electron-donor component value, γ_s^- , of the fiber-PEI with the concentration of RBB-R. In our opinion, the chemical interactions between the reactive acid groups of RBB-R molecule in water solution and the basic amino groups of PEI molecules previously adsorbed over Leacril surface could explain why electron-donor character of the surface falls from an initial value of 58 mJ/m² to 20 mJ/m² for the higher concentration of dye tested.

RBB-R C(M)	γ_s^{LW} (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s^- (mJ/m ²)	γ_s^{TOT} (mJ/m ²)
0	36±2	2.5±0.4	58±6	74±5
10 ⁻⁵	60±3	0.01±0.1	54±1	61±4
10 ⁻³	58±1	0.5±0.1	20±1	64±2
Pure RBB-R in solid phase	43.8±0.4	1.0±0.2	35.7±0.8	56±1

Table 3. Surface free energy components of Leacril pretreated with 5 g/l PEI and later dyed with RBB-R.

5. Effect of the tannic acid onto the zeta potential and surface free energy components of leacril fibers

In this part of the work we have used tannic acid as a surface active agent in the treatment of the Leacril fibers. This compound could be interesting to improve the conditions of dyeing the above acrylic fibers with a cationic dye (Chibowski et al., 1998). Chemical structure is shown in scheme 4.



Scheme 4.

Tannic acid, C₇₆H₅₂O₄₆, was A.R. grade from Merck, and it was used without further purification. It is a derivative of glucose in which five hydroxyl groups are substituted for digalic acid. The result is a large number of phenolic hydroxyl groups in the tannic acid molecule.

The adsorption measurements of tannic acid onto Leacril were conducted using 1 g of the fibers that was contacted with 100 mL of the solution in the concentration range from 10⁻⁶ to 10⁻² M in conical Pyrex flasks fitted with ground glass stoppers. The flasks were kept in a water bath at a desired temperature. Both the adsorption kinetic (from 5×10⁻⁵ M solution) and adsorption isotherms were determined at 275, 283, 293, and 303°K. The maximum absorbance was at λ = 271 nm. The adsorption equilibrium has been attained within 2-3 h. However, the adsorption measurements were conducted up to 24 h. To determine kinetics of the adsorption, first it was measured every second minute, up to the 30nd minute of the process duration, then every 4-5 min, and later for longer periods of time. Zeta potentials of

Leacril fibers versus tannic acid concentration were determined by the streaming potential method, and we have used the three different models of the capillary, although the significant levels were always higher than 95%, the best fit was obtained with the linear model of Goring and Mason. For determination of the surface free energy components by the thin-layer wicking method (42-4 strips of the fabric, 25 cm long and 2.5 cm wide, where first equilibrated in tannic acid solutions (10^{-5} – 10^{-2} M) for 24 h at 293°K, then dried in an oven at 313°K, and kept in a desiccators. Finally, to determine critical micelle concentration (c.m.c) in tannic acid solutions, the surface tension of the solutions was measured with a Rame-Hart goniometer.

First the adsorption kinetic of tannic acid on Leacril surface from 5×10^{-5} M solution was studied at four temperatures, 275, 283, 293, and 303°K. The results of the measurements are presented in Figure 9.

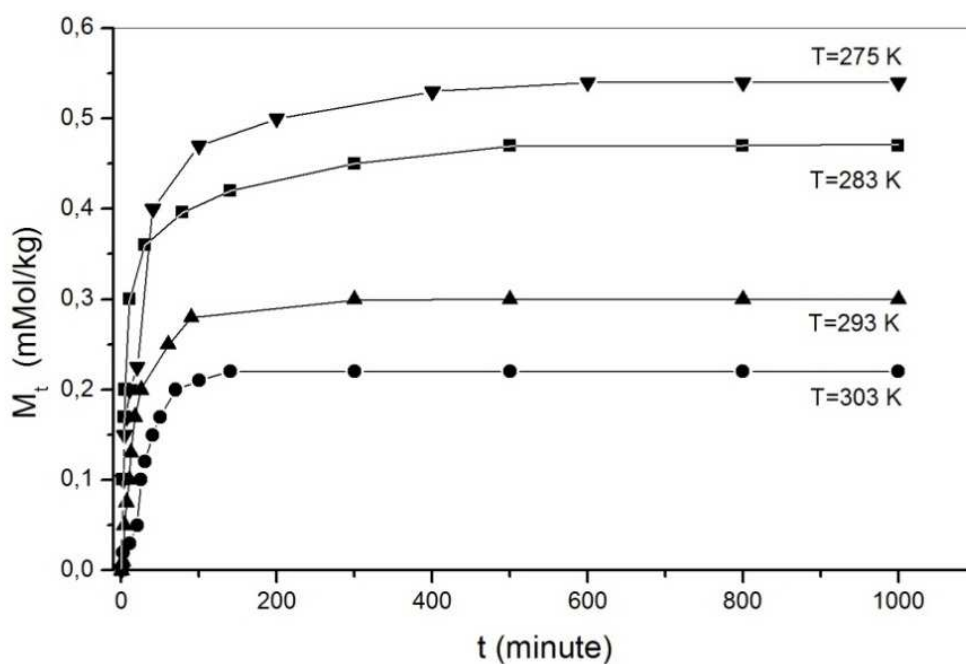


Fig. 9. Adsorption kinetic of tannic acid on Leacril surface at different temperature.

It is seen that even at the highest temperature, 303°K, the adsorption process lasts no more than 100 min and is very fast. The adsorbed amounts of tannic acid decrease with increasing temperature, which points out that the adsorption is physical in nature. To better visualize the adsorption kinetics, the parameters describing the process are listed in Table 4. Because the shape of the curves of adsorption kinetic suggests a first-order process, the rate constant can be determined from the following equation (Anders&Sones, 1965; Peters, 1975, Lyklema 1995)

$$M_t = M_{eq}(1 - e^{-kt}) \quad (6)$$

Where M_t is the adsorbed amount of tannic acid on the Leacril surface at time t , M_{eq} is equilibrium adsorbed amount, and k is the empirical rate constant. This equation has been solved numerically and thus obtained values of the rate constant are listed in Table 4 together with equilibrium amounts adsorbed, M_{eq} . Then, the half-adsorption times were calculated for particular temperatures, which for first-order processes are expressed as follows

$$t_{1/2} = \frac{\ln 2}{k} \quad (7)$$

which is independent of initial concentration of the adsorbate. These values are also placed in Table 4. Having determined the rate constant k , it is possible to calculate the activation energy of the adsorption process from an Arrhenius type equation

$$k = A \cdot e^{-(E/RT)} \quad (8)$$

whose logarithmic form should be a linear dependence against $1/T$, and this appeared to be the case in the studied system. As can be seen from Table 3, the rate constant k decreases with the adsorption process temperature increase. From the slope, the activation energy can be estimated. It was found to be 13.63 kJ/mol. Finally, Fick's equation may be applied to calculate the diffusion coefficient D at the cylindrical walls of the fibers, (Crank 1956)

$$\frac{M_t}{M_{eq}} = \frac{4}{\pi^{1/2}} \left(\frac{D \cdot t}{a^2} \right)^{1/2} \quad (9)$$

For short periods of time, t , a , is the fiber radius, which for this Leacril was 1.5×10^{-3} cm. This equation is only exact for a constant concentration of the surfactant on the surface, whose condition is actually never fulfilled exactly. Nevertheless, the calculated values may be informative for the total insight into the adsorption process. We observe that the apparent diffusion coefficient decreases from 5.39×10^{-10} to 1.14×10^{-10} cm²/s, if the temperature of adsorption increases from 275 to 303°K. This is obviously a consequence of the decreasing adsorption with the temperature increase and may be a result of higher thermal energy of tannic acid molecules in the solution. It is also possible to calculate the activation energy of diffusion, E^* , using again an equation of Arrhenius type

$$D = D_0 \cdot e^{-(E^*/RT)} \quad (10)$$

Here D is the diffusion coefficient and D_0 is a factor that may be interpreted as the diffusion coefficient for the activation energy being zero. The slope of logarithmic form of this equation (which is linear against $1/T$) allows calculation of the energy. For the system studied, the calculated value is 38.13 kJ/mol. This value is about twice that estimated for the activation energy of the diffusion for NCPCl on Leacril (48) and is much higher than that given above for the activation energy of this adsorption process (13.63 MJ/mol).

