The effect of N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate addition on washing properties of liquid laundry detergents

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ABSTRACT – REZUMAT

The effect of N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate addition on washing properties of liquid laundry detergents

The use of colorimetric analysis based on a CIELab system to determine detergency of commercial liquid laundry detergents before and after modification with SB3C14 sulfobetaine (N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate) is presented. The EMPA 101 standard cotton fabric soiled with carbon black and olive oil was used in washing tests under the following conditions: temperature 40°C, rotational speed 200 rpm, 30 minute washing cycle, water hardness 5.35 mval/l, the concentration of liquid laundry detergents 1.25–50 g/l. The physicochemical analysis of colour, form, odour, pH, density, viscosity and content of anionic surfactants showed compliance with the manufacturers' declarations. The studies demonstrated that with increasing laundry detergent concentration a gradual increase in detergency occurred. At the highest tested concentrations of 50 g/L, detergency of 18.1% and 22.2% for cheaper L1 and more expensive L2 products was achieved, respectively. Modification with the 5% addition of the zwitterionic sulfobetaine SB3C14 led to an improvement of the washing properties by 4.7% on average. At a concentration of 50 g/l, the modified L1 and L2 solutions demonstrated the highest detergency equal to 22.8% and 35.3%, respectively. This proves the existence of synergistic effect by the interaction of all ingredients in the solutions with higher concentrations. Microscopic analysis of EMPA 101 fabrics before and after washing processes showed no serious damage to the fibres, only the presence of slight fraying of individual ones. The results suggest that the SB3C14 sulfobetaine can be successfully used in liquid laundry detergents due to its very favourable surface properties.

Keywords: *surfactants, zwitterionic sulfobetaine, detergency quality, liquid laundry detergents, colorimetric analysis*

Influența adaosului de N-tetradecil-N, N-dimetil-3-amonio-1-propanesulfonat asupra proprietăților detergenților lichizi pentru rufe

Se prezintă utilizarea analizei colorimetrice bazată pe un sistem CIELab pentru a determina capacitatea de curățare a detergenților lichizi comerciali pentru rufe înainte și după adăugarea de SB3C14 sulfobetaină (N-tetradecil-N, N-dimetil-3-amonio-1-propanesulfonat). Materialul textil din bumbac EMPA 101 impregnat cu negru de fum și ulei de măsline a fost utilizat în testele de spălare în următoarele condiții: temperatura 40°C, viteza de rotație 200 rpm, ciclul de spălare de 30 de minute, duritatea apei 5,35 mval/l, concentrația detergenților lichizi pentru rufe 1,25–50 g/l. Analiza fizico-chimică a culorii, formei, mirosului, pH-ului, densității, viscozității și conținutului surfactanților anionici a arătat conformitatea cu declarațiile producătorilor. Studiile au demonstrat că odată cu creșterea concentrației de detergent pentru rufe a avut loc o creștere treptată a capacității de curățare. La concentrații ridicate de 50 g/l, s-a obținut o capacitate de curățare de 18,1% și 22,2% pentru produsele L1 mai ieftine și, respectiv, pentru produsele L2 mai scumpe. Adăugarea de 5% a sulfobetainei zwitterionice SB3C14 a condus la o îmbunătățire a proprietăților de spălare cu o medie de 4,7%. La o concentrație de 50 g/l, soluțiile L1 și L2 modificate au înregistrat cea mai ridicată capacitate de curățare, egală cu 22,8%, respectiv 35,3%. Aceasta dovedește existența unui efect sinergic prin interacțiunea tuturor ingredientelor din soluțiile cu concentrații mai ridicate. Analiza microscopică a materialelor textile EMPA 101 înainte și după procesele de spălare nu a arătat nicio deteriorare gravă a fibrelor, ci doar prezența unei ușoare destrămări a celor individuale. Rezultatele sugerează că sulfobetaina SB3C14 poate fi utilizată cu succes în detergenții lichizi de rufe datorită proprietăților sale de suprafață.

Cuvinte-cheie*: surfactanți, sulfobetaină zwitterionică, capacitatea de curățare, detergenți lichizi pentru rufe, analiză colorimetrică*

INTRODUCTION

Surfactants are one of the most important organic substances, used in large amounts in domestic and industrial applications, such as topical pharmaceutical formulations, antiseptics, cosmetics, shampoos, detergents, creams or lotions. Surface active agents are for to their amphiphilic properties used as emulsifers, suspending, wetting, solubilizing and stabilizing substances. Both ionic and nonionic surfactants are used. In this paper we will focus on a particular group of the compounds – zwitterionic surfactants and their potential application in liquid detergents. They contain both positively and negatively charged hydrophilic groups and the property leads to large dipole moments for zwitterionic surfactant molecules with hydrophilicites intermediate between ionic and nonionic surfactants [1]. Zwitterionic surfactants are mild to eyes and skin, exhibit very low toxicity [2], have a high foam stability and resistance to hard water and to degradation by oxidizing and reducing agents than many ionic surfactants [3–5]. Moreover, the temperature and the addition of electrolytes have little influence on their solution properties. Due to these useful properties, zwitterionic surfactants are often combined with anionic or cationic surfactants in many consumer products [6–8]. One of the most interesting properties of the zwitterionic surfactants is a strong interaction or complex formation with anionic surfactants, which is significant for the practical applications. Anionic surfactants are the main component for their detergency and foaming properties, and additionally the zwitterionics can act as a booster [9, 10]. In recent years, mixed nonionic/ionic, nonionic/nonionic, and ionic/ionic surfactant mixtures have been studied and reported in the literature [11–13].

