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Interactions between polysaccharide polymer thickener and bifunctional bireactive dye in the presence of nonionic surfactants. Part 2. Investigation of interactions using SEC method

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Abstract

Size exclusion chromatography used together with RI- and UV/VIS-detectors has proved to be a successful alternative method for identifying reaction products and complex formations between the bifunctional bivinylsulphonyl reactive dye, polysaccharide guar gum thickener and nonionic surfactant in a printing paste. It is shown that nonionic surfactants prevent undesired chemical interactions between the reactive dye and the guar gum thickener due to physical interactions (H-bonds, van der Waals forces) and chemical ether bonds between the surfactant and the guar gum thickener and in a smaller quantities between the surfactant and the reactive dye. The efficacy of surfactants decreases in direct proportion with the diminishing hydrophilic part ($C_{18}EO_{20} > C_{18}EO_{10} > C_{18}EO_4$) and with the growing length of the hydrophobic part ($C_{16}EO_{10} > C_{18}EO_{10}$) of the molecule. The efficacy of the surfactant also increases with the increasing concentration of the surfactant and with the increasing carboxymethylation degree of the polymer. The interactions between the reactive dye and guar gum are the least in case of the system containing $C_{18}EO_{10}$ surfactant and CMG = 1.1 thickener.

Keywords: Printing paste; Polysaccharides; Reactive dye; Nonionic surfactants; Chemical reactions; Size exclusion chromatography

1. Introduction

Some experimental methods investigate printing paste interactions by measuring macroscopic properties of a system (viscosity, viscoelasticity) and others determine changes indirectly by qualitative description of the results of printing (bending rigidity, color depth, dye penetration, sharpness of the contour) (Kokol, 1998, 2001). Both types of methods are useful for understanding the interactions of printing paste systems, but do not always provide a clear explanation/evidence. The determination of the fabric stiffness and the coloration of the printed cellulose fabric is so still the most important/appropriate analytical method for confirmation of undesired chemical reactions between the reactive dye molecules and the polysaccharide thickener during the dye fixation. The methods confirm that an appropriate nonionic surfactant added into the printing paste results in much softer fabric stiffness, a considerably poorer dye penetration and an acceptable depth of color in comparison with prints made without a surfactant (Kokol, Schneider, & Šostar-Turk, 2001). But, in order to establish the acting mechanism and the efficiency of a nonionic surfactant which is added to such a printing paste, i.e. to confirm the interactions between reactive dye and polysaccharide thickening before and after the nonionic surfactant addition, those methods are not sufficient anymore.

In the first paper the rheological (viscosity and viscoelasticity) method is used for determination of interactions between printing paste components. It is ascertained that a strong hydrophilic interactions between polysaccharide guar gum polymer and nonionic surfactant in such a mixture systems occur and are predominant. The measurements indicated that the physical and chemical binding of a surfactant molecules (under CMC) and a micelles (above CMC) on the polysaccharide cluster structures depending on the type and concentration of the surfactant used. The result is a complex formations, which in case of highly hydrophilic surfactant leads to a phase separation. The addition of a reactive dye in such a surfactant/guar gum mixture diminishes the hydrophilic interactions between the surfactant and guar gum polymer the most probably due the occurrence of interactions between the surfactant and reactive dye. The effect increases with the increasing

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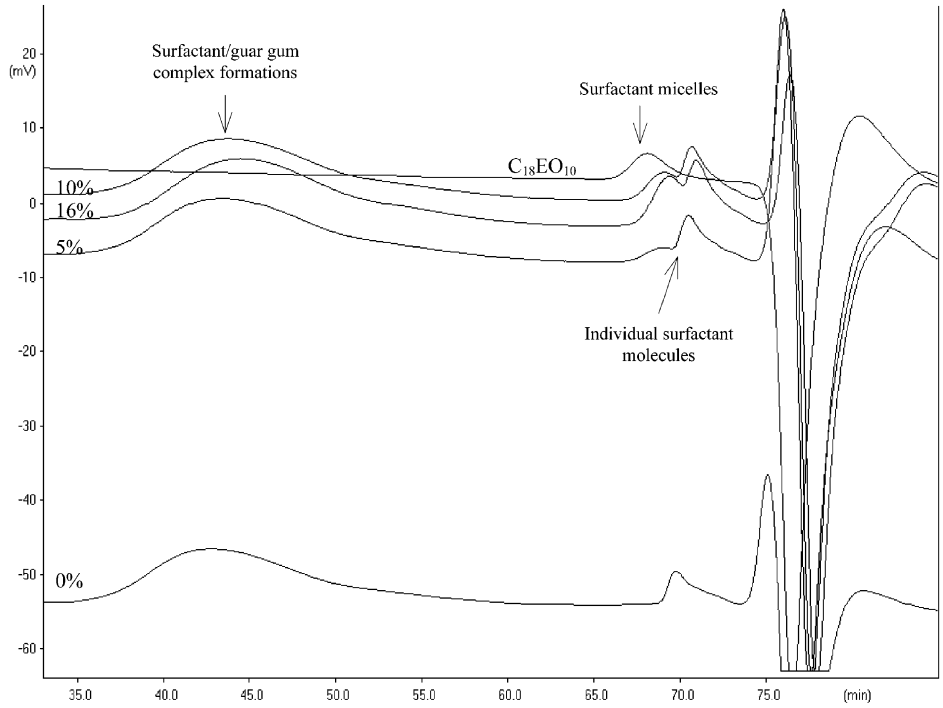


Fig. 1. SEC-RI chromatograms of NSG/0 solutions (with $NaHCO_3$) after the addition of $C_{18}EO_{10}$ surfactant of different concentrations (2. set).

DS of the polymer as well as the concentration of the reactive dye.

In this paper we study the interaction products or associations in different mixture systems between the reactive dye and guar gum polymer before as well as after the nonionic surfactant addition using the (size exclusion chromatography) SEC method. A combination of RI-concentration sensitive and VIS-absorption spectroscopy detectors were used for the identification of all uncolored (without reactive dye) and for all colored (with reactive dye) formations.

2. Experimental

2.1. Materials

Experimental materials (guar gums, nonionic surfactants and reactive dye) used are described in the first paper (part 1).