T (K)	k (min ⁻¹)	$\tau_{1/2} \cdot 10^{-3}$ (min)	M_{eq} (mmol/kg)	$D \cdot 10^{-10}$ (cm ² /s)
275	50.39	13.75	0.54	5.39
283	44.92	15.43	0.47	4.34
293	31.73	21.84	0.30	2.64
303	30.60	22.65	0.22	1.14

Table 4. Equilibrium adsorbed Amounts of Tannic Acid, M_{eq} , Adsorption rate constant, k , half time of adsorption, τ , and diffusion coefficient, D .

On the other hand, the adsorption isotherms of tannic acid at 275, 283, and 303°K versus its equilibrium concentration in the range of 10^{-6} - 10^{-2} M are presented in Figure 10. Similarly as in the kinetic experiments, the adsorption decreases with increasing temperature. The isotherms are concave and the adsorbed amount increases with the increase of equilibrium concentration. The behavior of both the adsorption kinetics and the adsorption isotherms

(Figures 9 and 10) of tannic acid with different temperatures, is similar, adsorption decreases with increasing temperature. This results, can be explained, probably, because of the hydrogen bonding generated between the reactive groups of Leacril and the phenolic hydroxyl groups in the tannic acid molecules adsorbed onto the surface of Leacril (Jacobash et al., 1985, 1988).

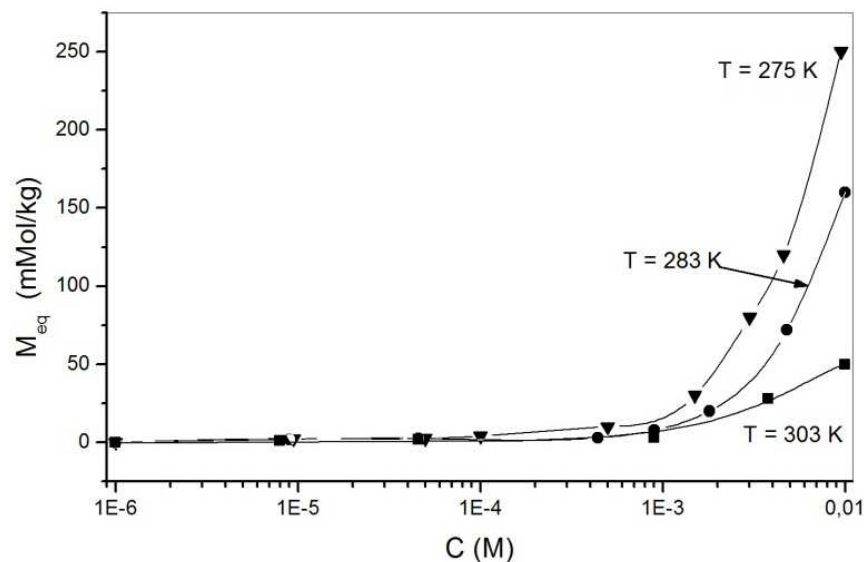


Fig. 10. Adsorption isotherms of tannic acid at 275, 283, and 303°K versus its equilibrium concentration in the range of 10^{-6} - 10^{-2} M.

The surface free energy components of Leacril bare and treated with tannic acid are shown in Table 5.

tannic acid C (M)	γ_s^{LW} (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s^- (mJ/m ²)	W_s (mJ/m ²)
0	43.3	0.00	60.5	-5.6
10^{-5}	51.2	0.66	62.2	9.2
10^{-4}	51.2	0.00	48.5	-5.4
10^{-3}	51.2	0.00	12.0	-41.4
10^{-2}	66.9	28.5	10.8	15.9

Table 5. Surface free energy components of Leacril surface and work of spreading of water of untreated and treated with different concentration of tannic acid.

It can be seen that the apolar Lifshitz-van der Waals interaction, γ_s^{LW} , increases slightly after the surface treatment with 10^{-5} - 10^{-3} M solutions, from 43.4 mJ/m² (untreated surface) to 51.2 mJ/m², but the component does not change after treatment in this concentration range. When the surface was equilibrated with 10^{-2} M solution, the component increases up to 66.9 mJ/m². The analysis of the electron acceptor component, γ_s^+ (Table 3), show how its values is practically zero for bare surface and with adsorbed tannic acid solutions from 10^{-5} to 10^{-3} M. However, it becomes significant (28.5 mJ/m²) if the surface was contacted with 10^{-2} M solution. The changes of the electron donor component, γ_s^- , are more complicated. At the lowest concentration of tannic acid (10^{-5} M) the component is practically the same as for the untreated surface, but the surface treated with higher tannic acid concentrations becomes

less electron-donating. To learn about hydrophobicity of the surface, the work of spreading for water was calculated. Some interesting conclusions can be drawn from these values. The work for the bare surface of Leacril is a small negative. This means, that a water droplet will not fully spread on its surface. Thus, the surface is slightly hydrophobic. After equilibration with 10^{-5} M tannic acid, it becomes low hydrophilic because positive work of spreading. With increasing concentration of tannic acid (10^{-4} and 10^{-3} M) it becomes increasingly hydrophobic, and finally when equilibrated with 10^{-2} M tannic acid, the surface converts to hydrophilic. To explain such behavior, determination of c.m.c for tannic acid could be helpful. The c.m.c was determined from surface tension measurements of its solutions. The results are shown in Figure 11, from which results show that c.m.c of tannic acid lies at ca. 3×10^{-4} M solution.

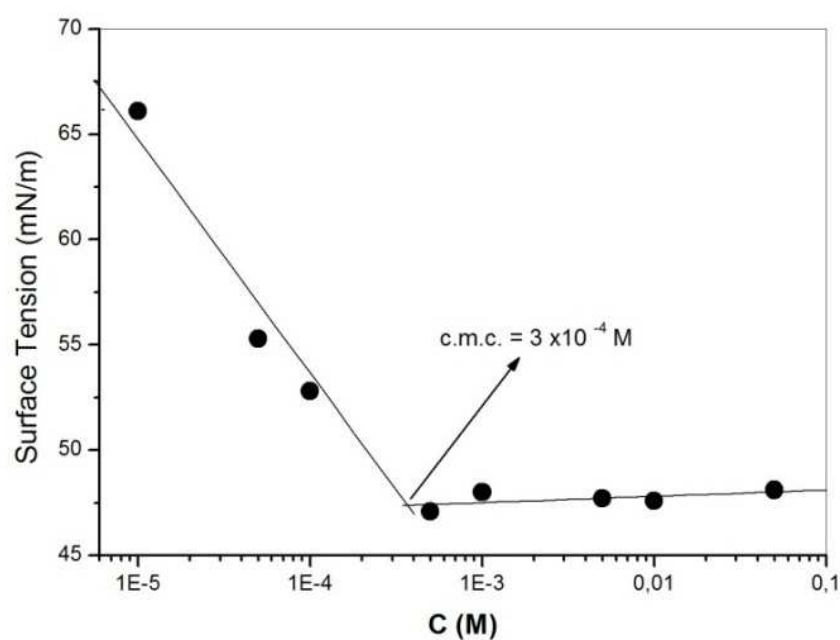


Fig. 11. c.m.c of tannic acid obtained from surface tension of tannic acid solutions against its concentration.

