THE SORPTION ABILITY OF TEXTILE FIBRES

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Obsah

THE SORPTION ABILITY OF TEXTILE FIBRES

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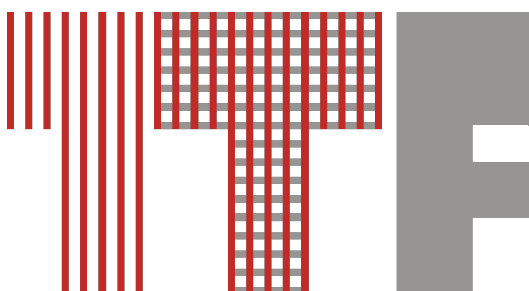
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Abstract: *Sorption capacity of textiles fibres for surfactants and water is discussed. Adsorption of surfactants is characterized through adsorption isotherms, adsorbed, desorbed and residual amount of ionic surfactants in variation of hydrophilic and hydrophobic part and concentration as well. Water sorption is expressed as moisture content and water retention value of textile fibres. Cationic and anionic surfactants are adsorbed on the cotton, wool, polyester and polypropylene fibres at 20°C for 60 minutes. Desorption of surfactants is performed at 20°C for 30 minutes. The results obtained indicate that the key parameters in adsorption process are concentration and composition of the surfactants, as well as the swelling capacity of textile fibres.*
Key words: *surfactants, adsorption, isotherms, desorption, micelles, fibres*

1   INTRODUCTION

The adsorption of surfactants at solid-liquid interface is influenced by a number of factors [1]: the nature of the structural groups on the solid surface (adsorbent); the molecular structure of the surfactant (adsorbate) and the environment of the aqueous phase. Therefore, the above mentioned factors indicate that possible interactions between adsorbent and adsorbate in the aqueous phase are complex [2-5]. An alternative to adsorption for additional surfactant molecules existing in solution is to build aggregates of colloidal dimensions named micelles. The spontaneous formation of micelles is clearly evident from the changes of physico-chemical properties of the surfactant solution, mostly characterized by narrow concentration range, known as critical micelle concentration (CMC). Micelles are not surface active; the significance of CMC is the equilibrium concentration, where surface chemistry ends and colloid chemistry begins. Micellisation and adsorption are two processes; in general the adsorption process is active at lower concentrations than micellisation, so when more of surfactant is added, it usually takes place first [6]. The electric double layer can be created when textile fibres are in contact with an aqueous solution, due to dissociation of suitable molecular groups or the preferential adsorption of one sort of ions or both [7, 8]. The electrical properties of solid surfaces depend on the pH of the aqueous solution. Most textile fibres have functional dissociable group or groups present at the surface. The complete dissociation of functional groups deals with maximum value of zeta potential (ξ_{max}) presented by the plateau of zeta potential in the function of pH [9]. The important and characteristic value of solid surface is an isoelectric point (IEP), labelled as the pH, at which zeta potential is zero. Possible interactions between fibre surface charge and dominant solution particles are important for monitoring or highlighting the adsorption mechanism [10]. A type of adsorption isotherm indicates adsorption mechanism depending upon the surfactant nature and concentration, as well as upon the composition and structure of textile fibres.

The paper deals with sorption ability of textile fibres, characterised by moisture regain, water retention value (WRV), surface charge, as well as by the adsorbed, desorbed and residual amount of ionic surfactants.

Adsorption of ionic surfactant in the concentration range (below and above of CMC) was studied in variation of hydrophilic and hydrophobic part.

2 EXPERIMENTAL

2.1 Adsorbent

Fibres were selected among different types of natural and synthetic ones. The characteristics of commercially available textile fibres, including processing parameters, were as follows:

-COTTON fibres (CO) of an average length of 29 mm, Maturity from 70 to 80 %, Micronaire from 3.8 to 4.2 and Pressley from 87000 to 90000; were pre-bleached with hydrogen peroxide;

-WOOL fibres (WO) of Australian origin with length 73.9 mm and fineness 22.3 μm; were washed in commercial conditions;

- Polyester (PES) fibres with linear density of 3.17 dtex
- Polypropylene (PP) fibres with linear density of 3.3 dtex.