2.2. Preparation of solutions for SEC analysis

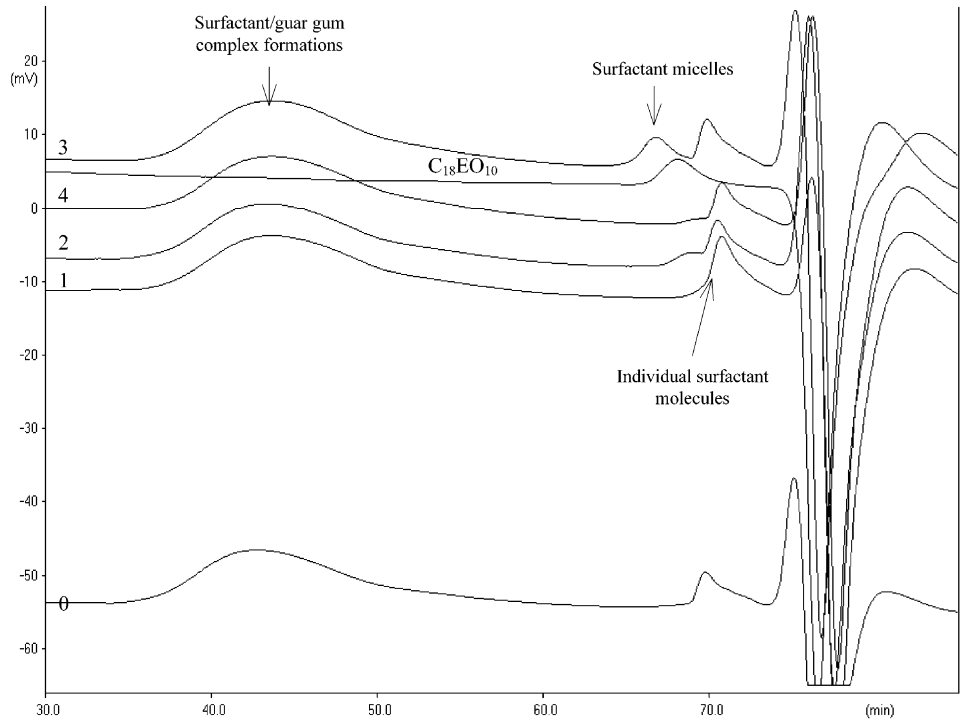
The solutions were prepared with and without guar gum thickener. The defined quantity of a thickener and demineralized water were stirred in a mixer and left in a refrigerator overnight to attain full swelling. To prepare the printing pastes 60% of the stock paste of each thickener, 2.5% of $NaHCO_3$, 0% (1, 5%) of reactive dye and required amount of demineralized water were stirred for another 15 min. The required amount (0, 1, 3, 5%) of individual surfactant was added to each paste and stirred again to obtain a homogeneous paste. The solutions without guar gum were prepared as the printing paste, considering different concentrations of dye and surfactant, but containing no thickener (stock paste).

Each of the prepared paste was divided into two parts: the first part was treated at extreme conditions ($T = 90$ °C and $t = 60$ min) to facilitate the monitoring of the occurrence of interaction products, whereas the second part was used without any further treatment. Solutions for SEC analysis were prepared from thermally treated as well as untreated printing pastes. The pastes were diluted with demineralized water in the ratio 1:10 prior to the analyses.

2.3. Method

SEC measurements were performed on a reservoir with the mobile phase (eluent), an eluent delivery system (L-6000A HPLC Pump, Merck-Hitachi), a simple injector (Rheodyne L.P., USA), hydroxy-ethyl-methacrylat gel cross-linked chromatograph columns (1. set: Hema Bio $40_{50\ mm}$, 2. set: Hema Bio $300_{30\ cm} + 2 \times$ Tosohaas PW XL $5000_{30\ cm}$), an UV/VIS-detector 430A (Kontron Instruments), a RI-detector ERC-7520 (Erma optical works Ltd, USA) and data processing software (Chromstar 4.0, firm SCPA, Germany). Sample solutions were filtrated through a 1.2 μm filter prior to injection (20 μl) into the column. Chromatography were performed with an eluent of 0.1N $NaNO_3$ ($M = 84.99$ g/mol, $pH_{(5.0\%\ water\ solution)} = 5.0$–7.5 Merck GmbH, Germany) at a flow rate of 0.4 ml/min and a pressure of 4.0 bar. The eluent was degassed by the depression method for 1 h before usage to remove air bubbles and to increase column efficacy.

Elute solutions were monitored by two selective detectors: a



No.	Sample		Retention time t_r [min] / Area					
-	**$C_{18}EO_{10}$**	**5%**	**68.14**	/	/		/	
0		**0%**	**42.63**	/	**69.70**	**0.25 10^6**	**75.10**	**2.50 10^6**
1	$C_{18}EO_4$	5%	43.39	/	70.70	0.52 10^6	76.16	2.28 10^6
2	$C_{18}EO_{10}$	5%	43.42	/	70.46	0.25 10^6	76.00	2.95 10^6
		10%	43.72	69.10	70.63	0.22 10^6	76.10	2.74 10^6
		16%	44.43	69.38	70.90	0.16 10^6	76.40	2.34 10^6
3	$C_{18}EO_{20}$	5%	43.66	66.85	69.83	0.30 10^6	75.16	2.57 10^6
4	$C_{16}EO_{10}$	5%	43.63	/	70.70	0.29 10^6	76.23	2.73 10^6
		10%	43.77	69.38	71.00	0.29 10^6	76.40	2.52 10^6
		16%	44.10	69.39	71.03	0.30 10^6	76.46	2.85 10^6

/ - no peak

Fig. 2. SEC-RI chromatograms of NSG/0 solutions (with $NaHCO_3$) after the addition of 5% of different nonionic surfactants (2. set).

differential refractometer (RI-detector), which measures the difference in the refractive index between the initial mobile phase and the mobile phase in which the dissolved sample passes through the column, and a photometric VIS-detector which measured the light absorption at a wavelength of 600 nm. The measurements were performed for 40 min (for all solutions without the reactive dye) and for 100 min (for all solutions containing the reactive dye). Elution curves (chromatograms) are direct results of separation processes that show the amount of the sample elute through the column in a certain retention time (t_r).

3. Results and discussion

Owing to the heterogeneity of inter-molecular interactions (see part 1) which can be formed in the printing paste containing the polysaccharide guar gum thickener and a bifunctional bireactive dye before as well as after the nonionic surfactant addition, the research was focused on the study of the following interactions: surfactant/guar gum, surfactant/reactive dye and surfactant/reactive dye/guar gum. In order to characterize the interactions between different paste components the SEC chromatograms of their pure solutions as well as their mixtures were studied.

Since the substrate printed with such a printing paste is a subject of thermal treatment during the fixation process (Kokol, 1998, 2001; Kokol et al., 2001), all investigated solutions were analyzed before and after the thermal treatment. The results of SEC analysis have shown great differences between thermally treated and thermally untreated solutions (Kokol, 2001). According to better interpretation of inter-molecular interactions between printing paste components in this paper only the results of thermally treated solutions will be presented.