Taking this into account, the changes in the hydrophobicity of tannic acid treated Leacril can be explained as follows. At low concentration (10^{-5} M) only a few molecules of tannic acid are adsorbed on the Leacril surface (see Figure 10), probably by hydrogen bonding between phenolic hydroxyl groups of the acid and sulphonate and sulfate end groups of the Leacril, as well as electrostatic interaction. The molecules may lie flat. With this, more polar hydrogen bonding interactions appear on the surface, and the surface becomes slightly hydrophilic. When the concentration of tannic acid increases, there is less and less room for the adsorbed molecules and they have to pack, probably, with polar groups directed toward the Leacril surface. This leads to increasing hydrophobization of the surface (10^{-4} and 10^{-3} M). However, at concentrations above 3×10^{-4} M micellization takes place, and on the surface pre-micelles and then micelles adsorb. It is possible to imagine that in the case of, say two-molecule pre-micelles, they have mutually saturated polar interactions thus giving rise to hydrophobicity of the Leacril surface. However, when micelles are already formed and adsorbed on the surface, their polar $-OH$ groups will interact with the Leacril surface, as well as directed toward liquid phase (water), thus causing hydrophilization of the surface,

which results from Table 5. Thus, it seems that the changes of surface free energy components of Leacril caused by the adsorbed tannic acid molecules can be explained with a help of c.m.c of tannic acid solutions.

To evaluate possible electrostatic interaction, determinations of the zeta potential were conducted by means of the streaming potential method. As was discussed in above paragraph, three models of the capillary bundles were considered, and it seems to us that the most appropriate one is that Goring and Mason. Zeta potential values as a function of tannic acid concentration applying three models of capillary bundles are plotted in Figure 12.

It is seen that the zeta potentials are small negative, but the absolute values drop practically to zero when the concentration is higher than 10^{-4} M. In our previous paper (Chibowski et al., 1998), we have found that the hydrogen and hydroxyl ions are potential determining for the Leacril surface and the isoelectric point occurred at pH= 2.2. The decrease in zeta potentials in tannic acid solutions with its increasing concentration may be explained by adsorption of tannic acid molecules whose polar groups are partially dissociated, thus possessing positive charge. Anyway, from the results presented in Figure 12 it can be concluded that the electrostatic interaction plays a minor role in the adsorption process of tannic acid and total interfacial interactions, because the zeta potentials are low. It may be postulated that apolar Lifshitz-van der Waals and polar Lewis acid-base interactions are the dominant ones.

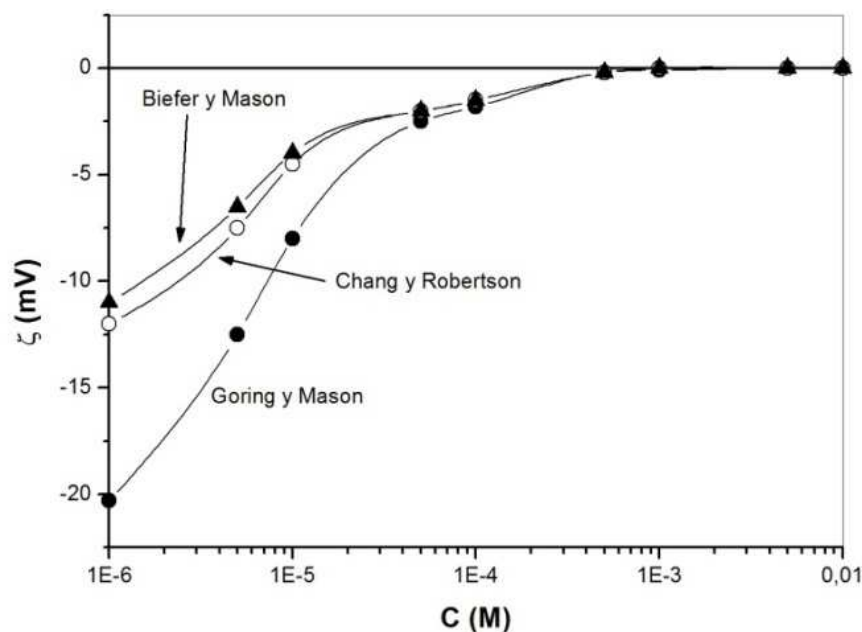


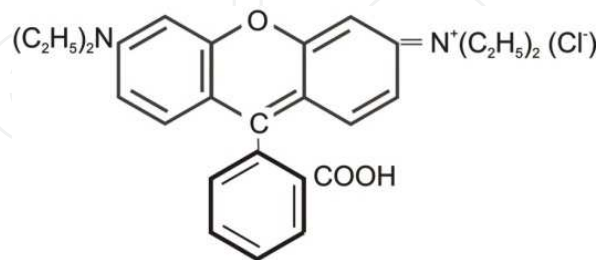
Fig. 12. Zeta potential of Leacril fibers as function of tannic acid concentration.

6. Effect of tannic acid on the sorption of a cationic dye onto leacril fibers

Our purpose in this study is to investigate both the electrokinetic behavior of Leacril fabrics in the process of adsorption of a cationic dye where the Leacril fibers were previously treated with tannic acid and the behavior of the surface free energy components in the above treatment of fibers and also in the adsorption process of the cationic dye on Leacril pretreated with tannic acid. These studies are very interesting with the aim of improving the dyeing properties of Leacril, as has been observed before with cellulosic fibers. (Espinosa Jimenez et al., 1986). To explain the interactions between Leacril pretreated with tannic acid

and later died with the cationic dye, the electrostatic contribution will be analyzed from data of the ζ potential of the system Leacril pretreated with tannic acid/cationic dye at different concentrations of dye in the liquid phase.

The cationic dye used is Rhodamine B (C.I. 45170). The molecular structure of this dye is shown scheme 5.



Scheme 5.

Temperatures tested in our experiments of adsorption were 283, 293, 303, and 313°K. The adsorbed amount was determined after conditioning the fibers with the solution under study for 96 h, this time being sufficient to attain the equilibrium. We have measured the optical absorbance of the dye solutions at a wavelength of 554 nm.

Figure 13 shows the behavior of the zeta potential of the system untreated Leacril/Rhodamine B at different concentrations of the cationic dye in solution for the different models of capillary bundles above described, but, the model that presents the highest correlation coefficient to obtain the data of the zeta potential of the system is the linear model of Goring and Mason that is the model to be employed to obtain zeta potential of the different pretreatments of the Leacril with tannic acid.

We can observe that the zeta potential increases in absolute value for concentrations of dye from 10^{-6} to 5×10^{-6} M of dye solution. The negative value of the zeta potential of the fiber at the lowest concentrations of dye in solution can be attributed to the existence on the surface of Leacril of the sulphonate and sulfate end groups ionized at pH 4, which is the pH condition. On the other hand, the increase in absolute value of the zeta potential of the system shown in Figure 13 for concentrations of the cationic dye from 10^{-6} to 5×10^{-6} M in solution can be explained by the increase of the ionization of the carboxyl group of the Rhodamine B in the molecule of dye at the mentioned value of pH 4. Also this behavior can be explained by the increase in the hydrophobic attractions between the hydrophobic chains of the dye and the Leacril fiber in aqueous media. This fact favors the approximation of the carboxyl groups of the cationic dye to the surface of the fiber. For concentrations above 5×10^{-6} M Rhodamine B in solution one can observe a strong decrease in the absolute value of ζ potential of the system. For the highest range of concentration of dye in solution the zeta potential of the system changes its sign. This change of sign is shown between ca. 10^{-4} and 10^{-2} M of cationic dye in solution. The mentioned decrease of the zeta potential and the change of the sign observed in this parameter can be attributed to the electrostatic attraction between the sulphonate and sulfate end groups of the Leacril and the amine groups of the Rhodamine B. The low values observed in the zeta potential of the system for 10^{-4} to 10^{-2} M of dye in solution also can be attributed to the compression of the electric double layer.