Betaine surfactants are an important kind of zwitterionic surfactants and they are widely used as boosters in hair conditioners or shampoos, because they can stabilize foams against the antifoaming action of oil droplets [14]. Compared to other surfactants, betaines have many excellent advantages, such as high interfacial activity at low concentrations [15–18]. They can reduce the interfacial tension to an ultralow value within a wide concentration range (0.005–0.3%) [19, 20]. Sulfobetaines belong to surfactants that contain both amino and sulfonate groups. The compounds are divided into several subgroups differing the length and structure of the hydrocarbon chain, which separates the quaternary ammonium centre from the sulfonate group [21, 22].

Sulfobetaines have higher surface activity than betaine ones [23] and exhibit amphoteric properties at all pH values, thus they adsorb to charged surface at all pH values without forming a hydrophobic film [24]. The literature shows that sulfobetaines are widely used in industries concerned with adhesives, textiles, coatings, flocculants, dispersion agents, surfactants, protective colloids, hair conditioners, shampoos, etc. [25–27].

In this study, zwitterionic sulfobetaine N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (SB3C14) has been chosen to examine its washing properties when added to liquid laundry detergents. The interaction of the sulfobetaine with other surfactants and components has not been studied and reported yet. Especially it is necessary to investigate the synergistic effect of the combined substances to demonstrate positive or negative changes in their surface properties.

EXPERIMENTAL SECTION

Materials

Liquid laundry detergents were selected on the Polish market due to their price category: cheap (L1) and expensive (L2). Their composition and gross sales prices are presented in table 1.

In these studies, the liquid laundry detergents were modified with the amphoteric surfactant: sulfobetaine N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (formula: $C_{19}H_{41}NO_3S$; abbreviation: SB3C14; molecular weight 363.6 g/mol; solubility in water is 50 mg/mL; melting point 245°C; flash point 110°C; topological polar surface area 65.6 Å^2) in the amount of 5% (m/m). The compound was synthesized in our laboratory [28] based on the literature [21, 22]. The crystalline substances were separated from the reaction mixture by filtration and next purified by the recrystallization process. Finally, white SB3C14 solids were obtained with high purity (99.9%) and yield and taken into this research. Thermodynamic and surface parameters of the SB3C14 sulfobetaine at different temperatures are listed in table 2 [29]. The surface tension at temperature 25°C (for critical micellar concentration (CMC) = 0.377 mmol/l) is 31.8 mN/m. The measurements of surface tension were conducted using the drop-volume method in a water thermostat control at temperature range 25–45°C in

Table 1

TESTED COMMERCIAL LIQUID LAUNDRY DETERGENTS

Liquid laundry detergents	Compositions based on manufacturer's information	The retail price range of detergents (euro/l)
L1	5–15% ethoxylated (EO 9) fatty alcohol (C_{12}–C_{18}), 5–15% sodium lauryl (C_{12}–C_{14}) ether (EO 2) sulfate, 5–15% soap, <5% phosphates, enzymes, fragrance (benzyl salicylate, hexyl cinnamal, butylphenylmethylpropional), preserving agents (1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one)	1.7–2.0
L2	5–10% sodium dodecylbenzenesulfonate, 1–5% sodium dodecylpoly(oxyethylene) sulphate ($C_{14}H_{29}NaO_5S$), 1–5% (C_{10}–C_{16})alkyl benzenesulfonic acid - monoethanolamine salt, 1–5% ethoxylated (EO 7) fatty alcohol (C_{14}–C_{15}), <1% hexyl salicylate, phosphonates, soap, enzymes, preserving agents (1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one), fragrance (α-isomethyllonone, butylphenylmethylpropional, citronellol, geraniol, linalool)	3.6–3.9

Table 2

THERMODYNAMIC AND SURFACE PARAMETERS OF MICELLIZATION FOR SB3C14					
Temperature (°C)	**ΔG°_{mic} (kJ/mol)**	**ΔH°_{mic} (kJ/mol)**	**ΔS°_{mic} (kJ/mol×K)**	**$-T\Delta S^{\circ}_{mic}$ (kJ/mol)**	**CMC (mmol/l)**
25	–29.505	–28.611	0.003	–0.894	0.377
30	–29.520	–16.333	0.044	–13.187	0.456
35	–29.940	4.265	0.111	–34.205	0.468
40	–30.630	15.090	0.146	–45.720	0.433
45	–31.400	17.595	0.154	–48.995	0.389

a time range of 5 to 50 minutes up to a state of equilibrium. Then, the surface tension (γ) was calculated according to the equation 1:

$$\gamma = \frac{F V \Delta p g}{R} \quad (1)$$

where R is the tip's radius, Δp – the difference of the two phases, g – the local gravity acceleration, V – the volume of one drop, $F(R/V)^{1/3}$ – a correction factor that takes into account the drop's non-sphericity. The CMC were signified from the sudden change in the slope of γ versus Log C plot. The thermodynamic values of micellization (free energy ΔG°_{mic}, enthalpy ΔH°_{mic}, entropy ΔS°_{mic}) were estimated according to the equations 2–4:

$$\Delta G^{\circ}_{mic} = RT \ln CMC \quad (2)$$

$$\Delta H^{\circ}_{mic} = \Delta G^{\circ}_{mic} + T\Delta S^{\circ}_{mic} \quad (3)$$

$$\Delta S^{\circ}_{mic} = (\delta \Delta G^{\circ}_{mic} / \delta T) \quad (4)$$