3.1. Interactions between surfactant and guar gum

In Fig. 1 are presented the SEC-RI chromatograms of NSG/0 solutions before and after the addition of different

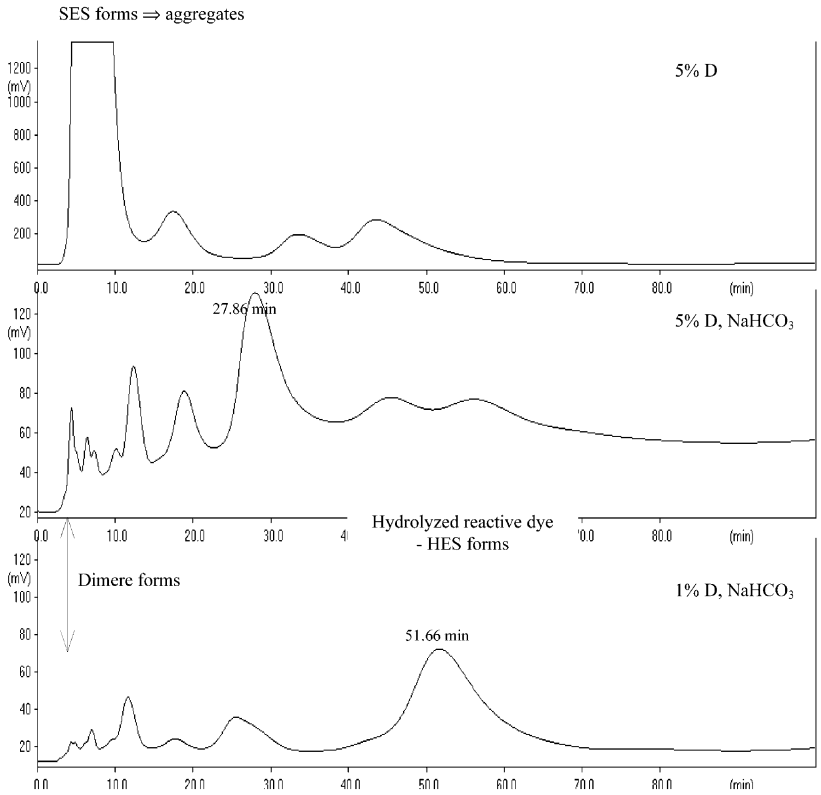


Fig. 3. The influence of $NaHCO_3$ on the SEC-VIS chromatograms of reactive dye solution (1. set).

concentration of $C_{18}EO_{10}$ surfactant. According to the exclusion mechanism theory, i.e. the fact that the samples with the highest hydrodynamic volume elute first (Kokol, 2001), the 1. peak in the SEC-RI chromatogram of the NSG/0 solution corresponds to the largest polymer clusters. The shifting of the 1. elution peak to a higher retention or to a lower-molecular region (from 42.63 to 43.42 min; Fig. 2, table) after the addition of the $C_{18}EO_{10}$ surfactant and considering the fact that the elution peak of the pure $C_{18}EO_{10}$ surfactant solution (it elutes at 68.14 min) is not present anymore confirm the complex formations between the surfactant and guar gum. The addition of the surfactant to the NSG/0 solution obviously causes the contraction of polysaccharide macromolecules to more dense and more compact systems with smaller hydrodynamic volumes. It can be also observed that the 1. peak shift to higher retention times with the increasing surfactant concentration (from 43.42 min at 5% to 43.72 min at 10% and to 44.43 min at 16% surfactant) which consequently indicate that the density of the system increases. At very high surfactant concentrations ($\geq$10%) a new elution peak appears at about 69.00 min that additionally increase at 16% concentration. Since this peak does not appear below the 5% of surfactant addition, but only at higher surfactant concentrations, it should be a consequence of the elution of surfactant molecules associated in a micellar aggregate. This indicate that the surfactant molecules or micelles are incorporate into the complex formations with guar gum macromolecules only up to a certain concentration, which we could call the 'saturation' concentration. The results correspond to the anticipations resulting from viscosity measurements present in the part 1 of the paper.

The peaks appearing in a higher retention region (at about 70.00 min) probably correspond to the remaining (in association structures not-included) individual surfactant molecules, smaller guar gum molecules (monomers) and/or impurities in the polymer whereas the peak at about 75.00 min is most probably the consequence of the elution of added salt.

As it is evident from the table in Fig. 2, the retention times of individual fraction elutions and corresponding elution peak areas of NSG/0 solutions with $C_{16}EO_{10}$ surfactant show the similar effect.

The SEC-RI chromatograms of NSG/0 solutions before and after the addition (5%) of different nonionic surfactant are present in Fig. 2. It can be noticed that the shifting of the 1. peak to higher retention times (from 42.63 min at pure NSG/0 solution to 43.39 min at $C_{18}EO_4$/NSG/0, to 43.42 min at $C_{18}EO_{10}$/NSG/0, to 43.63 min at $C_{16}EO_{10}$/NSG/0 and to 43.66 min at $C_{18}EO_{20}$/NSG/0 system) is linearly proportional to the decreasing degree of etoxylation ($C_{18}EO_{20} > C_{18}EO_{10} > C_{18}EO_4$). The retention time of the 1. peak in case of the $C_{16}EO_{10}$ surfactant addition is between the retention time of $C_{18}EO_{20}$ and $C_{18}EO_{10}$ mixtures; $C_{16}EO_{10} > C_{18}EO_{10}$. It is obvious that the greater the 1. peak shifting, the greater the effect of surfactant molecules