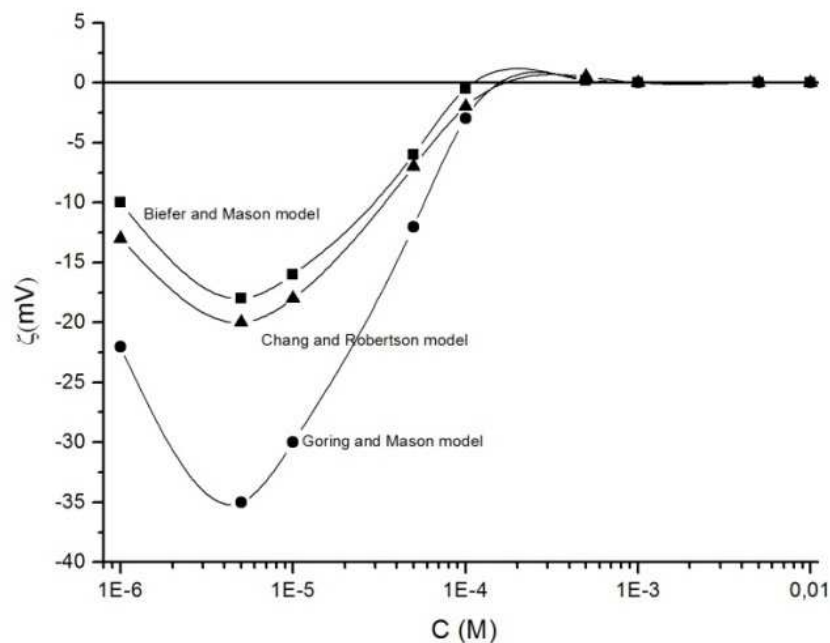


Fig. 13. Zeta potential of the system untreated Leacril/Rhodamine B at different concentrations of the cationic dye in solution for the different models of capillary bundles.

On the other hand, we have carried out adsorption experiments of Rhodamine B on Leacril at different temperatures. Figure 14 shows the amount of Rhodamine B adsorbed on Leacril, M_{eq} , at different temperatures as a function of the final (equilibrium) concentration of the dye in solution.

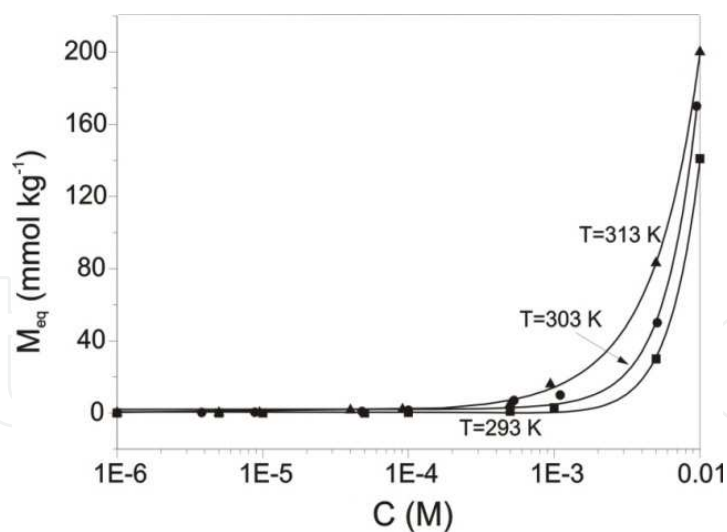


Fig. 14. Amount of Rhodamine B adsorbed on Leacril, M_{eq} , at different temperatures as a function of the equilibrium concentration of the dye in solution.

It can be seen that M_{eq} increases in all cases with both increasing concentration of dye in solution and increasing temperature of adsorption. The amount of dye taken up by Leacril is low when the equilibrium concentration is lower than 10^{-4} M of dye and increases abruptly above this value, attaining a value of ca. 200 mmol/kg at 10^{-2} M of dye in solution and 313°K. The observed increase in M_{eq} with the increase in temperature of adsorption can be

attributed to the increasing ionization of the sulphonate and sulfate end groups of the Leacril with increasing temperature of the system. The fact that the values of zeta potential of the system are very low in the range of concentration higher than 10^{-4} M of dye in solution and, on the other hand, the values of adsorption, M_{eq} , obtained in the same range of concentration increase with the concentration of dye and with temperature of adsorption shows that the electrostatic interaction cannot be the only interaction responsible for the uptake of dye by Leacril: some sort of specific interactions between Leacril and the dye must exist. Given the hydrophobic character of Leacril and the amphiphilic nature of the dye molecules, hydrophobic attractions between the fiber and the hydrophobic part of the dye might account for the interaction, explaining the sorption of Rhodamine B on the Leacril even when it is hindered by electrostatic repulsion. However, the behavior of the zeta potential, practically constant, at the highest range of concentration of dye in the liquid phase also must be a consequence of electrical double layer compression.

With the aim of improving the dyeing process of Leacril with a cationic dye, we have treated the Leacril fibers with different concentrations of tannic acid and later the treated fibers have been dyed with increasing concentrations of Rhodamine B from 10^{-6} to 10^{-2} M of dye in solution. Figure 15 shows the behavior of the zeta potential of untreated Leacril and Leacril pretreated with two concentrations of tannic acid versus the molar concentration of the dye in solution. The obtained values of the zeta potential of the system shown in this figure have been obtained from the linear model of Goring and Mason, which has the highest correlation coefficient.

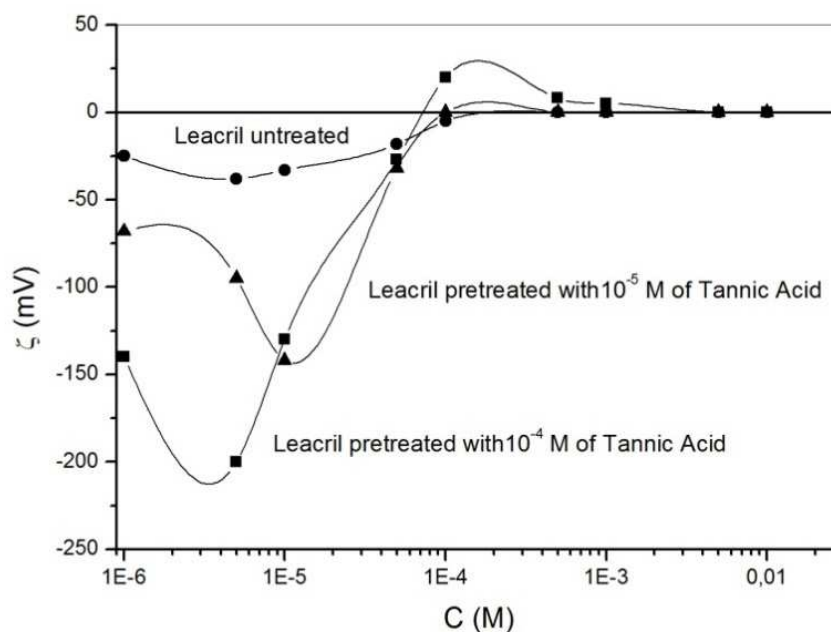


Fig. 15. Zeta potential of Leacril untreated and pretreated with two concentrations of tannic acid versus the molar concentration of the Rhodamine B in solution.