All the solutions of liquid laundry detergents applied in the research were prepared using deionized water at hardness 5.35 mval/l, which was prepared by mixing hydrated calcium chloride with hydrated magnesium sulphate(VI) in certain proportions in accordance with Polish Standard PN-C-77003. The EMPA 101 fabric (cotton soiled with carbon black and olive oil) and EMPA 210 (cotton fabric, pattern, bleached, without stains) were obtained from the company EMPA Testmaterialien AG plant (Switzerland). EMPA swatches were stored at room temperature (23±1°C) in dark polypropylene foil in an desiccator in order to keep samples dry and under normal pressure. EMPA fabrics meet all the requirements of the model fabrics and are suitable for washing tests. Carbon particles present in the fibres are chemically neutral and do not form any strong physical or chemical bonds with cotton fibres, which could interfere with their removal. The size of carbon particles is very small (~ 0.1 μm) and their diffusion coefficient for aqueous solutions (calculated from the Stokes-Einstein equation) is about ~10^{-12} m^2/s [30]. The construction parameters of the fabrics are shown in table 3.

Methods

Evaluation of colour, form and odour of liquid laundry detergents, determination of density by picnometry, pH measurements (pH meter HI 221, Hanna Instruments), viscosity using Höppler viscometer (KF-20, Brookfield) were carried out in accordance with the literature and Polish standards [31–35]. Determination of anionic surfactants content in liquid detergents was carried out using a direct manual two-phase titration method [36]. The structure analysis was performed by a Fourier transform attenuated total reflection (FT-IR ATR) using Spectrum 100 (Perkin-Elmer, Waltham, USA).

Detergency experiments were carried out using EMPA 101 cotton fabric soiled with carbon black and olive oil under the following conditions: 40°C, rotational speed 200 rpm, 30 minute washing cycle, water hardness 5.35 mval/l, the concentration of liquid laundry detergents ranged from 1.25 to 50 g/L, the concentration of SB3C14 added was 5% (m/m). During each process three EMPA 101 swatches (5×5 cm) were washed in detergent solutions (500 mL) under the same conditions [37–39]. After washing processes fabric samples were rinsed in deionized water and dried at room temperature (23 ± 1°C) for 24 hours. The colour measurements were carried out in the CIELab (CIE – *Comission Internationale de l'Eclairage*) colour space using a colorimeter Minolta CR-300 (Konica Minolta). Calibration parameters for

Table 3

CONSTRUCTION PARAMETERS OF TESTED COTTON FABRICS EMPA 101 AND EMPA 210										
Cotton fabrics	**Sample mass 5×5 cm (g)**	**Thickness (mm)**	**Surface mass (g/m^2)**	**Linear mass of a single thread (g/m, tex)**	**Relative water absorption capacity (%)**	**Absolute water absorption capacity (g/m^2)**	**Mass of warp threads (g/m^2)**	**Count of warp (pcs/cm)**	**Mass of weft threads (g/m^2)**	**Count of weft (pcs/cm)**
EMPA 101	0.231±0.003	0.16±0.01	91.08±0.8	9±0.001	144.4±1.2	132.3±1.1	54.6±0.1	50	39.8±0.1	43
EMPA 210	0.468±0.002	0.29±0.01	180.2±0.7	33±0.04	129.4±0.9	231.9±1.3	104.6±0.1	27	78.5±0.1	22

a light source D_{65} were as follows: Y = 94.0, x = 0.3174, y = 0.3330. The system of coordinates was designated as L^*, a^* and b^*. The symbol L^* is the vertical coordinate of a three-dimensional system of colours, which has values from 0 (black) to 100 (for white). The symbol a^* is the horizontal coordinate the values of which range from –80 (green) to +80 (red), and b^* is the horizontal coordinate, the values of which range from –80 (blue) to +80 (yellow). Colour coordinates are calculated by the following equations 5–7:

$$L^* = 116(Y/Y_0)^{1/3} - 16 \quad (5)$$

$$a^* = 500\left[(X/X_0)^{1/3} - (Y/Y_0)^{1/3}\right] \quad (6)$$

$$b^* = 200\left[(Y/Y_0)^{1/3} - (Z/Z_0)^{1/3}\right] \quad (7)$$

The values X_0 = 94.81, Y_0 = 100.0 and Z_0 = 107.3 are standardized values, which are related to a theoretical ideally white specimen [40, 41, 44, 45].

The colour measurements were repeated 10 times for two sides of each sample. Colour differences ΔE between the sample (EMPA 101) and the reference (EMPA 210) was determined based on the measured L^*, a^*, and b^* values according to the equation 8:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (8)$$

Depending on the parameter ΔE visible differences in change in the colour are described in table 4 [42]. Detergency D [%] was calculated according to the equation 9:

$$D = \left[\frac{(\Delta E - \Delta E_1)}{(\Delta E_0 - \Delta E_1)}\right] \times 100\% \quad (9)$$

Table 4

DEGREES OF COLOUR CHANGE DUE TO THE ΔE PARAMETER

Values of parameter ΔE	**Assessment of colour change by a standard observer**
$0 < \Delta E < 1$	A standard observer cannot see the colour difference
$1 < \Delta E < 2$	Only an experienced observer can see the colour difference
$2 < \Delta E < 3.5$	An inexperienced observer can see the colour difference
$3.5 < \Delta E < 5$	An observer (everyone) can see the colour difference clearly
$5 < \Delta E$	An observer can see two distinct colours

The values ΔE and ΔE_1 denote the average colour difference (degree of brightness) of the fabric sample after and before washing, respectively, and ΔE_0 is the average colour difference of the standard unsoiled fabric sample as a reference. Detergency D [%] means the efficiency of removing soil from fabrics.