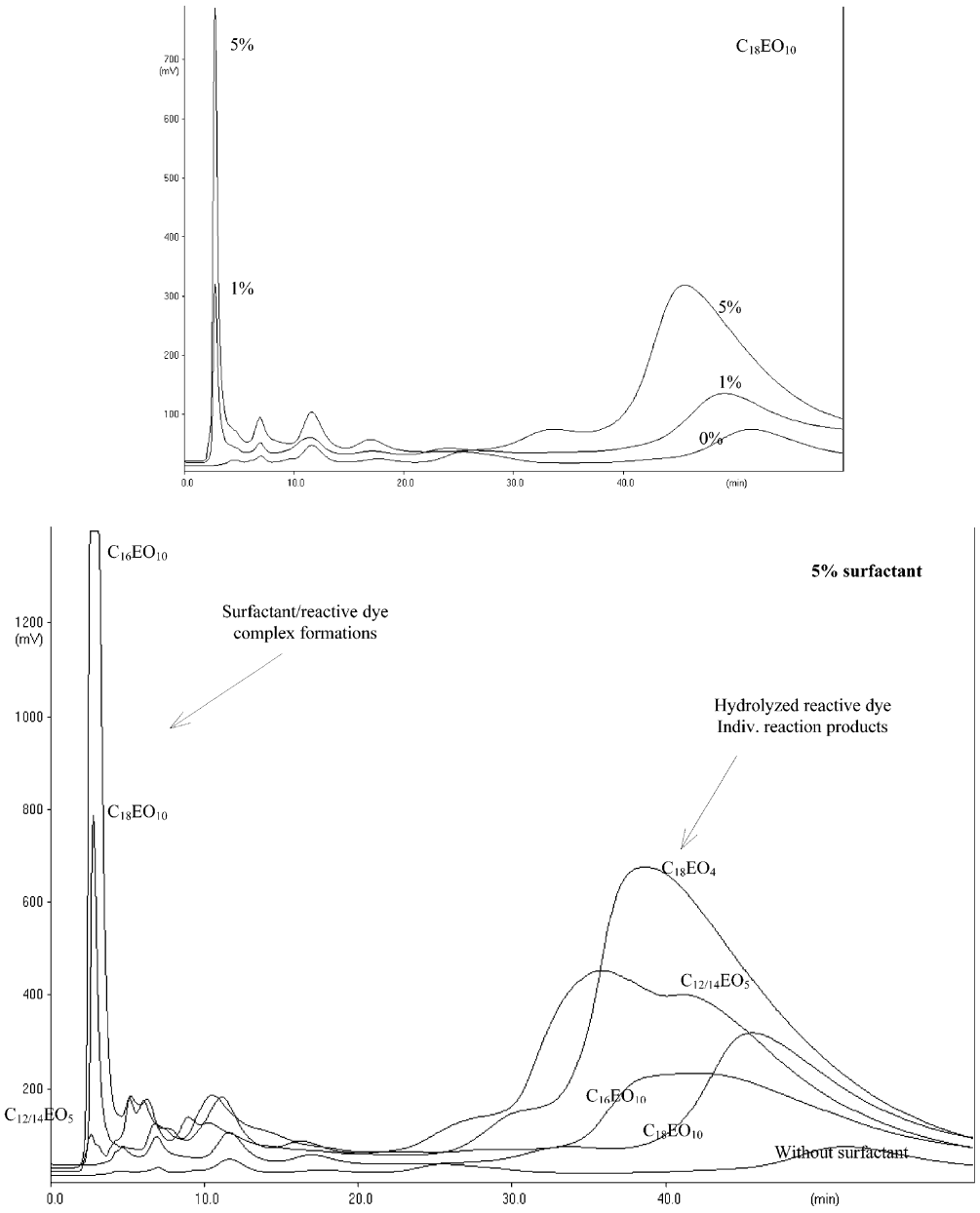


Fig. 4. SEC-UV chromatograms of 1% reactive dye solution (with $NaHCO_3$) after the addition of 1 and 5% of different nonionic surfactants (1. set).

on the rearrangement of the primary cross-linking structure which forms NSG/0 macromolecules in an aqueous solution. The findings again coincide with the results of the viscosity measurements.

3.2. Interactions between surfactant and reactive dye

In order to get more accurate information about the nature of interactions between the surfactant and the reactive dye we first studied the influence of $NaHCO_3$ and then the influence of different nonionic surfactants. It is well known (Motomura, Kim, & Morita, 1991) that the reactive dye, which is as a commercial product in the non-reactive ester sulphatoethylsulphone (SES) ([D]–$SO_2CH_2CH_2$–OSO_3Na) form, converted into the reactive vinylsulphone (VS) ([D]–$SO_2CH{=}CH_2$) form after the alkali addition and that the presence of water leads to the occurrence of β-hydroxyethylsulphone (HES) ([D]–$SO_2CH_2CH_2$–OH). Because of the reaction between VS and HES forms the occurrence of dimere form ([D]–$SO_2CH_2CH_2$–O–CH_2CH_2–[D]) is also possible. It is also known that at pH $<$ 8 only the SES and at pH $>$ 11 only the VS and HES products occur, whereas at pH 8–11 the occurrence of all products are possible.

As it is evident from Fig. 3, the SEC-VIS chromatogram of 5% reactive dye solution without $NaHCO_3$ shows four peaks, which means that the reactive dye used is not pure. The greatest area of the 1. elution peak at 9.50 min indicates that the greater part of the dye elutes in this region. The dye

molecules are probably in the SES form which they should be associated into aggregates since the elution takes place in a higher-molecular region. The addition of $NaHCO_3$ (pH 8–9) causes the occurrence of the 1. peak already at about 4.00 min which followed a great number of new and differently greater peaks, the greatest appears at 51.66 min. In the case of 1% reactive dye solution appear the same effect only that the majority of the dye elutes at 27.86 min. It could be also noted that in case of 5% reactive dye solution an additional hour was necessary for complete dye elution probably due to the great affinity of different types, above all HES and dimere forms, of reactive dye for the stationary phase of the column. In case of 1% reactive dye solution it elutes in 1 h.

From the analysis of chromatograms it can be concluded that after the thermal treatment of the alkaline solution the reactive dye appears predominantly in the HES and in smaller quantity in the dimere forms. The dimere form of the dye most probably elute first and then the hydrolyzed dye which also corresponds to the greatest peak areas in the lower-molecular region. The other elution peaks most probably correspond to other different types of reaction products resulting from the impurity of the dye.

As it is evident from Fig. 4 that the thermal treatment of reactive dye solutions containing the surfactant reveals the disappearing of earlier mentioned peaks and the appearance of new peaks depending on the structure and the concentration of the surfactant. In case of all surfactant additions ($C_{18}EO_{10}$, $C_{16}EO_{10}$, $C_{12/14}EO_5$), except the $C_{18}EO_4$, the 1. peak appears in a higher-molecular region or at lower retention time (between 2.56 and 2.96 min) in comparison with the reactive dye solution without a surfactant (the 1. peak appears at 4.33 min). The result indicate on the hindering of the occurrence of aggregates of the reactive dye molecules at dimere forms after the surfactant addition and the occurrence of new complex formations (Jocić, Trajković, & Jovanović, 1991). The complex formations between the surfactant and the reactive dye are the most probable since the greatest hydrodynamic volume of the 1. elution and the fact that they are perceived by the VIS-detector—they undoubtedly contain the dye molecules.