2.2 Adsorbate

The ionic surfactants of analytical grade were purchased from Sigma-Aldrich. The choice of cationic surfactants was based on the variation of hydrophilic group: quat and pyridinium group. Additionally, alkyl chain, from C12 to C16 was varied only in the case of quat group, while pyridinium group was attached to the C 16 alkyl chain. The series of cationic surfactants included:

- Dodecyl trimethyl ammonium bromide **(DDTMAB)**
- Hexadecyl trimethyl ammonium bromide **(HDTMAB)**
- Hexadecyl pyridinium chloride **(HDPC)**

Various hydrophilic groups were included in the series of anionic surfactants: sulphate and sulphonate; sulphate attached to the C 12 alkyl chain and sulphonate to C12 alkyl aryl chain. The series of anionic surfactants included:

- Sodium dodecyl sulphate **(SDS)**
- Sodium dodecylbenzene sulphonate **(SDBS)**

2.3 Adsorption isotherms, adsorption and desorption

Adsorption isotherms of tested ionic surfactants were designed selecting different concentrations: below, near and above CMC (Table 1).

Ionic surfactants of different concentrations (Table 1) were adsorbed on the 5 g of textile fibres at pH 7 in the bath ratio of 1:20 at 20°C for 60 minutes. The process was performed in the Linitest apparatus, Original, Hanau until equilibrium was reached.

Textile fibres were separated afterwards and centrifuged for 60 seconds at 1420 rpm. Drying followed at 40°C for 60 minutes.

After the adsorption (A) of surfactant from the solutions in the concentrations (c_2 and c_4 from Table 1), desorption (D) of surfactants from dried fibres was carried out in distilled water, also in Linitest apparatus at 20°C in the bath ratio of 1:40 for 30 minutes.

Table 1 CMC of tested anionic and cationic surfactants and selection of applied concentrations for adsorption isotherms

SURFACTANTS					
CATIONIC	CMC [mmol/L]	c_1 [mmol/l]	c_2 [mmol/l]	c_3 [mmol/l]	c_4 [mmol/l]
DDTMAB	14	4.8648	9.7295	14.5943	19.4590
HDTMAB	0.91-1.6	0.2744	0.6860	1.3719	2.0579
HDPC	1.24	0.4190	0.8380	1.2570	1.6760
ANIONIC	CMC [mmol/L]	c_1 [mmol/l]	c_2 [mmol/l]	c_3 [mmol/l]	c_4 [mmol/l]
SDS	8.6	2.9475	5.8950	8.8425	11.7900
SDBS	1.1	0.3444	0.861	1.0331	1.722

2.4   Methods

Potentiometric titration method was applied for the determination of surfactants using automatic titrating instrument Titrino 736 GP (Metrohm, Swiss). The commercial ion selective electrode, ISE 6.0507.150, was used as appropriate for anionic and cationic surfactants with adequate variation of pH. Sigma-Aldrich products were applied as titrants, benzethonium chloride (Hyamine 1622) for anionic and sodium dodecyl sulphate (SDS) for cationic, both in the concentration of 4 mmol/l.

Streaming current method was applied to measure electrokinetic potential of textile fibres using Electrokinetic Analyzer (EKA) designed by Anton Paar GmbH, Graz, Austria. Cylindrical cell was used as the most appropriate for fibrous material. Prior to measuring zeta potential, textile fibres were purified in an organic solvent following the procedure according DIN 54278. The fibres were rinsed in deionized water afterwards, until conductivity lower than 4×10^2 µS/m was reached. The electrolyte solution (1 mmol/l KCl) was forced through the cell. Streaming potential was measured versus pressure by means of Ag/AgCl electrode in dependence of pH. Zeta potential was calculated according to the Smoluchowski equation [11].

Water retention value (WRV) was chosen as an appropriate and certain parameter for the determination of fibre swelling capacity. The method according to DIN 53814 is based on the fibres swelling capacity as well as the ability of water retention under controlled conditions (2 g of fibres were soaked during 2 hours and centrifuged during 5 and 20 minutes).

Moisture regain of cotton, wool, PES and PP fibres was determined according to ASTM D 2654 89a. Textile fibres were exposed to standard atmosphere following the standard DIN 53802.

3   RESULTS AND DISCUSSION

Sorption properties of selected adsorbents are characterized by water retention value (WRV) and moisture regain (% H_2O), Table 2.