The fabric swatches were observed before and after detergency processes using the Amplival microscope (Carl Zeiss Jena, Germany) and a EVO40 scanning electron microscope (SEM) (Carl Zeiss, Germany), which is equipped with a secondary electron (SE) detector and a backscattered electron detector–extended variable pressure (BSD–XVP).

RESULTS AND DISCUSSION

To begin with, the SB3C14 amphoteric sulfobetaine was synthesized and next characterized by FT-IR spectroscopy. The following peaks were observed at the FTIR spectrum: 914 cm^{-1}, 941 cm^{-1} (nitrogen group C–N, stretching), 1032 cm^{-1} (sulfonate group S–O, stretching), 1196 cm^{-1} (sulfonate group S=O, asymmetric stretching), 1468 cm^{-1} (nitrogen group CH_3–(N^+), bending), 2851 cm^{-1} (symmetric CH_2, stretching), 2918 cm^{-1} (asymmetric CH_2, stretching). Similar results were reported by Viana et al. and the following bands were shown: 2944 cm^{-1} (ν_{as} CH_3), 2873 cm^{-1} (ν_{sym} CH_3), 2954 cm^{-1} (ν_{sym} N–CH_3), 2920 cm^{-1} (ν_{as} CH_2), 1465 cm^{-1} (δ CH_2), 1378 cm^{-1} (CH_2 umbrella mode), 1402 cm^{-1} (δ_{sym} N–CH_3), 912 cm^{-1} (ν C–N stretching), 1133–1280 cm^{-1} (ν_{as} SO_2), 1038 and 1058 cm^{-1} (ν_{sym} SO_2) [43]. Based on the findings, there is no ν_{as} CH_3 vibration when the packing density is larger than 10^{17} molecules/cm^2. In case higher densities, only a band in 2954 cm^{-1} related to the ν_{sym}N–CH_3 is revealed. In our analysis a peak in 2918 cm^{-1} is present and it is an indicative of a crystalline conformation. The CH_2 asymmetric stretching and the CH_2 scissoring vibration are dependent on the SB3C14 packing density. On the other hand, the CH_2 symmetric feature is not linearly dependent on the sulfobetaine packing density. The 1300–1400 cm^{-1} region, in which peaks are related to the *d-g* and *e-g* conformation, is characterized by the CH_2 wagging deformations. The 900–1000 cm^{-1} region contains ν C–N stretching for packing densities larger than 10^{16} molecules/cm^2. The $\nu_{as}SO_2$ peaks are present for densities lower than 10^{16} molecules/cm^2 in the range of 1133–1280 cm^{-1}. The $\nu_{sym}SO_2$ bands in 1038 and 1058 cm^{-1} are noticed for densities larger than 10^{17} molecules/cm^2. Additionally, the interaction between the H_3O^+ ion and the sulfonate group may appear and consequently a split for the $\nu_{sym}SO_2$ mode is reported [43].

Selected physical and chemical properties were determined and the results are presented in table 5. The results proved to be in line with declarations of the detergents manufacturers. After the addition of SB3C14 (5%, m/m), a slight change in colour, odour, pH, density and viscosity was observed.

The standard EMPA 101 fabrics have been washed using liquid laundry detergents before and after modification with SB3C14. Based on the colorimetric measurements of colour change of EMPA fabrics, the calculated ΔE values were observed to be higher than 5. Thus, in accordance with table 4, the observer was able to see two distinct colours during comparative analysis of samples before and after washing processes. Nevertheless, modification did not cause changes to the extent enabling the observer to see the colour differences with unaided eye, hence only colorimetric measurements could provide this detailed information. The results showed that as the concentration of detergents solutions increases (form 1.25 to 50 g/l), detergency also increases (figure 1). However, no detergent was able to completely remove the carbon black and olive oil dirt from the fabrics. The applied dirt is difficult to remove and often used as a standard during the research on detergency at many research centres. At the highest tested concentrations of 50 g/l, only the detergency of 22.2% (L2) and 18.0% (L1) was achieved. The more expensive L2 product showed better washing properties than the less expensive L1 one.

Modification of commercial liquids with the SB3C14 sulfobetaine added improved detergency. Figure 1 shows a steady upward trend as concentration increases. The best washing performance (35.3%) was observed for the L2 solution modified with SB3C14 at a concentration of 50 g/l. The modified L1 liquid has better detergency in the initial concentration range from 1.25 g/l to 20 g/l. Only at the concentration greater than 20 g/l, the addition of SB3C14 had a more favourable effect on the efficiency of the L2 solution. The synergism of action of all the components of the liquid detergents was strengthened at a greater concentration in the washing solution. The addition of SB3C14 (5%, m/m) to the products resulted in an increase in detergency by 4.7% on average. It can be stated that enriching the detergent composition with the addition of an amphoteric surfactant has a positive effect on the efficiency of removing dirt from cotton fabric.

The process of removing dirt in a washing solution is divided into several stages. This starts with wetting and penetrating the fabric fibres along with the impurities present on it with a detergent solution that is able to reduce the interface tension. Wetting can occur quickly and efficiently if the interfacial tension is reduced by surfactants to 30 mN/m or lower value [50]. Thanks to surfactants, the dirt layer is well wetted and evenly covered with an aqueous solution.