From the comparison of SEC-VIS chromatograms of reactive dye solutions containing different surfactants is obvious that the greater the portion of EO units (52.4/49.0% at $C_{12/14}EO_5$, 62.0% at $C_{18}EO_{10}$, 76.5% at $C_{18}EO_{20}$; Table 2 in Kokol (2002)) or the higher the HLB value (10.5/9.8, 12.4, 15.3), the greater the area of the 1. peak. This confirms the increase of surfactant/reactive dye complexes with the increasing number of EO units. The comparison of SEC-VIS chromatograms of reactive dye solutions after the addition of $C_{18}EO_{10}$ or $C_{16}EO_{10}$ surfactant (surfactant with the same length of the hydrophilic part and different length of the hydrophobic part) confirms the influence of hydrocarbon chain length on the peak area. In the case of the surfactant with a shorter hydrocarbon chain ($C_{16}EO_{10}$, HLB = 12.9) the area of the 1. peak is greater than in the case of the surfactant with a longer hydrocarbon chain ($C_{18}EO_{10}$, HLB = 12.4). We can conclude that a shorter hydrophobic part causes an increase of complex formations between the surfactant and the dye that must be the result of an increase of hydrophilic interactions.

It is also evident from chromatograms that the majority of the reactive dye elutes in the lower-molecular region (between 30.00 and 50.00 min) which represent the hydrolyzed portion of the dye. With respect to the size of the obtained peak area, it could be assumed that elute so the individual surfactant molecules as well as the individual surfactant molecules to which individual reactive dye molecules are covalently bounded. Namely, the area of this peak decreases with the increasing surfactant concentration as well as with the decreasing portion of EO units at constant dye concentration, probably because of the incorporation of the surfactant into the occurrence of complex formations with the dye molecules (the 1. peak increases). In a constant concentration of reactive dye solution the quantity of complex formations increases with the increasing surfactant concentration.

According to the results of chromatographic measurements and due to the structure of the surfactant molecule it must be consider the possibility for the occurrence of interactions so with the hydrophilic as well as with the hydrophobic part of the surfactant molecule with the vinylsulphonic reactive dye. The occurrence of complex formations is possible due to:

(a) hydrophilic interactions:

1.1. covalent bonds between the end –OH group of the surfactant molecule (surfactant–$(CH_2–CH_2–O)_n$–$CH_2–CH_2–OH$) and the reactive VS or HES group of the dye molecule via nucleophilic addition or etherification mechanism ([D]–$SO_2CH_2CH_2–O–CH_2–CH_2–(O–CH_2–CH_2)_n$–surfactant),

1.2. H-bonds between the end –OH group of the surfactant molecule and the sulphate ($–OSO_3^-$) group, the sulphonic ($–SO_3^-$) group or π electrons of the azo (–N=N–) group of the reactive dye,

1.3. H-bonds between oxygen atoms on EO units or the end –OH group of the hydrophilic part of the surfactant molecule and the hydroxyl (–OH) or amino ($–NH_2$) group of the reactive dye;

(b) hydrophobic interactions: van der Waals forces (dispersion, induction) between the hydrocarbon chain or the hydrophobic part of the surfactant molecule and the non-polar part of the reactive dye molecule (Jocić et al., 1991).

At higher surfactant concentrations, where the surfactant molecules are set in micellar aggregates, they also incorporate the covalently bounded reactive dye molecules. The possibility for the occurrence of hydrophilic interactions is just as great as the possibility for the occurrence of hydrophobic interactions since the reactive dye molecules can be

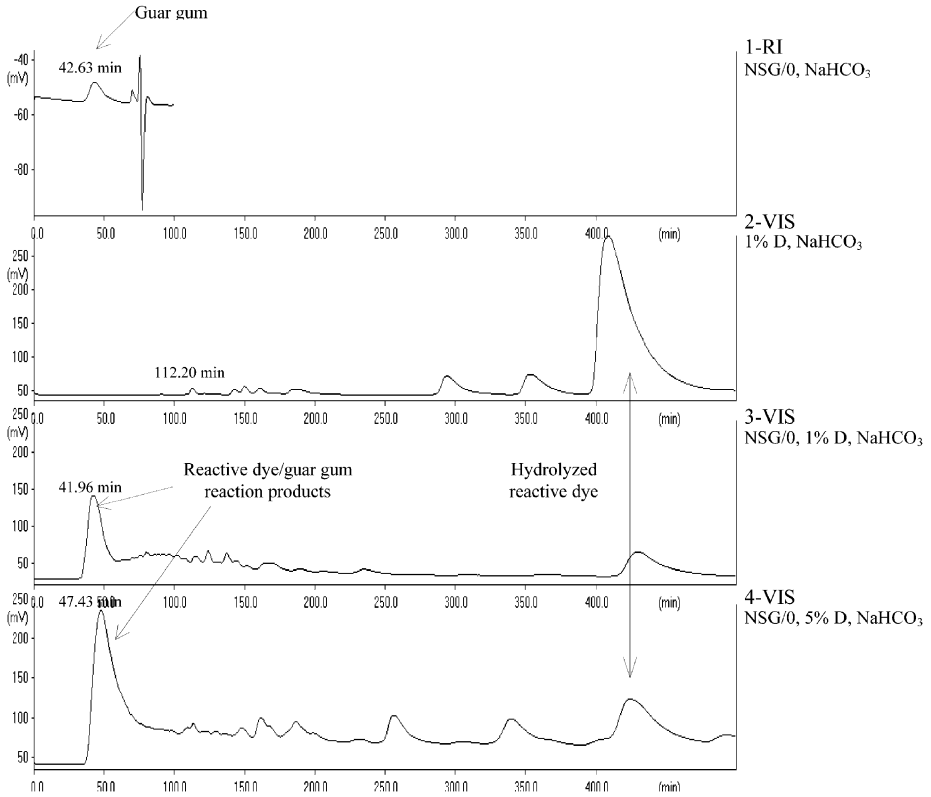


Fig. 5. SEC chromatograms of NSG/0 solutions (with $NaHCO_3$) after the addition of 1 and 5% of reactive dye (2. set).