Table 2 Moisture regain and WRV of selected textile fibres

Fibres	% H_2O	WRV/5	WRV/20
CO	8.34	39.6	35.3
WO	11.91	36.5	34.0
PES	0.93	0.9	0.3
PP	0	0	0

There is a significant difference between natural and synthetic fibres, indicating that the composition of textile fibres causes variation in sorption ability. Higher values of water sorption and retention in the case of natural fibres are influenced by accessible reactive groups. The sorption capacity of PES fibres is low. No water uptake of PP fibres is influenced by hydrophobic nature.

Electrokinetic properties of the adsorbent are evaluated by zeta potential, as an important parameter for surface characterisation, especially in wet processing of textiles, Figure 1.
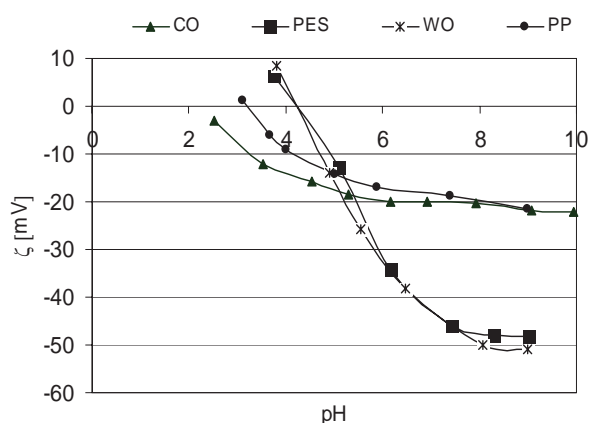

Figure 1 Zeta potential of cotton, PES, wool and PP fibres in dependence of pH 1 mmol/l KCl

Cotton fibres are negatively charged in an alkaline and neutral aqueous solution, mainly due to the presence of hydroxylic or carboxylic groups. Previous results showed that the stage of pre-treatment process significantly affected swelling properties, the accessibility of reactive groups and surface charge [12]. It is confirmed by titration with

an acid (0.1 mol/l HCl) and back titration with a cationic surfactant (0.002 mol/l HDPC). Amphoteric properties of wool fibres are the result of the amino (-NH$_2$) and carboxylic (-COOH) groups. The dissociation of wool fibres in aqueous solutions depends on pH; Wool fibres are positively charged in an acid medium (pH < IEP), because of the dissociation of –NH$_2$ groups. Negative charge of the wool fibres in neutral and an alkaline medium (pH > IEP) results from the dissociation of –COOH groups. Wool fibres have a high value of zeta potential in alkaline and neutral aqueous solutions, compared to cotton fibres.

Most hydrophobic synthetic fibres, including PES fibres, have a highly negative value of zeta potential (according to Jacobasch from -40 to -80 mV) [7]. Esterified carboxylic groups of PES fibres result in strongly negative zeta potential values. Polypropylene fibres have a considerably lower negative zeta potential than the polyester ones, due to specific structure, very low sorption ability, presence of non-polar CH$_2$ groups in the chain and CH$_3$ groups at the end of the chain. Adsorption of the surfactants, dyes, polyelectrolytes, etc. which all have the opposite charge to the adsorbent, adsorption may take place in Stern layer and extend into the surface layer of swollen fibres. Specific hydrophobic-hydrophilic or polar-nonpolar nature of surfactant molecule enables their wide application in textile finishing. They change electrokinetic properties of the adsorbent. The magnitude depends on the distribution and length of hydrophobic part, as well as on the charge and position of hydrophilic group in the surfactant molecule [4]. Adsorption isotherms of cationic

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surfactant, DDTMAB on cotton, wool, PES and PP fibres are presented in Figure 2.
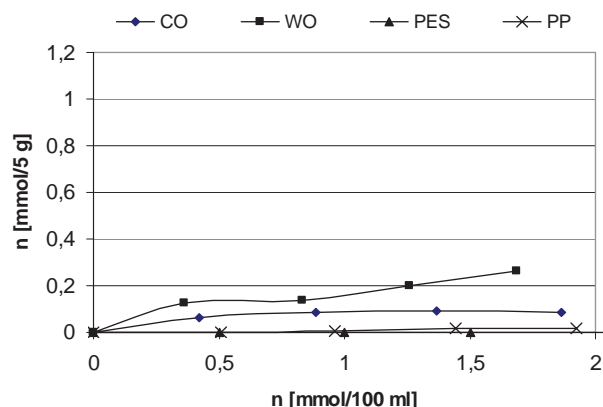