Penetration of impurities is facilitated by solubilizing surfactants, sequestrants, alkaline compounds or acids by selective elution of dirt components, causing erosion of its compact layer and facilitating the penetration of the washing solution deep into dirt. Water, solubilizers and organic solvents, interacting with alkalines, increase the volume and softness of dirt as a result of penetrating the dirt structure, which facilitates the removal of dirt from the surface. In the second stage, the active ingredients are adsorbed on the surface of the fabric fibres and penetrate the structure of the impurities. Active ingredients, having a high affinity for active centres of the washed surface, adsorb more strongly than dirt, facilitating its removal. In the third stage, solid carbon black dirt is dispersed. Contaminants are thoroughly surrounded by surfactants and released from the adjacent surface (*"rolling-up"* phenomenon). The dirt sphere stays in the washing solution all the time and prevents it from settling on the fabric again. The surface of the fabric is also covered entirely by surfactants. This increases the negative electrostatic charge of dirt and fabric, making them more repulsive. The aqueous alkali solution penetrating deep into the impurities causes alkaline hydrolysis reactions. As a result, the cohesion decreases and the dirt solubility increases. The result is an emulsion/dispersion consisting of an aqueous solution and dirt particles surrounded by surfactants (the last stage). The solution is then removed and the fabric washed out of the emulsion/dispersion residues and detergent components [50, 51].

In the aqueous solution, the carbon black particles contain both hydrophobic and hydrophilic groups that can provide steric or electrostatic interaction with amphiphilic particles. The attraction of hydrophobic particles is stronger to the fibre surface than that of hydrophilic ones, probably due to coulombic attraction. Another important aspect of soil removal is the surface energy of the fabric substrate. Cellulose in cotton fabrics has high surface energy (as well as high critical surface tension) for wetting in air, however, it has low surface energy for wetting in water. Therefore, cellulose exhibits high resistance to wet soiling by hydrophobic dirt that also means its easy

Table 5

RESULTS OF PHYSICO-CHEMICAL MEASUREMENTS

Properties (T = 23±1°C)	L1	L1 + SB3C14	L2	L2 + SB3C14
Colour	white, milky, opaque	white brighter, more intense	green-blue, opaque	green-blue brighter, opaque
Physical state	liquid	liquid	liquid	liquid
Odour	less pleasant, slightly irritating	less pleasant, slightly irritating	pleasant	pleasant
pH	8.51 ± 0.03	8.87	8.26 ± 0.03	8.57
Density [g/ml]	1.01 ± 0.0006	0.93	1.06 ± 0.0004	0.95
Viscosity coefficient η (mPa • s)	349 ± 4,3	—	186 ± 3,8	—
Content of anionic surfactant (%)	6,62 ± 0.07	—	10.28 ± 0.08	—

removal during washing processes [52]. Carbon black has an acid-base character, hence the surface groups present on its surface may gain or lose a proton depending on the pH of the aqueous solution. Some investigators observed that the isoelectric point (IEP) of carbon particles in water is achieved at about pH 6.5 when the zeta potential $\zeta = 0$ (the net surface charge is zero) [53, 54]. At higher pH values the surface charge becomes negative. In the present studies, pH of L1 and L2 washing solutions was equal to 8.51 and 8.26, respectively. At this pH, the negatively charged surface of carbon particles attracted the head groups of cationic surfactants during the adsorption. Amphoteric sulfobetaine SB3C14 at pH > 8 takes on a negative electrostatic charge.

Thanks to this, in washing bath SB3C14 repels the negatively charged carbon black particles on the fibres in accordance with the *"roling-up"* mechanism. In addition, low interfacial tension of SB3C14 promotes the wetting and dirt removal process of the fibre surface. The above interpretation can probably explain the increased amount of carbon black removed after adding the sulfobetaine to the washing solution.

The assessment of the structure of fabric fibres before and after the washing process was carried out using an optical microscope and SEM. Figure 2 shows the fabrics EMPA 210 (100% cotton, white, not soiled) and EMPA 101 (100% cotton, soiled with carbon black and olive oil) before the washing process. Weft and warp threads are arranged in an orderly manner and only slight pilling is visible. The SEM images showed no pilling or damage to individual threads. Figures 3 and 4 show samples of EMPA101 fabric after washing processes in L1 and L2 laundry liquids before and after modification (at concentrations of 1.25 g/l, 20 g/l, 25 g/l, 35 g/l, 50 g/l). At a microscopic approximation of 359x, no serious fabric damage was found in the concentration range tested. However, SEM images showed damage in the form of single fibre delamination. Moreover, it was observed with the unaided eye that few pilling appeared on the samples after washing processes. One reason may be the movement of the agitator blades, rubbing against the surface of the fabric during the process.