It can be observed that the effect of the tannic acid on the zeta potential of the system pretreated Leacril/Rhodamine B is a general increase in the absolute value of the zeta potential of the system for the all the range of concentration of dye in solution tested. The effect of the tannic acid is more marked at the higher concentrations of this compound in the pretreatment of Leacril. For the concentration range lower than 10^{-4} M of dye in solution and pretreatment

with 10^{-5} M tannic acid, it can be observed an increase of the zeta potential of the system from 10^{-6} to 10^{-5} M of dye, where a maximum value of the zeta potential exists. At still higher concentrations of dye in solution (from 10^{-5} to 10^{-4} M), an abrupt decrease in the zeta potential of the system can be observed. The increase in the zeta potential of the system from 10^{-6} to 10^{-5} M can be explained by the formation of hydrogen bonding between the phenolic hydroxyl groups of the tannic acid and the sulphonate and sulfate end groups of Leacril. In this process the negative charge is increased and hence the zeta potential of the system is also increased. Also, this behavior can be explained by the increase in the hydrophobic attractions between the hydrophobic groups of the dye and the pretreated Leacril fiber in aqueous media. This fact favors the approximation of the carboxyl group of the cationic dye to the surface of the fiber being this group ionized at the acid medium ($\text{pH} = 4$). Figure 15 shows that increasing the concentration of tannic acid in the pretreatment of Leacril results in an rise up of zeta potential of the system due to increasing formation of hydrogen bonding between the phenolic hydroxyl groups of tannic acid and the sulphonate and sulfate end groups of Leacril, even, the observed maximum of zeta potential of the system is displaced to the lowest concentration of cationic dye in solution. This fact is in according with the hypothesis proposed before.

The strong decrease observed in the zeta potential of the system for concentrations higher than 10^{-5} M of dye in solution in the two pretreatments of Leacril with tannic acid can be explained by the electrostatic attractions between the amine groups of the Rhodamine B and the sulphonate and sulfate end groups of Leacril. This fact is particularly marked for increasing pretreatment of Leacril with the tannic acid. It can also be observed that in the range of concentration from ca. 4×10^{-5} to 10^{-4} M of dye in solution, the zeta potential of the system changes its sign. The change of sign is displaced to the lowest range of concentration of dye in the liquid phase when the Leacril fibers are pretreated with increasing concentrations of tannic acid. This fact shows that the tannic acid increases its effect on the dyeing of Leacril with the cationic dye at increasing concentration of tannic acid in the treatment of the fibers. The low values observed in zeta potential of the system from 10^{-4} to 10^{-2} M of dye in solution also can be attributed to the compression of the electric double layer.

On the other hand, we have carried out adsorption experiments of Rhodamine B on pretreated Leacril (with 10^{-5} and 10^{-4} M tannic acid) at different temperatures of adsorption. Figures 16 and 17 show the amounts of Rhodamine B adsorbed on Leacril, M_{eq} , at different temperatures as a function of the final (equilibrium) concentration of the dye in solution. It can be seen that M_{eq} increases in all cases with increasing concentration of dye in solution. Also, it can be observed that at the highest temperature the amount adsorbed decreases. This behavior can be explained by the formation of hydrogen bonding between the carboxyl group of Rhodamine B and the phenolic hydroxyl groups of the tannic acid preadsorbed onto the fiber. (Hiemenz, 1986). Also, this fact can be explained by the electrostatic attraction between the cation of the dye and the negative charge of the fiber generated by the existence of phenolic hydroxyl groups on the fiber and the existence of sulphonate and sulfate end groups of Leacril. When comparing the values of adsorption, M_{eq} , in Figures 16 and 17 for the two treatments of Leacril with tannic acid, one can see that the adsorption of Rhodamine B on Leacril is favored by the increasing tannic acid concentration in the pretreatment. This shows the effect of tannic acid on the sorption of a cationic dye onto Leacril. On the other hand, the behavior of the zeta potential in Figure 15 at the highest range of concentration of dye in solution, where the values of the zeta potential are very low, suggests the existence of other interactions in the systems mentioned above. Hence it is necessary to carry out other studies with the aim of understanding this behavior, such as determinations of evolution of surface free energy components of Leacril with the treatment.

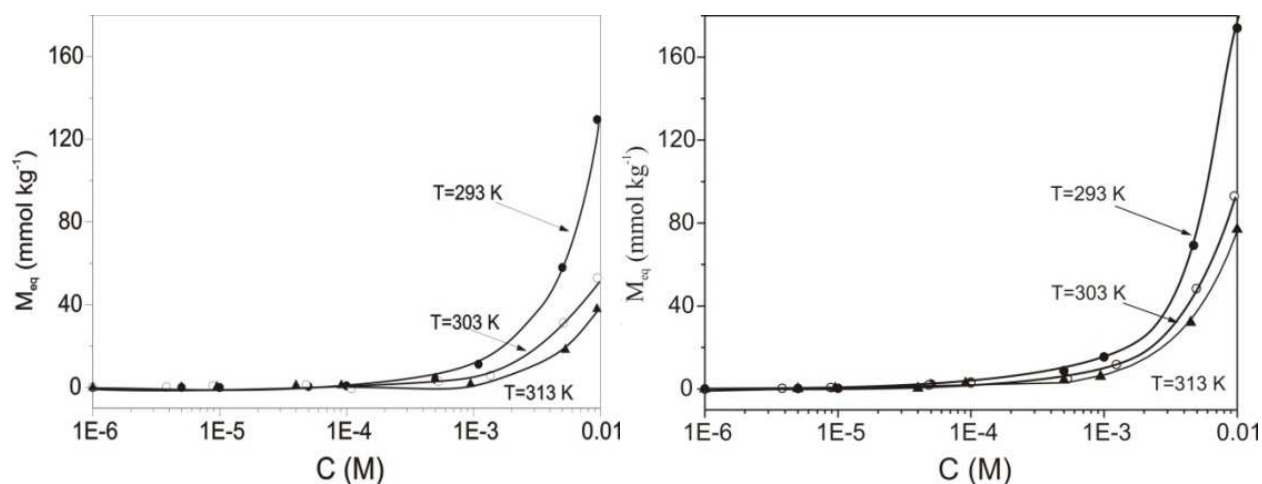


Fig. 16. and 17. Amount of Rhodamine B adsorbed on Leacril pretreated 10^{-5} M and 10^{-4} M of tannic acid, M_{eq} , at different temperatures as a function of the equilibrium concentration of the dye in solution, respectively.

Surface free energy components of treated Leacril dyed with Rhodamine B are shown in Table 6. To explain the behavior shown in Table 6, Table 7 shows the values of surface free energy of untreated Leacril of tannic acid and Rhodamine B in solid phase, from contact angle measurements.

Rodamine B C(M)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
10^{-5}	60.8 ± 0.02	0.7 ± 0.4	61.7 ± 0.4
10^{-4}	47.5 ± 0.5	0.5 ± 0.5	53.6 ± 0.5
10^{-3}	38.1 ± 0.3	1.3 ± 0.4	52.3 ± 0.1
10^{-2}	37.4 ± 0.4	1.4 ± 0.5	51.6 ± 0.1

Table 6. Surface free energy components of Leacril treated with different concentration of Rhodamine B.

Material	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
Untreated Leacril ^a	43.3 ± 0.4	0 ± 0.5	60.5 ± 0.1
Tannic acid	38.2 ± 0.3	0.4 ± 0.4	58.7 ± 0.1
Rhodamine B ^b	38.6 ± 0.2	1.4 ± 0.4	51.7 ± 0.4
Leacril treated with 10^{-4} tannic acid	51.2 ± 0.2	0 ± 0.1	48.5 ± 0.3

Table 7. Surface free energy components for untreated Leacril, tannic acid and Rhodamine B pure in solid phase, and Leacril treated with 10^{-4} M of tannic acid.