Figure 2 Adsorption isotherms of **DDTMAB** on cotton (CO), wool (WO), PES and PP fibres

Critical micelle concentration (CMC) of DDTMAB is rather high, due to a shorter hydrophobic chain (C12), Figure 2. The lowest concentration applied (1.5 g/l) is below CMC, and at the same time the only one technologically acceptable. It is obvious that synthetic fibres, PES and PP, exhibit rather poor adsorption of this cationic surfactant, despite the negative surface charge. Hydrophobic properties prevail in adsorption, together with low swelling ability of the fibres (Table 3). Wool fibres absorb somewhat higher amount than cotton, which is especially noticeable in the area above CMC. Complex wool fibres, with good swelling ability, have partially broken the micelles, which results in lower concentration than CMC in the solution.

The amount of adsorbed (A), desorbed (D) and residual (R) amount of cationic surfactant, DDTMAB, in dependence of textile fibres composition is presented in Figure 3
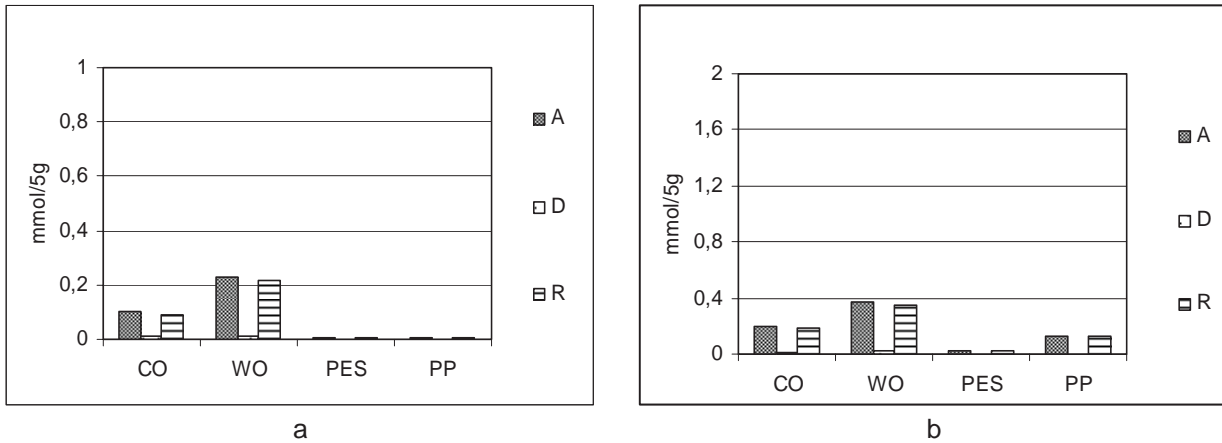
Figure 3 Adsorbed (A), desorbed (D) and residual amount (R) of **DDTMAB**
selection of concentration for adsorption a: $c_1 = 0.9729$ mmol/100 ml; b: $c_2 = 1.9459$ mmol/100 ml

The amount of adsorbed DDTMAB on natural fibres of relevant sorption capacity is low despite of the opposite charges (surfactant and fibres surface), Table 3, Figures 1 and 3. Low amount of adsorbed DDTMAB is mostly retained during desorption in rinsing process.

Adsorption isotherms of the surfactant HDTMAB, Figure 4, are of different shape and slope compared to DDTMAB.

Its adsorption on the PES and PP fibres is somewhat higher. The CMC of HDTMAB is lower than CMC of DDTMAB, as the length of the hydrophobic chain has an impact on CMC.

The amount of adsorbed HDTMAB on cotton fibres is higher than on the wool ones. It proves that electrokinetic potential is not dominant in the adsorption of HDTMAB. The surfactant applied in the concentrations below CMC is fully adsorbed. Cotton and wool fibres intensively adsorb selected surfactant concentrations in the regions near to and above CMC.

The amount of adsorbed and desorbed HDTMAB shows strong sorption and retention ability of natural fibres, as compared to synthetic ones. The lengthening of the alkyl chain in the hydrophobic part of HDTMAB results in lower CMC and adsorption increases in comparison to DDTMAB, Figure 5.