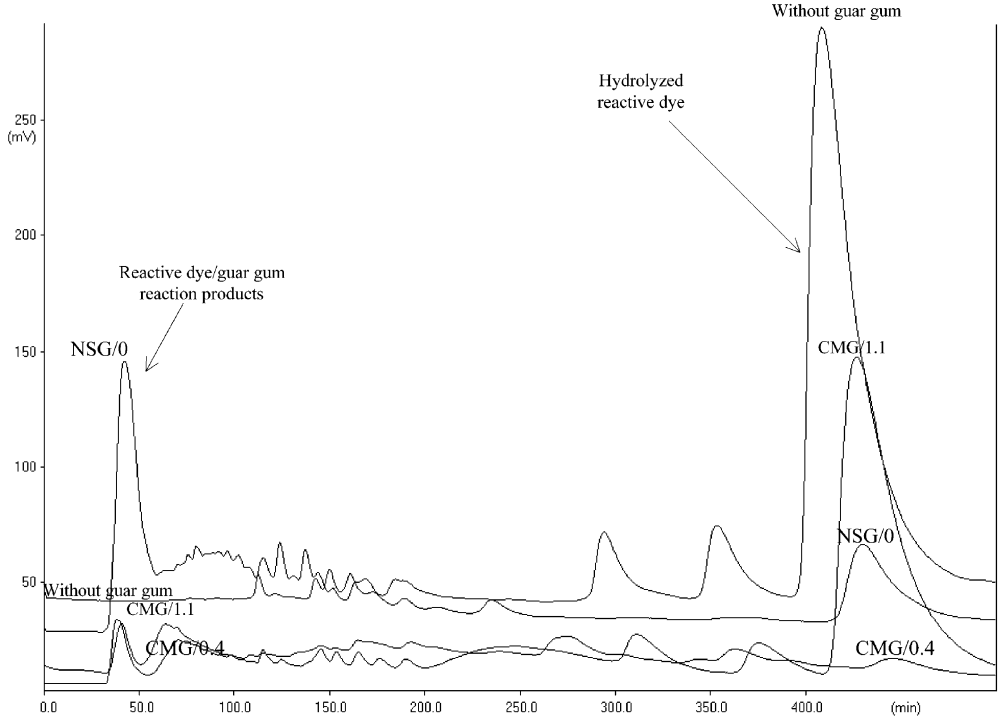
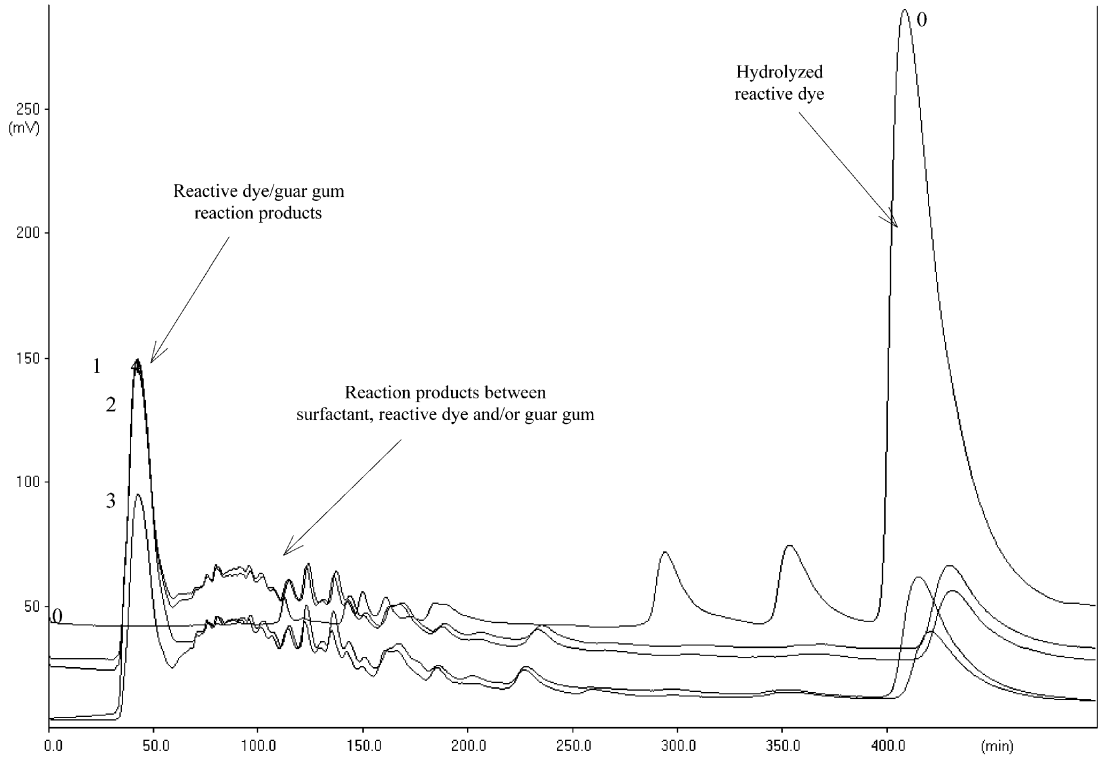


Fig. 6. SEC-UV chromatograms of different guar gum thickeners (with $NaHCO_3$) containing 1% of reactive dye (2. set).



0-1% D, $NaHCO_3$, **1**-without surfactant, **2**-with $C_{18}EO_{10}$, **3**-with $C_{16}EO_{10}$, **4**-with $C_{18}EO_4$

Fig. 7. SEC-UV chromatograms of NSG/0 solutions (with $NaHCO_3$) containing 1% of reactive dye and 5% of different surfactants (2. set).

included in the interior of such a micellar aggregates (Jocić et al., 1991) (Fig. 10).

3.3. Interactions between surfactant, reactive dye and guar gum

The combination of a polysaccharide guar gum thickener and a reactive dye in an alkali aqueous solution causes, as it is well known, a covalent binding of the reactive dye with the thickener (Kokol, 1998), where one part of the reactive dye is hydrolyzed (Majcen Le Marechal & Lobnik, 1990). Since we wanted to study the influence of the surfactant on the occurrence of interactions between the reactive dye and guar gum, we must first determine the interactions between the reactive dye and the guar gum thickener, and then tried to ascertain the influence of the chemical structure and concentration of the surfactant, the influence of the reactive dye concentration, and the influence of the DS of the guar gum thickener.

3.3.1. Interactions between reactive dye and guar gum

The comparison of SEC-VIS and SEC-RI chromatograms presented in Fig. 5 confirms the occurrence of reaction products between the reactive dye and guar gum: the shifting of the 1. peak in SEC-VIS chromatograms of the 1% reactive dye solution from 112.20 min (No. 2) to 41.96 min (No. 3), or to 47.43 min (No. 4) in the case of both mixtures (1, 5%) that correspond to the 1. peak at 42.63 min in the SEC-RI chromatogram of the NSG/0 solution (No. 1), and the decrease of the peak at about 450 min, which represents the hydrolyzed portion of the reactive dye. The greater the portion of the reactive dye that reacts with the guar gum thickener (i.e. the greater the area of the 1. peak), the smaller the portion of hydrolyzed dye (i.e. the smaller the area of the peak at about 450 min). This also indicate that the reaction of the reactive dye with water molecules is slower than the reaction with guar gum macromolecules.