In table 6 we can observe that the Lifshitz-van der Waals component, γ_s^{LW} , decreases with the increase in the amount of Rhodamine B taken up by the fabric, up to the value of 37.4 mJ/m². This value is very close to the value of 38.6 mJ/m² obtained for pure Rhodamine B with contact angle measurements. These results can be explained by the greater fixation of the dipoles of the molecules involved in these processes of adsorption. On the other hand (Table 7), the electron-acceptor component γ_s^+ , increases slightly from 0.7 to 1.4 mJ/m²,

which corresponds to the value of this component obtained for Rhodamine B from contact angle measurements. The electron-donor component, γ_{S^-} , decreases from 61.7 to 51.6 mJ/m². These values correspond practically to the obtained values of this component for untreated Leacril and Rhodamine B, respectively. This observed behavior of the components, $\gamma_{S^{LW}}$, γ_{S^+} , and γ_{S^-} , for the dyeing of Leacril with the cationic dye can be explained for the total covering of the Leacril fabric with the cationic dye due to the adsorption of this chemical component onto the Leacril surface. The high values of the electron-donor component, γ_{S^-} , observed in Table 6 can be attributed to the presence of both amine and carboxyl groups in the molecule of Rhodamine B, these groups being strong donors of electrons. Also, the value of 61.7 mJ/m² for the dyeing of Leacril with 10⁻⁵M Rhodamine B can be attributed to the presence of the above groups on the surface of the Leacril and mainly the presence of sulphonate and sulfate end groups on the Leacril fabric that at lowest concentration range of dye in solution are not totally blockaded for the molecules of the cationic dye.

On the other hand, Table 7 shows the values of the components of the surface free energy, $\gamma_{S^{LW}}$, γ_{S^+} , and γ_{S^-} , for the dyeing of Leacril with increasing concentrations of Rhodamine B, this fabric being pretreated with 10⁻⁴ M tannic acid. It can be seen in this table, that the Lifshitz-van der Waals component, $\gamma_{S^{LW}}$, of the system notably decreases with increasing concentration of Rhodamine B used in this treatment. This fact can be due to the increasing of the adsorption of the dye onto Leacril at increasing concentration of this cationic dye, which is favored by the presence of the mordant, tannic acid, in the pretreatment. These results can be explained by the greater fixation of the dipoles of the molecules involved in these processes by the presence of the tannic acid in the surface of the fabric which produces a greater adsorption of the cationic dye according to the results shown in Figures 16 and 17 of this work. The obtained value of $\gamma_{S^{LW}}$ for pretreated Leacril and dyeing with 10⁻³ M Rhodamine B, 37.6 mJ/m² is close to the value of 38.6 mJ/m² obtained for pure Rhodamine B (Table 7) and the general behavior of this component is to decrease their value in the presence of tannic acid preadsorbed onto the fabric. These facts show that the effect of tannic acid is to favor the adsorption of the cationic dye onto the Leacril fabric.

Rodamine B C(M)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
10 ⁻⁵	55.7±0.6	1.6±0.5	40.8±0.2
10 ⁻⁴	38.9±0.2	2.37±1	60±5
10 ⁻³	37.6±0.2	4.6±0.4	65.9±0.2

Table 8. Surface free energy components for Leacril pretreated with 10⁻⁴M of tannic acid and died with different concentration of Rhodamine B.

In Table 8 it can be seen that the electron-donor component, γ_{S^-} , of the surface free energy increases from 40.8 to 65.9 mJ/m² for Leacril pretreated with 10⁻⁴ M tannic acid and subsequently dyed with increasing concentrations of the cationic dye Rhodamine B. This behavior can be explained by the increasing presence on the surface of Leacril of the hydroxyl end groups of the tannic acid taken up by Leacril in its treatment and also by the presence on the surface of the fabric of both the carboxyl groups and amine groups of the chromophore of the Rhodamine B taken up by Leacril in its dyeing. These groups have a strong electron-donor character and their effects on the behavior of the surface free energy are additive. Hence the high value of γ_{S^-} obtained for 10⁻³M Rhodamine B by the

pretreatment of the fabric with the tannic acid, this value being 65.9 mJ/m, is higher than the value obtained for this component by Rhodamine B (Table 7). This fact shows the additive effects of the groups mentioned above on the behavior of γ_s^- in these processes of dyeing Leacril with the assistance of the mordant, tannic acid. The behavior of the electron-acceptor component, γ_s^+ , observed in Table 5, where an increase of this component is observed, having the value of 4.6 mJ/m² for 10⁻³M Rhodamine B can be due to the formation of micelles of the cationic dye since the c.m.c of Rhodamine B is close to 10⁻³ M (this data was obtained from conductivity measurements). In these conditions the micelles are adsorbed, but now with polar heads directed also towards the solution phase. Hence this fact leads to an increase in the electron-acceptor component, γ_s^+ , for the higher concentration range of Rhodamine B in solution.

7. Study of the leacril dyeing process by a cationic dye from an emulsion system

In this part of the work a dye-in-emulsion dyeing process onto Leacril was investigated using a cationic dye, Rhodamine B. The process was analyzed through the changes in surface free energy of the Leacril. To our knowledge, no work has been reported in the literature dealing with the application of the dye-in-emulsion system to improve the adsorption onto Leacril. The Leacril used is the same of the above studies. The emulsion of Rhodamine B was prepared in the following way: 0.15 ml of n-hexadecane was dissolved in 7.7 ml of 2-propanol (p.a.) placed in a 100-ml flask, and then 10 ml of 0.01 M tannic acid was added (as a surfactant) in which 48 mg of Rhodamine B (as a cationic dye) was dissolved. The content was mixed and doubly distilled water (Milli-Q System) was added up to a volume of ca. 50 ml. Next, the flask was placed in an ultrasonic bath for 15 min and again water was added to reach the final volume of 100 ml. Finally, the obtained emulsion was shaken vigorously by hand.

Studies of the kinetics of Rhodamine B adsorption onto Leacril fibers were carried out, both from its solution alone or from the emulsion (Chibowski et al., 2001). In both systems the dye concentration was 10⁻⁵M, and in the case of the emulsion tannic acid was present as a mordant agent and/ or stabilized the emulsion. For the experiments of adsorption kinetics, in Pyrex conical flasks fitted with ground glass stoppers, 1 g Leacril fiber samples were conditioned with 250 cm³ of a 10⁻³ M aqueous solution of Rhodamine B or the emulsion. The flasks were immersed in a water bath and the temperature was kept constant within $\pm 0.1^\circ\text{K}$. The adsorption was carried out at 293, 313 and 333 K. The amount of adsorbed dye on the Leacril fibers was determined from absorbency as measured with a Hitachi U-2000 spectrophotometer at a 554-nm wavelength, at which the maximum absorbency occurred. Moreover, desorption experiments were also carried out for Rhodamine B from the Leacril surface. These experiments were conducted by washing with deionized water 1g samples of Leacril fibers dyed under the described above conditions. Desorption experiments were carried out in a thermostated bath at constant agitation and a temperature of 293°K. The zeta potentials of the Leacril suspensions in water (Milli-Q system) and in tannic acid solutions were determined electrophoretically. The water pH was regulated with the help of HCl or NaOH concentrated solutions. Zetameter ZetaPlus/Pals (Brookhaven Co) was applied for this purpose. To obtain Leacril powder the fibers were ground in a coffee mill after being cooled in liquid nitrogen. To determine the Leacril surface free energy components the thin-layer wicking technique was applied.