The introduction of the pyridine ring in the hydrophilic part of the surfactant molecule HDPC impacts CMC, Figure 6. The shape and slope of the HDPC adsorption isotherm is similar to the HDTMAB isotherm for all the fibres tested.
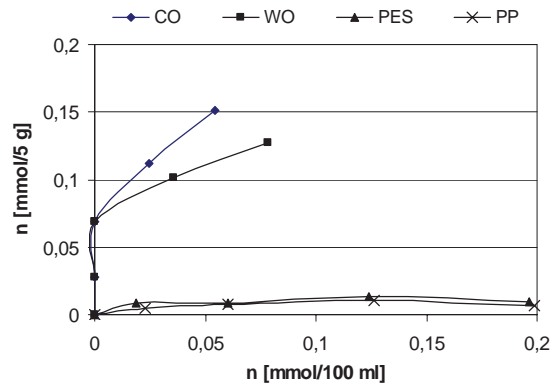

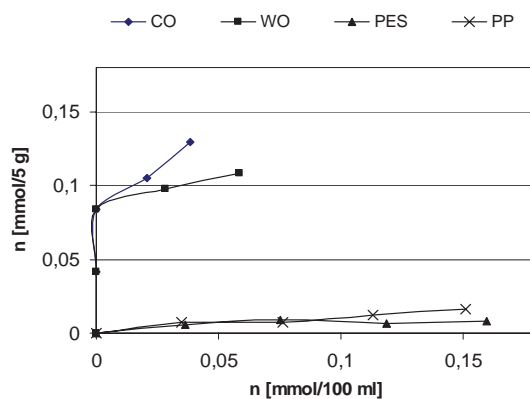**Figure 4** Adsorption isotherms of **HDTMAB** on cotton (CO), wool (WO), PES and PP fibres

Figure 6 Adsorption isotherms of **HDPC** on cotton (CO), wool (WO), PES and PP fibres
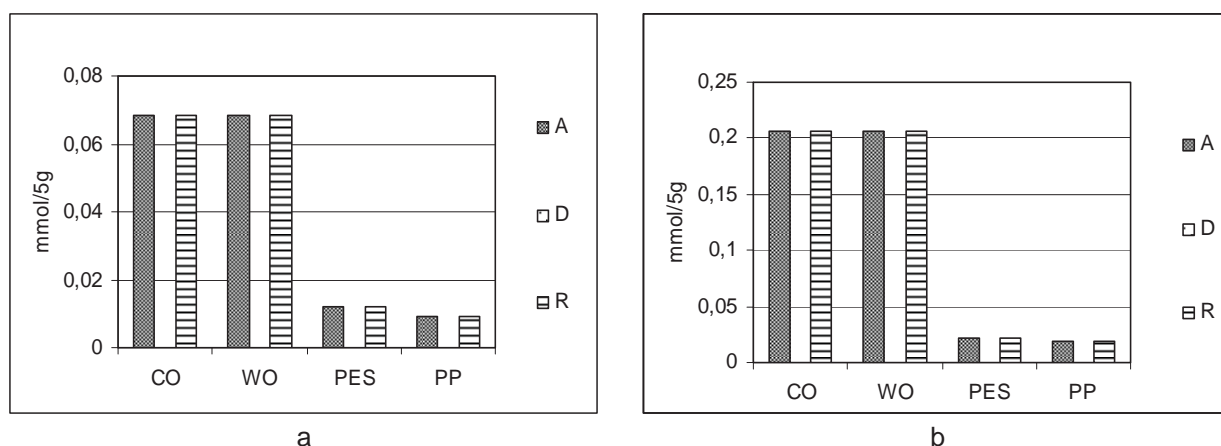
Figure 5 Adsorbed (A), desorbed (D) and residual amount (R) of **HDTMAB**
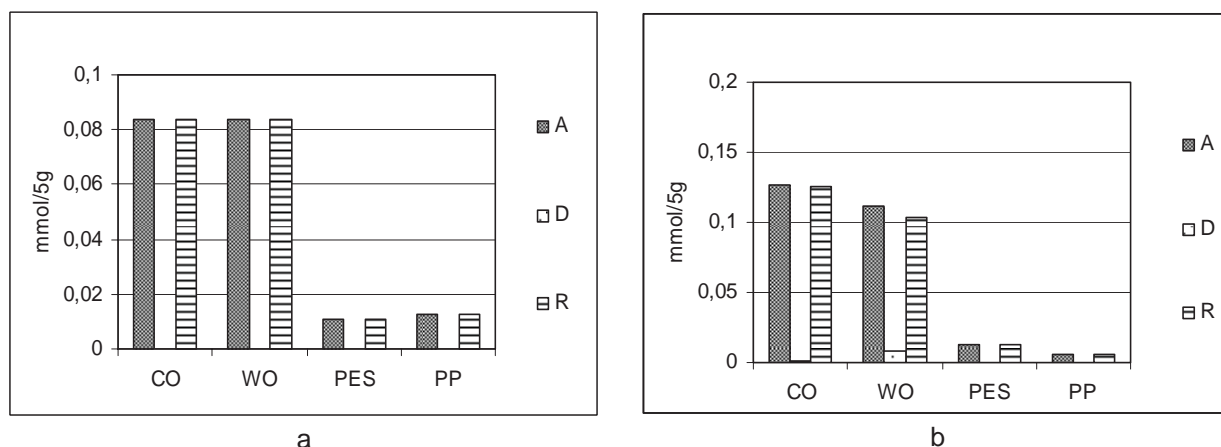selection of concentration for adsorption a: c_1=0.0686 mmol/100 ml; b: c_2=0.2057mmol/100 ml