From SEC-VIS chromatograms shown in Fig. 6 it is evident that the area of the 1. peak decreases intensively when carboxymethylized guar gum is used (note: all the guar gums eluted at similar retention times since they have comparable values of average molecular weights as well as polydispersity values: $M_w \cong 147{,}000$, $P \cong 2.7$ (Kokol, 2001)). Therefore, the covalent interactions between the reactive dye and guar gum decrease with the increasing DS of the thickener since anionic $-COO^-$ groups on guar gum macromolecules prevent the covalent binding with the reactive dye. In the case of mixtures containing CMG thickeners we can also notice the occurrence of additional peaks in the time region between 64.46 and 73.13 min. The peaks could indicate on the reaction of reactive dye molecules with smaller molecules (monomers, oligomers) of guar gum, since we know that the remaining guar gum molecules elute in this region (at about 70.00 min, Chapter 3.1). At the same time, the intensity of the hydrolyzed portion of the reactive dye (peak at about 450 min)

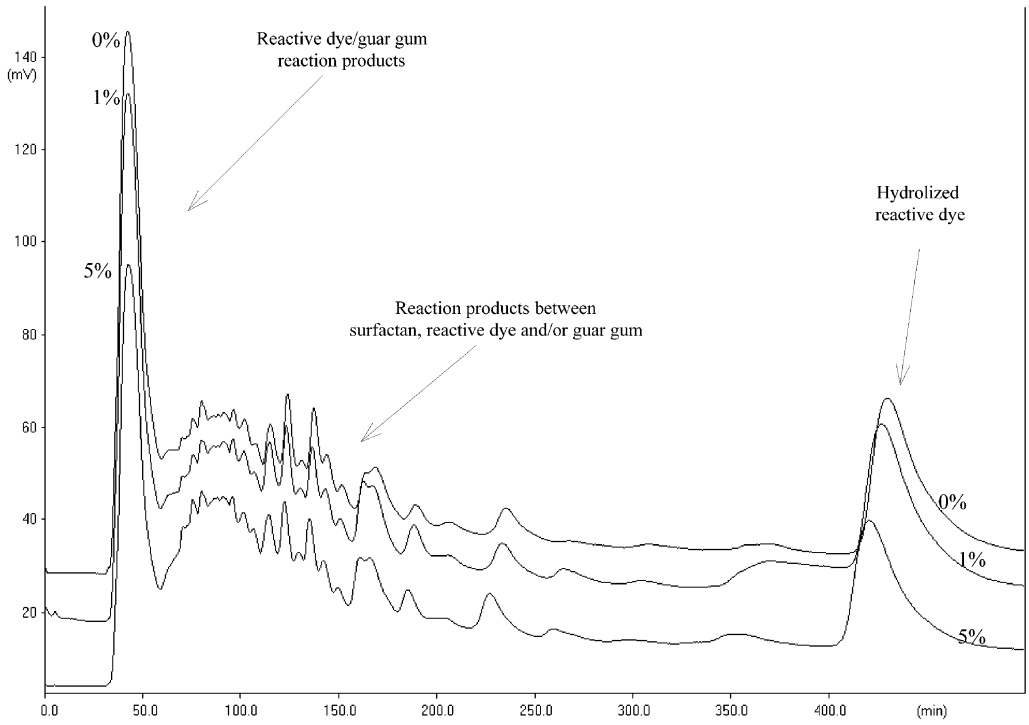


Fig. 8. SEC-UV chromatograms of NSG/0 solutions (with $NaHCO_3$) containing 1% of reactive dye and 0, 1 or 5% of $C_{16}EO_{10}$ surfactant (2. set).

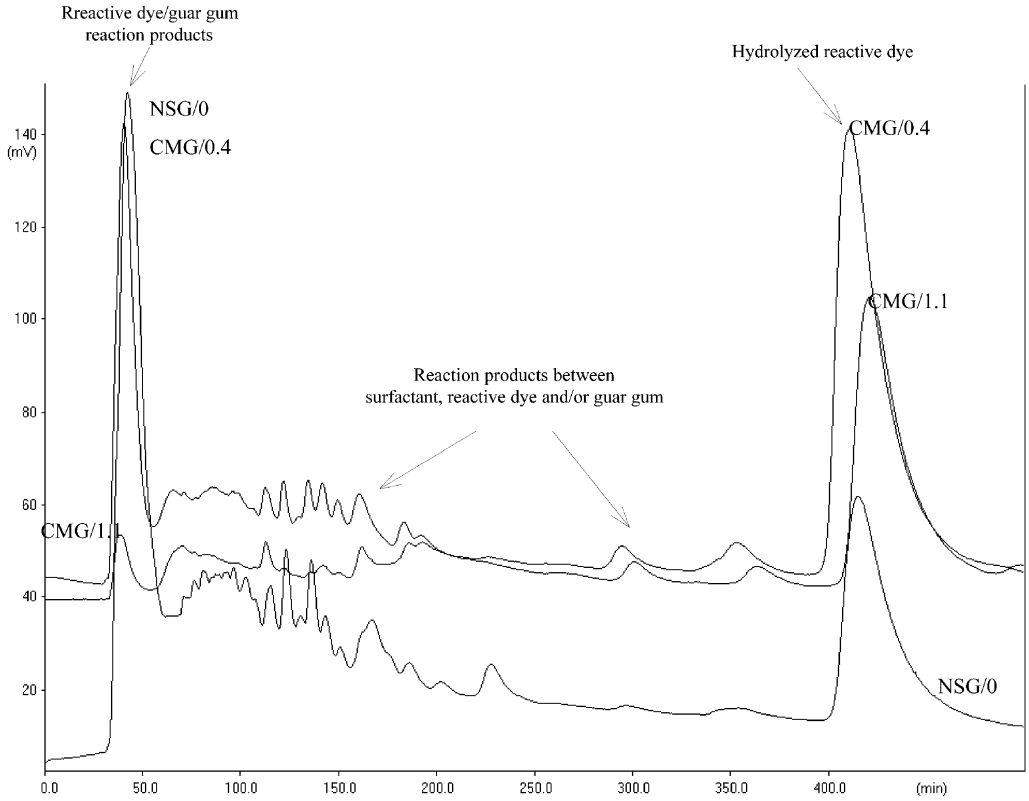


Fig. 9. SEC-UV chromatograms of different guar gum thickeners (with $NaHCO_3$) containing 1% of reactive dye and 5% of $C_{18}EO_{10}$ surfactant (2. set).