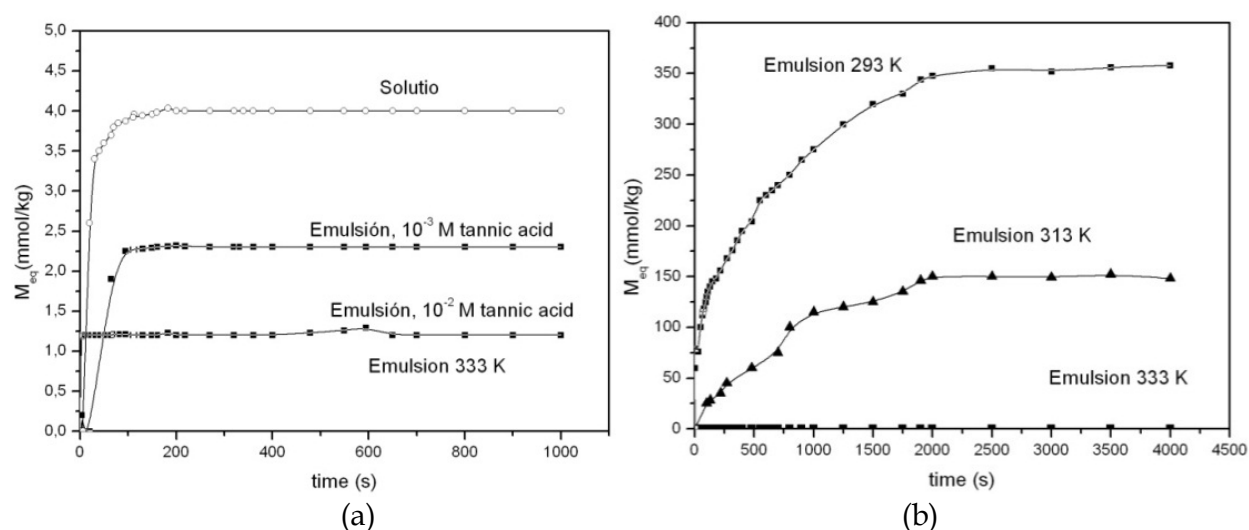


Fig. 18. (a) Amount of Rhodamine B adsorbed onto Leacril from its 10^{-3} M emulsion phase containing 10^{-3} M tannic acid at 293, 313, and 333°K, as function of time. (b) Amount of Rhodamine B from its 10^{-3} M solution onto Leacril, as function of time.

Isothermal rates of adsorption are shown in Figures 18A and 18B. The curves in Figure 18A relate amounts of cationic dye Rhodamine B adsorbed onto Leacril from its 10^{-3} M solution in the emulsion phase containing 10^{-3} M tannic acid at 293, 313, and 333°K, respectively. In Figure 18B are shown the adsorbed amounts of Rhodamine B from its 10^{-3} M solution alone. Because the adsorption from the emulsion at 333°K is small, therefore in Figure 18B is also shown adsorption of Rhodamine B from the emulsion at this temperature. From Figures 18A and 18 B it is evident that at 293 and 313°K the adsorption of dye on the Leacril is much higher in the case of the emulsion. However, at 333°K the adsorption of dye is much lower from the emulsion than from the solution of Rhodamine B. Moreover, with increasing temperature the adsorbed amount decreases from emulsion, while it increases from solution. A decreasing adsorption with increasing temperature of the process is typical for physical adsorption. The shape of the adsorption isotherms is evidence of the first-order process and therefore the adsorption rate constant can be estimated from an equation relating adsorption vs time [6]. We have determined the values of the rate constant and half-adsorption time eq. [7] presented in Table 9.

Temp. (°K)	$k \times 10^3$ (min ⁻¹)	$t_{1/2}$ (min)	M_{eq} (mmol/kg)	$D \times 10^{10}$ Cm ² /s)
Emulsion of the Dye				
293	125.7	5.51	325.2	9.75
313	124.4	5.57	140.6	1.30
333	107.6	6.44	3.15	1.10
Solution of the Dye				
293	65.5	10.3	21.85	0.44
313	77.3	8.96	32.2	1.12
333	120.8	5.73	55.51	1.52

Table 9. Equilibrium adsorbed Amounts of Rhodamine B, M_{eq} , Adsorption rate constant, k , half time of adsorption, t , and diffusion coefficient, D for the systems 10^{-3} M Rhodamine B in emulsion/Leacril and systems 10^{-3} M Rhodamine B in solution/Leacril.

As it can be seen from this table, when Rhodamine B was adsorbed from the emulsion system the rate constant k decreased a little with increasing temperature, and for adsorption from the solution k increased markedly. The adsorption rate constants from emulsion are practically the same at 293°K and 313°K, and they are much higher than those determined for adsorption from the solution at the same temperatures.

Looking for an explanation for such relationships the activation energies and diffusion coefficients for the adsorption process were determined next. Applying the equation [8] of this work, the activation energies E of the adsorption process of the dye in the case of both emulsion and solution were then estimated. The results obtained are $E=3.2$ kJ/mol, for the emulsion system, and $E=11.7$ kJ/mol, for the adsorption from solution. These values show that the activation energies are low and hence it can be concluded that both processes are governed by interactions of a physical nature. On the other hand, applying equations [9], we have obtained the values of the apparent diffusion coefficient, D , for the adsorption process from both the emulsion and solution, respectively. These values are also presented in Table 9. Moreover, it is also possible to determine the activation energy of diffusion process, E^* , applying the equation [10] of this work. The calculated results for E^* in the diffusion process of the dye from emulsion and solution are following $E^* = 45.0$ kJ/mol for the emulsion and $E^* = 25.4$ kJ/mol for the solution. It appears that the activation energy for the diffusion process is much higher in the emulsion system than in the solution. From the data given in Table 9 and the determined activation energies of adsorption and diffusion one may conclude that the adsorption process in both systems is diffusion controlled. It is much faster in the case of the emulsion than the solution system although it needs higher activation energy. If one assumes that the hydrocarbon forms a film on the Leacril surface, then the diffusion activation energies would indicate that a higher energy is needed to diffuse through the film into the surface. Another reason might be that the Rhodamine B molecules interact (hydrogen bonding) with tannic acid which stabilizes the emulsion droplets. Therefore, a higher energy is needed to adsorb such "complexes" on the Leacril surface, possibly together with the hexadecane droplets. At higher temperatures (313 and 333°K) the diffusion coefficients are practically the same for both systems (Table 9), and both processes occur at similar rates. It is worth mentioning that no visible extraction take place from the aqueous solution of Rhodamine B to the hexadecane phase after vigorous shaking of the system. The same was true if the dye was dissolved in 1 M isopropyl alcohol. This concentration corresponds to that used in the emulsion. We have also found that tannic acid caused formation of a very stable emulsion of water droplets in hexadecane. This means that tannic acid because of its molecule structure is a very good stabilizing agent for both oil-in-water and water-in-oil emulsions. These observations support the above discussion.

The adsorption strengths were also tested by desorption experiments. It was realized by means of a washing process with deionized water. The dyed fibers were placed in a bath with a mechanical stirrer at the temperature of 293°K. These results are presented in Figure 19. The desorbed amounts of the dye are much higher for the sample dyed from 10^{-3} M solution of Rhodamine B (ca. 4 mmol/kg) than for the sample dyed from the emulsion phase and the same concentration of tannic acid (ca. 2.5 mmol/kg). Moreover, the desorption of the dye decreases essentially when the dyeing process have been conducted from the emulsion system and at an increased amount of tannic acid present (10^{-2} M). The results in Figure 19 clearly show that at room temperature the dyeing process of Leacril with Rhodamine B from the emulsion is of a superior efficiency, especially when 10^{-2} M tannic acid is present as a stabilizing agent, whose role seems to be crucial.

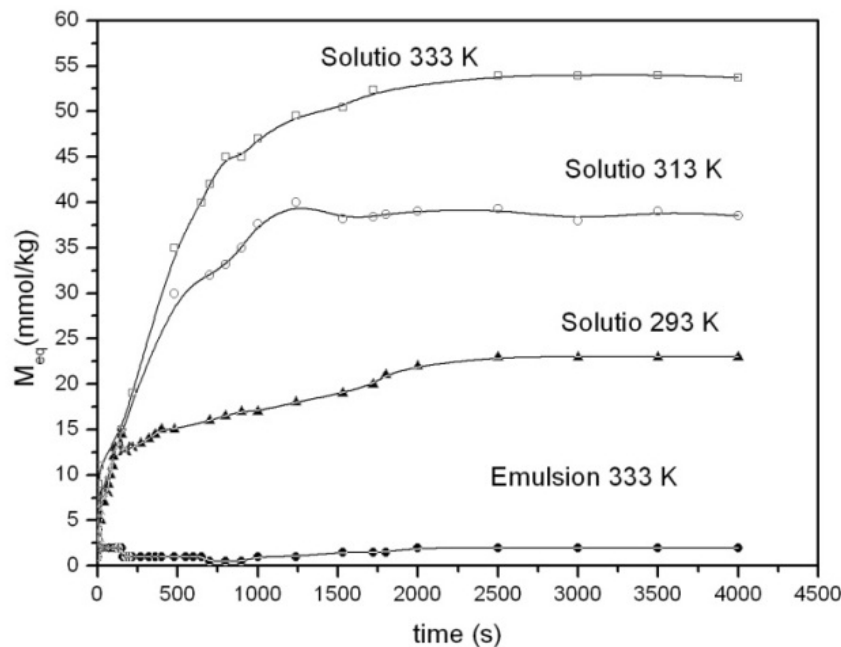


Fig. 19. Kinetic of Rhodamine B desorption from Leacril surface at 293°K adsorbed from 10^{-3} M solution or emulsion.