Figure 7 Adsorbed (A), desorbed (D) and residual amount (R) of **HDPC**
selection of concentration for adsorption a: c_1=0.0838 mmol/100 ml; b: c_2=0.1676 mmol/100 ml

The type of adsorption isotherms indicates the importance of surfactant composition, as well as the equilibrium of the hydrophilic and hydrophobic parts of the surfactant for its adsorption to particular textile fibre, Figure 7. Weaker adsorption of HDPC applied above CMC is primarily the result of more prominent steric barrier. Possible additional reason can be lower CMC of HDPC in comparison to HDTMAB.

The adsorption of anionic surfactants is possible if the potential barrier of the negatively charged fibre surface has been overcome. The tendency is decreased by electrostatic repulsive interactions, Figures 8 - 11.

The adsorption potential of textile fibres for SDS is generally poor. Cotton fibres also exhibit poor adsorption of this surfactant, regardless of the concentration range, below and above CMC alike, Figure 8. Among the fibres tested, wool exhibits the best adsorption properties, regardless of the concentration range applied, both below and above CMC, Figure 8.
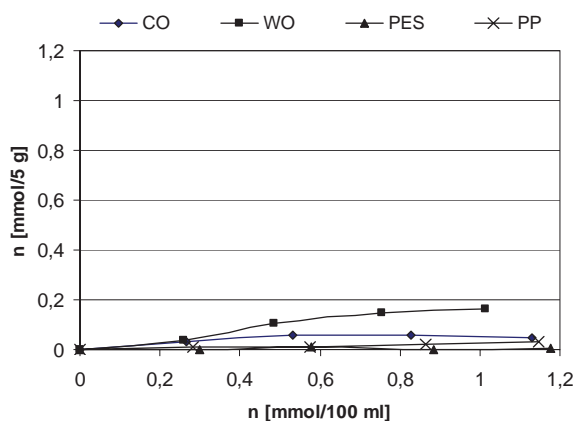
Figure 8 Adsorption isotherms of **SDS** on cotton (CO), wool (WO), PES and PP fibres

Desorption of SDS, from cotton and wool fibres during rinsing, is low. The adsorbed and desorbed amounts are mostly the result of sorption power expressed through WRV, Figure 9.

The surfactant SDBS is a constituent of the washing agent used. The presence of benzene ring in the hydrophobic part results in lower CMC, compared to SDS, Figure 10. This contributes to higher adsorption than is the case with SDS. Higher adsorption of this surfactant is also recorded on synthetic fibres. Cotton and wool fibres completely adsorb SDS at the lowest concentration