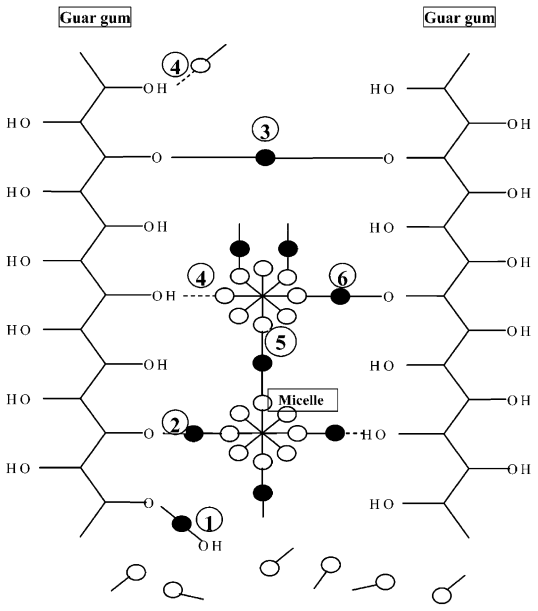


Fig. 10. Schematic presentation of interactions between nonionic surfactant, nonsubstituted polysaccharide thickener and bifunctional bivinylsulphonyl reactive dye.

increases intensively with the increasing DS of the guar gum thickener (in the case of the CMG/1.1 mixture): a greater portion of the dye elutes at higher (>450 min) retention times (in the case of the CMG/0.4 mixture).

It can be concluded that the SEC is the first method which confirms, on the basis of the disappearing primary peaks and the appearing of new chromatograph peaks, the occurrence of reaction products or covalent bonds between the reactive dye and polysaccharide macromolecules, and quantitative decreasing of the mentioned interactions with the increasing DS of the thickener.

3.3.2. Interactions between surfactant, reactive dye and guar gum

From SEC-VIS chromatograms of printing paste solutions with the NSG/0 thickener and 1% of reactive dye (Figs. 7 and 8) it can establish the efficiency (i.e. the decreasing portion of the reactive dye/guar gum reaction product) of different surfactants added to the printing paste. The decreasing of the 1. peak area, the occurrence of additional peaks and the portion of hydrolyzed reactive dye in surfactant/reactive dye/guar gum mixtures show the influence of the type and the concentration of the surfactant on the occurrence of inter-molecular interactions.

The addition of the (1%) $C_{18}EO_{10}$ or $C_{18}EO_4$ surfactant to the printing paste with a lower reactive dye concentration (1%) (Fig. 7) practically does not change the area of the 1. peak, while it strongly decreases in case of the (1%) $C_{16}EO_{10}$ surfactant. This means that the presence of the $C_{16}EO_{10}$ surfactant prevents the chemical reaction between the reactive dye and guar gum thickener to a certain extent. Since a great number of new peaks occurs at the same time in a retention region between 60.00 and 170.00 min, we can assume that they correspond to the occurrence of different reaction products or complex formations between the reactive dye, surfactant and guar gum macromolecules, which are schematically shown in Fig. 10. Considering this outcome we can conclude that the reaction of the reactive dye molecule with the molecules of the surfactant is faster than with the guar gum macromolecules, which is understandable since the surfactant molecules are much smaller and also more mobile.

The strong influence of the surfactant concentration is also obvious since the 1. peak area in the surfactant/reactive dye/guar gum mixtures (Fig. 8) decreases and the area of peaks between 60.00 and 170.00 min increases with the increasing surfactant concentration. At the same time the portion of the hydrolyzed dye (peak at about 450 min) shows no particularly changes.

In the case of printing pastes containing a surfactant, reactive dye and carboxymethylized guar gum thickener (CMG/0.4 or CMG/1.1) the course of SEC-VIS chromatograms (Fig. 9) is similar to that of the nonsubstituted (NSG/0) guar gum thickener. But, with the increasing DS of the thickener, the 1. peak that corresponds to the reaction product between the reactive dye and the guar gum thickener decreases considerably and the peak at about 450.00 min increases. The DS of the guar gum thus additionally reduces the possibility for the occurrence of covalent interactions between the reactive dye and guar gum and at the same time increases the portion of the hydrolyzed dye. Regarding this, the printing paste with the CMG/1.1 thickener and 5% $C_{18}EO_{10}$ surfactant the covalent interactions between the reactive dye and the guar gum thickener are quantitatively the smallest, which indicate that this is the most effective paste mixture.

It can be concluded that the surfactant exerts influence on the: quantitative decreasing of the reaction products between the reactive dye and guar gum macromolecules, qualitative and quantitative increase of different reaction products or complex formations, occurring between the reactive dye, the surfactant and guar gum (Fig. 10), and quantitative increase of the portion of hydrolyzed dye.

This kind of prevention of chemical reaction between the reactive dye molecules and guar gum thickener in the presence of nonionic surfactant molecules is very important since it can lead to softer fabric handle of so printed cellulose substrate. The portion of the un-reacted (hydrolyzed)

reactive dye namely could correspond to the portion of the reactive dye which can bind on the cellulose fiber during printing. The results of those investigations are present in (Kokol, 2001; Kokol et al., 2001).

4. Conclusions

SEC analysis in combination with RI- and UV/VIS-detectors has proved to be the alternative method that enables quantitative and qualitative monitoring of differing types of reaction products and complex formations in a printing paste. It is shown that the addition of a nonionic surfactant into the printing paste containing the polysaccharide guar gum thickener and the bifunctional bivinylsulphonyl reactive dye (pH 8–9; $T = 95$ °C, $t = 60$ min) decreases the undesired covalent interactions between the reactive dye and guar gum due to the occurrence of interactions between the surfactant and the guar gum thickener as well as between the surfactant and the reactive dye whereas the occurrence between all three components is also possible. At the same time a large portion of the reactive dye remain hydrolyzed.

The results of interactions between the surfactant and guar gum correspond the anticipations resulting from the rheological measurements which are presented in the first paper, whereas the interactions between the surfactant and the reactive dye is better determinable by SEC method. It is ascertained that interactions between the surfactant and the reactive dye are a consequence of intensive hydrophilic interactions (covalent and H-bonds between oxygen atoms of EO units and end –OH group of the surfactant and $-OSO_3^-$, $-SO_3^-$, or –OH groups of the reactive dye) and less intensive hydrophobic interactions (van der Waals forces between the hydrocarbon chain of the surfactant and the nonionic part of the reactive dye molecule) resulting to the complex formations. At a constant concentration of the reactive dye the interactions increase with the increasing number of EO units ($C_{18}EO_4 < C_{18}EO_{10} < C_{18}EO_{20}$) due to the hydrophilic interactions and with the shortening of the hydrocarbon chain ($C_{18}EO_{10} < C_{16}EO_{10}$) caused by hydrophobic interactions.

The efficiency of the surfactant to prevent the interactions between the reactive dye and guar gum thickener in a printing paste increase as the concentration of the surfactant and the DS of the guar gum thickener increases. The interactions between the surfactant and guar gum are quantitatively greater than the interactions between the surfactant and reactive dye. The interactions between the reactive dye and the polysaccharide thickener cannot be prevented totally, but they can be reduced to a minimum using the $C_{18}EO_{10}$ surfactant and a highly carboxymethylized (DS = 1.1) guar gum thickener.

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