Figures 5 and 6 show FT-IR spectra of EMPA 101 cotton fabrics before and after washing processes using tested detergents. As it is seen, both spectra are very similar and typical bands of cellulose, lignin and hemicellulose are revealed. The strong peak at 3333.9 cm^{-1} is typical for the stretching vibration of hydroxyl groups present in cellulose, lignin and water [46]. The peak at 2899.8 cm^{-1} is related to the stretching vibration of C–H present in hemicellulose and cellulose [47]. The peak at about 1620 cm^{-1} is characteristic for water present in the fibres [48]. The peak at 1428 cm^{-1} refers to CH_2 symmetric bending in cellulose. Bending vibrations of the C–H and C–O groups of the aromatic rings in cellulose (polysaccharides) are associated with the peaks at 1360 and 1314.7 cm^{-1}, respectively. The peak at 1245 cm^{-1} corresponds to the stretching vibration of hydroxyl-bound carbon. The C–O bond stretching vibration occurred at 1165 and 1107.9 cm^{-1}. The intense bands at 1053.3 and 1028.8 cm^{-1} refer to the C–O and O–H stretching vibrations in hemicellulose and lignin (polysaccharides). β-glycosidic connections between

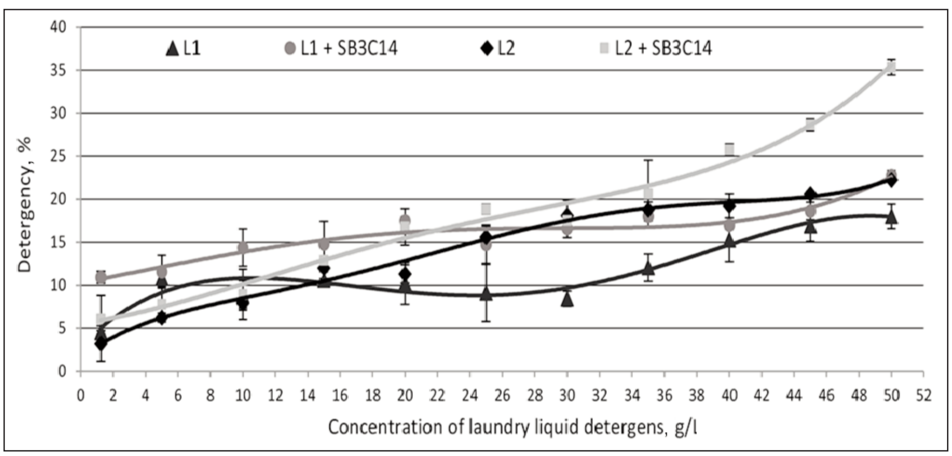
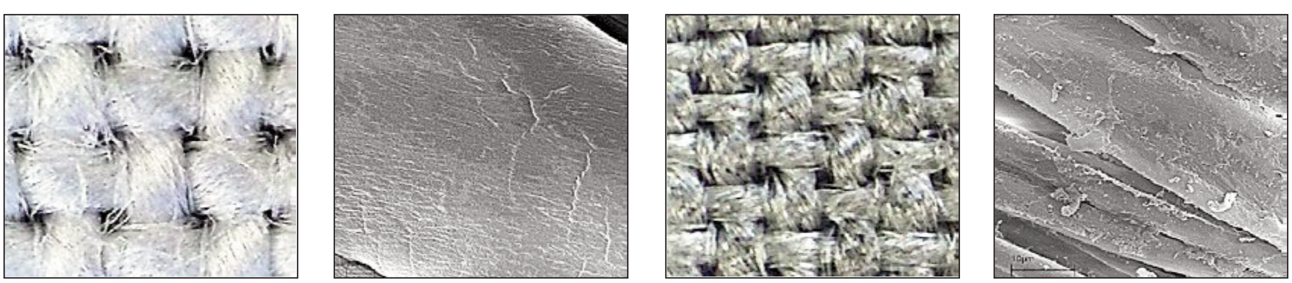


Fig. 1. Detergency of liquid laundry detergents (L1, L2) before and after modification with SB3C14



a *b* *c* *d*

Fig. 2. Cotton fabrics: before washing processes: *a* – EMPA 210, white, uncontaminated (magn. 1346×); *b* – EMPA 210 (15000×); *c* – EMPA 101 (359×); *d* – EMPA 101 (5000×)