(0.15 g/l). Wool and cotton fibres adsorb the surfactant at higher concentration as well, with the adsorption coefficient dropping to below 50 %. Adsorption and low desorption of SDBS from cotton and wool fibres are the result of fibre sorption and retention ability. The adsorption of SDBS on the synthetic fibres results from hydrophobic and steric interactions mostly dominant due to the presence of benzene ring in the hydrophobic part, Figure 11.
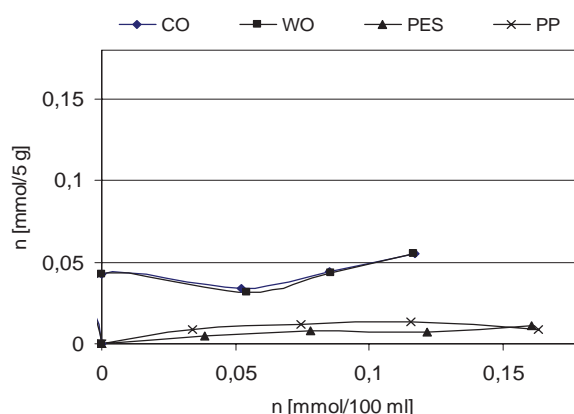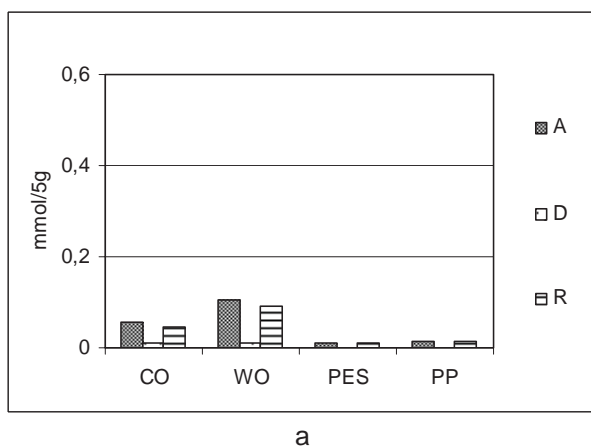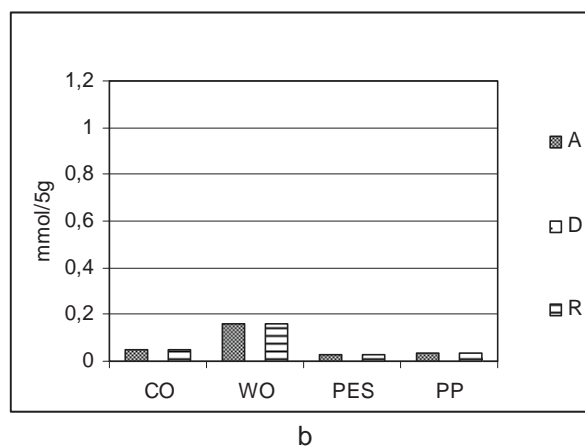

Figure 10 Adsorption isotherms of **SDBS** on cotton (CO), wool (WO), PES and PP fibres

Figure 9 Adsorbed (A), desorbed (D) and residual amount (R) of **SDS**
selection of concentration for adsorption a: c_1=0.5895 mmol/100 ml; b: c_2=1.179 mmol/100 ml
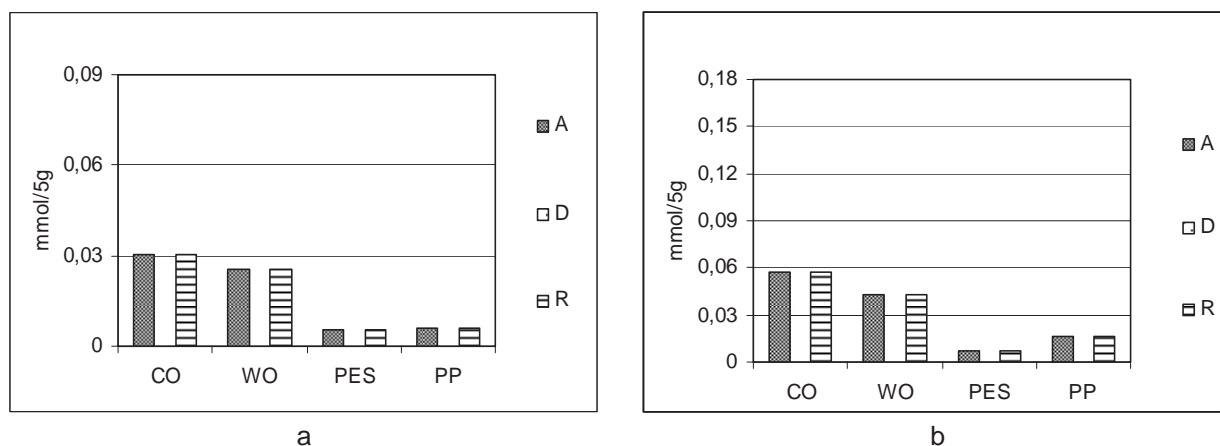
Figure 11 Adsorbed (A), desorbed (D) and residual amount (R) of **SDBS**
selection of concentration for adsorption a: $c_1 = 0.0861$ mmol/100 ml; b: $c_2 = 0.1722$ mmol/100 ml