To obtain more information about the dyeing processes of Leacril from both the emulsion and solution of the cationic dye used, the surface free energy components of the Leacril samples dyed at various temperatures and different conditions were determined. The components are collected in Tables 10 and 11, together with calculated values of the work of spreading for water, W_s .

Temp of dyeing (K)	γ_s^{LW} (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s^- (mJ/m ²)	W_s (mJ/m ²)
293	53.7	0.0	58.4	0.01
313	52.5	0.2	54.6	1.1
333	53.8	0.1	24.5	-23.9

Table 10. Surface free energy components and work of spreading of Leacril dyed with 10^{-3} M Rhodamine B from emulsion containing 10^{-3} M of tannic acid at different temperatures.

Sample of Leacril	Temp (K)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	W_s (mJ/m ²)
0	293	51.9	0.02	53.9	-2.8
10^{-3} M Tannic acid treated	293	59.3	0	56.6	2.3
10^{-3} M Tannic acid treated	333	54.0	0.41	52.1	2.4
10^{-2} M Tannic acid treated	293	63.6	0	66.9	11.5
10^{-3} M Rodamine dyed	293	31.8	1.3	52.3	-3.4
10^{-3} M Rodamine dyed	333	53.7	0.4	55.1	4.2

Table 11. Surface free energy components and work of spreading of Leacril dyed with 10^{-3} M Rhodamine B from solution and treated with different concentration of tannic acid at different temperatures

In Table 10 are shown the components of Leacril samples dyed (10^{-3} M Rhodamine B) at various temperatures from the emulsion system and with 10^{-3} M tannic acid. The Lifshitz-van der Waals component, γ_s^{LW} , is practically the same, but the electron-donor component, γ_s^- , decreases markedly with increasing temperature. It may be due to a partial change in the surface structure, from a crystalline at 293 K to an amorphous one above 353°K. However, the results presented in Table 11 deals with the Leacril dyed surface in the system where hexadecane was present. The low value of the electron-donor component (24.5 mJ/m^2) for the surface dyed from the emulsion at 333°K indicates that the surface became less polar after the adsorption process had taken place. Indeed, the work of spreading is highly negative, being their value of $W_s = -23.9 \text{ mJ/m}^2$, so the surface is hydrophobic and although the adsorbed amount of the Rhodamine was low (Table 8 and Figures 18A and 18B) the surface hydrophobicity protects against its dewashing from the surface (Figure 19). Because for the same system at lower temperatures (293 and 313 °K) the polar component is much higher, one would conclude that the decrease in polarity is mainly due to the surface structure transition. However, it seems this is not the only reason, if one compares the results presented in Table 10. It should be mentioned that the apolar and electron acceptor components for untreated Leacril surface shown in this table are somewhat different than those obtained previously (38.1 and 1.3 mJ/m^2 , respectively), while the electron donor component is practically the same (previously 52.3 mJ/m^2). This is probably due to a different lot of the Leacril sample used in these experiments.

From Table 10 it can be seen that treatment of the surface with tannic acid (10^{-3} M or 10^{-2} M) at 293°K causes an increase in nonpolar, γ_s^{LW} , and electron-donor, γ_s^- , components, while at 333 °K the changes are minor relative to the untreated sample of Leacril. But, the treatment of the surface with Rhodamine B solution (10^{-3} M) alone at both temperatures does not change much the polar component. It shows that the role of hexadecane in lowering the electron-donor interaction of the Leacril surface at 333°K is probably also important. Obviously, the studied systems are very complicated and an unambiguous mechanism of the observed changes cannot be given yet. The changes in polar components are surely due to changes in kind and density of the polar groups present on the Leacril surface originating from tannic acid, Rhodamine B molecules, and the Leacril surface itself. Thus the decrease in γ_s^- must be due to a decrease in the surface density of the electron-donor groups and/or shielding of these groups by the hexadecane film. In Fig.18 B it was observed an increase in adsorption from its solution with the temperature, in this situation electrostatic mechanism of the adsorption can be considered.

In Figure 20 are shown zeta potentials of Leacril surface as a function of pH. As can be seen from this figure the Leacril surface is negatively charged above pH 3, because of the presence of some amounts of sulfate and sulfonate end-groups. On the other hand, Rhodamine B molecules possess positively charged amine groups. With increasing temperature the number of the dissociated groups may increase, which is reflected in the increased adsorption (Figures 18A and B). On the other hand in tannic acid solutions (10^{-5} - 10^{-2} M) the zeta potential of Leacril is practically constant and amounts to $-12.5 \pm 1 \text{ mV}$, as determined by electrophoresis and using the Smoluchowski equation. This means that tannic acid is not potential determining for the Leacril surface and the zeta potentials are about the same as those in water in this pH range.

To summarize briefly, dyeing of the Leacril surface with a cationic dye, Rhodamine B, from the emulsion phase at 313°K and in the presence of tannic acid as a stabilizing agent is more efficient than the dye solution alone. The dyeing systems tested are very complicated and

need further studies for us to better understand the processes that take place in these systems.

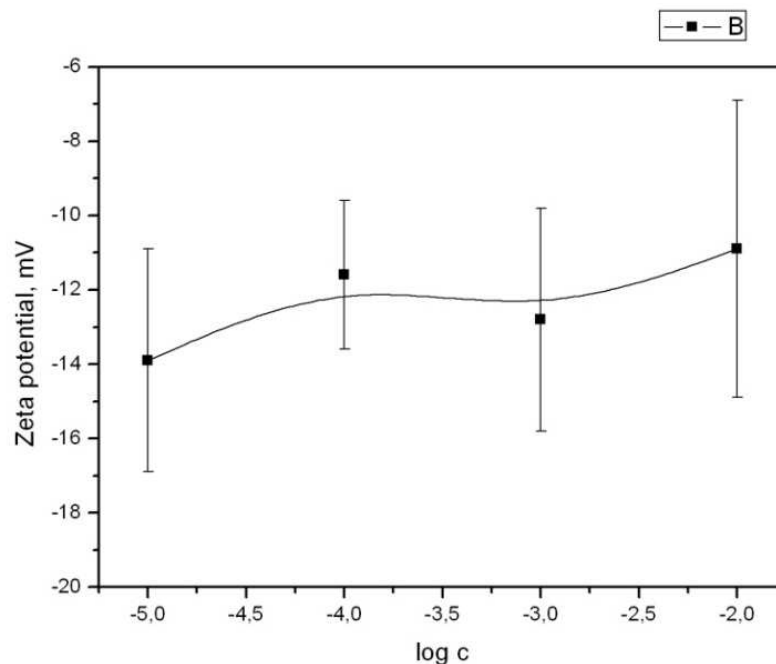


Fig. 20. Zeta potential of Leacril suspension in tannic acid solution determined by electrophoresis.

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Textile Dyeing

Edited by Prof. Peter Hauser

ISBN 978-953-307-565-5

Hard cover, 392 pages

Publisher InTech

Published online 14, December, 2011

Published in print edition December, 2011

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