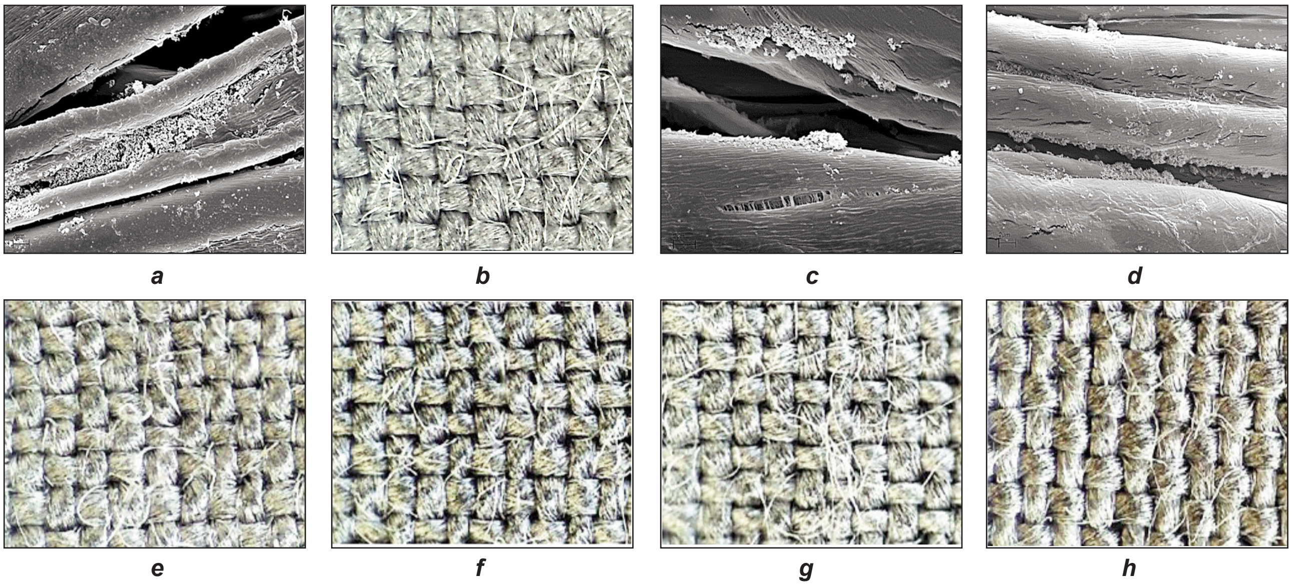


Fig. 3. The images of EMPA 101 cotton fabrics after washing processes at various concentrations of the L1 laundry detergent solutions: *a* – 1.25 g/l (magn. 10000×); *b* – 20 g/l (359×); *c* – 25 g/l (13750×); *d* – 50 g/l (10000×); L1 modified with SB3C14; *e* – 1.25 g/l; *f* – 20 g/l; *g* – 35 g/l; *h* – 50 g/l (359×)

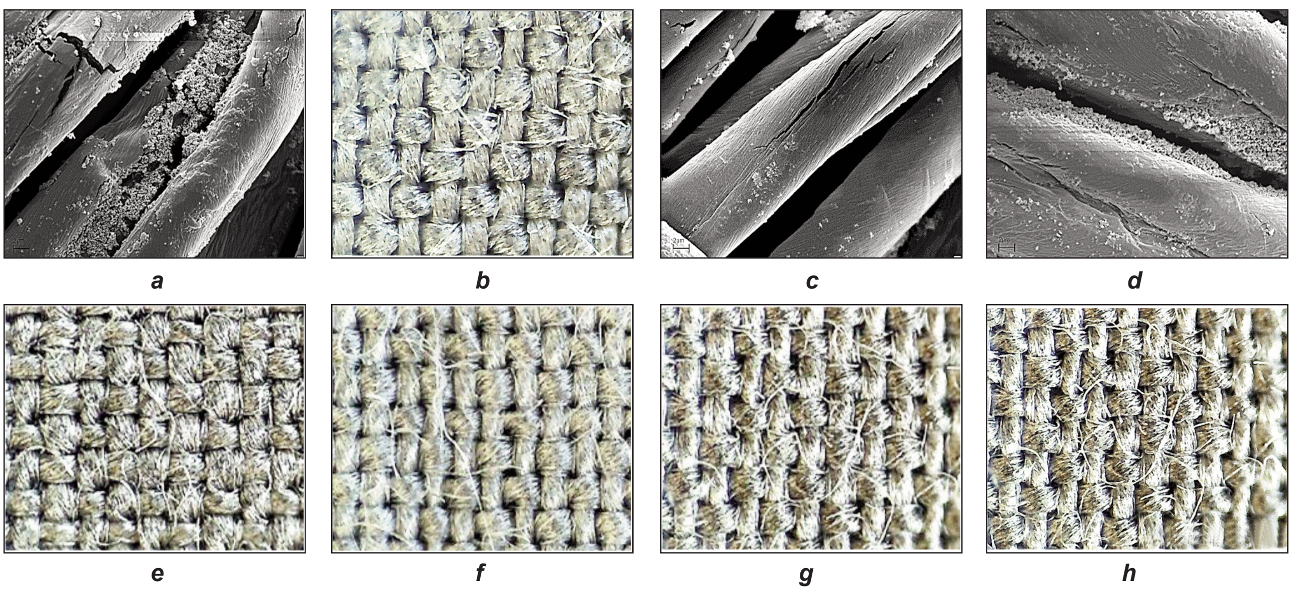


Fig. 4. The images of EMPA 101 cotton fabrics after washing processes at various concentrations of the L2 laundry detergent solutions: *a* – 1.25 g/l (magn. 10000×); *b* – 20 g/l (359×); *c* – 25 g/l (10000×); *d* – 50 g/l (10000×) L2 modified with SB3C14; *e* – 1.25 g/l; *f* – 20 g/l; *g* – 35 g/l; *h* – 50 g/l (359×)

monosaccharides are visible at 894 cm^{-1} [49]. The washing processes with L1 and L2 detergents and modified detergents with SB3C14 resulted in a slight change in the intensity of the peaks towards higher values of transmittance.

CONCLUSIONS

In this work, commercial liquid laundry detergents: cheaper L1 and more expensive L2 before and after modification with SB3C14 sulfobetaine (N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate, 5% m/m) were used for physicochemical and detergency tests. EMPA 101 cotton fabric soiled with carbon black and olive oil was tested for washing performance.