4 CONCLUSIONS

The adsorption isotherms of anionic and cationic surfactants on cotton, wool, PES and PP fibres are interesting and complex. Adsorbent and adsorbate properties like: hydrophilic-hydrophobic ratio in a surfactant molecule, its solubility and dissociation, as well as fibre structure and active groups and their properties respectively are the most prominent ones.

Results obtained indicate that the key parameters in adsorption process are the concentration and composition of the surfactants, as well as the composition of textile fibres. The influence of zeta potential is essential in the study of selected surfactants. The results show a significant impact of fibre swelling and retention capacity on the adsorbed and desorbed amount of ionic surfactants.

5 REFERENCES

1. Rosen, M.J.: Surfactants and Interfacial Phenomena, Wiley, New York, 1989.
2. Pušić T., Grancarić A.M., Soljačić I.: The Influence of Bleaching and Mercerization on the Changes of Electrokinetic Potential, Vlákna a textil, 8 (2001) 2, 121-124
3. Pušić T.: Adsorption properties of alkali treated cotton fibres, 1st International Textile Conference-Magic World of Textiles, (Prof. Zvonko Dragčević, Ph.D.), October 06th to 09th 2002, Dubrovnik, Croatia
4. Wurster J.: Untersuchungen zur Sorption und Desorption von Tensiden auf textilien Substraten, Melliand Textilber., 57 (1976) 7, 587-593
5. Grancarić A.M. et al.: Electrokinetic behaviour of textile fibres (in Croat) Polimeri, 23 (2002) 6, 121-128
6. Zoller, U.: Handbook of Detergents: Part A, Marcel Dekker, New York 1999.
7. Jacobasch H.J.; Bauböck G.; Schurz J.: Problems and results of zeta potential measurements on fibres, Colloid & Polymer Sci., 263 (1985), 3-24
8. Jimenez-Espinoza M.; Gonzalez-Caballero E.: The electrokinetic properties of cellulose fabrics and their significance in dyeing processes, Cellulose Chem. Technol., 52 (1991), 65-77
9. Pušić, T. Et al.: Adsorption and desorption of ionic surfactants, Tenside Surfactants Detergents 47 (2010) 3, 173-177
10. Weatherburn A.S.; Bayley C.H.: The Sorption of Synthetic Surface-Active Compounds by Textile Fibres, Textile Res. J., 22 (1952) 12, 797-804
11. Ribitsch, V.; Jacobasch, H.J. & Boerner M.: Advances in Measurement and Control of Colloidal Processes, Butterworth-Heinemann (1991), 354-365
12. Grancarić & al.: Influence of electrokinetic potential on adsorption of cationic surfactants, Text.Chem.Colorist, 29 (1997) 12, 33-35

SORPČNÁ SCHOPNOSŤ TEXTILNÝCH VLÁKIEN

The translation of article
The sorption ability of textile fibres

V príspevku sa skúma sorpčná kapacita textilných vlákien vzhľadom na povrchovo aktívne činidlá (detergenty) a vodu. Adsorpcia detergentu je charakterizovaná adsorpčnými izotermami, adsorbovaným, desorbovaným a zvyškovým obsahom iónového detergentu pri striedaní hydrofilnej a hydrofóbnej časti a tiež koncentráciou. Sorpcia vody je vyjadrená ako obsah vlhkosti a zádrž vody v textilných vláknach. Katiónový a aniónový detergent sa absorboval na bavlnené, vlnené, polyesterové a polypropylénové vlákna 60 min pri 20°C. Desorpcia sa uskutočnila 30 min pri 20°C. Získané výsledky ukazujú, že rozhodujúce parametre pri adsorpčných procesoch sú koncentrácia a zloženie detergentov a tiež kapacita napúčania textilných vlákien.