The assessment of colour, form, odour, pH, density, viscosity and content of anionic surfactants showed compliance with the declarations of detergent producers. The addition of SB3C14 did not cause significant changes in these properties. An increase in detergency was observed with increasing detergent solution concentration (1.25–50 g/l). At the highest tested concentrations of 50 g/L, detergency of 18.1% (L1) and 22.2% (L2) was achieved. Synergistic effect between all the components strengthened at a higher concentration in the washing solution. Modification of liquid compositions with the 5% addition of the amphoteric surfactant sulfobetaine SB3C14 resulted in an improvement of the washing efficiency by 4.7% on average. The best washing performance (35.3%)

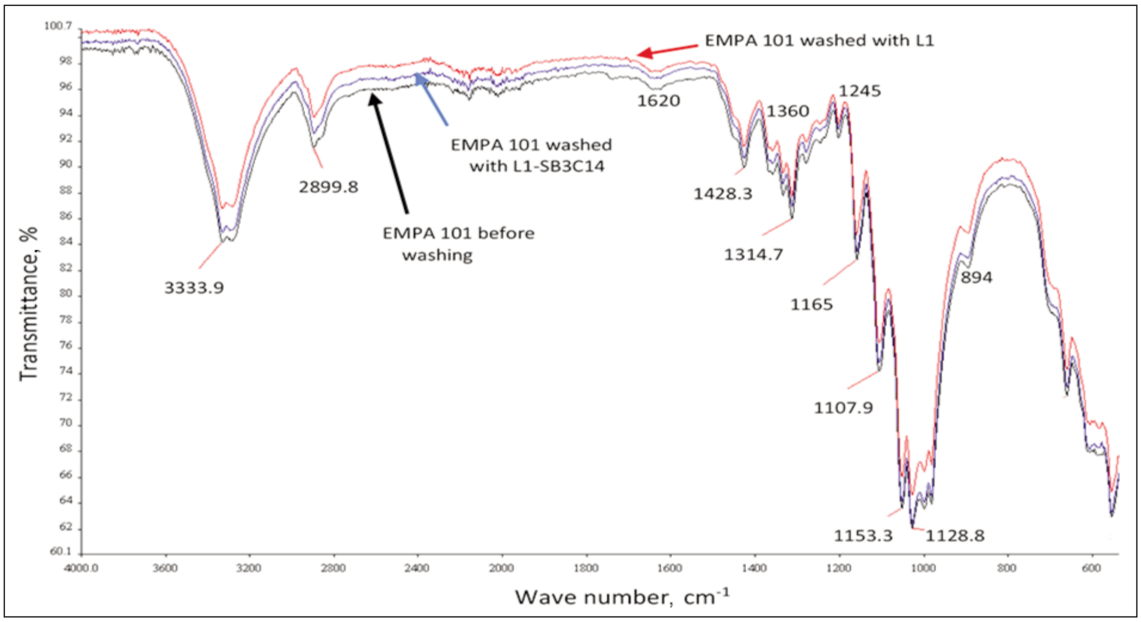


Fig. 5. FT-IR spectrum of EMPA 101 cotton fabric before and after washing processes using L1 detergent

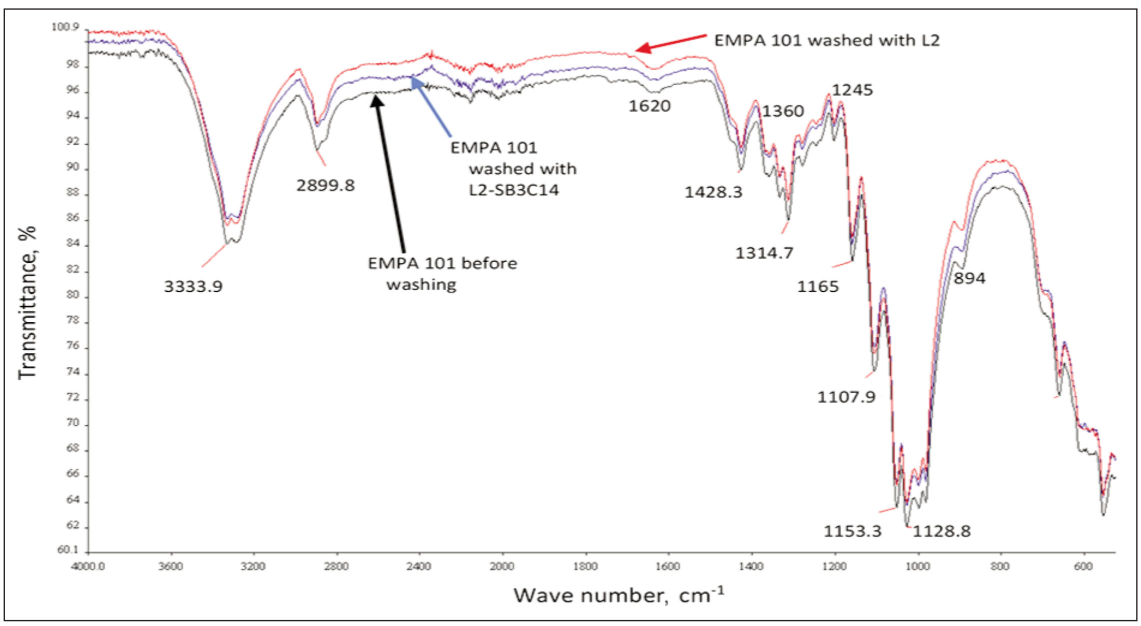


Fig. 6. FT-IR spectrum of EMPA 101 cotton fabric before and after washing processes using L2 detergent

was obtained with the L2 modified solution at a concentration of 50 g/l. The positive effect of the modification was too small for the observer to see colour differences with unaided eye, so changes can only be seen by colorimetric measurements. Microscopic analysis of images of EMPA 101 fabrics before and after washing processes showed only the occurrence of single ruffled fibres.

To sum up, it can be stated that enriching the composition of the washing liquids with the addition of SB3C14 sulfobetaine has a positive effect on the efficiency of removing dirt from cotton fabric. The research results suggest that the tested sulfobetaine can be potentially used as an ingredient in liquid laundry detergents.

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