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NEW ORANGE DYES: NITRODERIVATIVES OF SULFONEFLUORESCEIN

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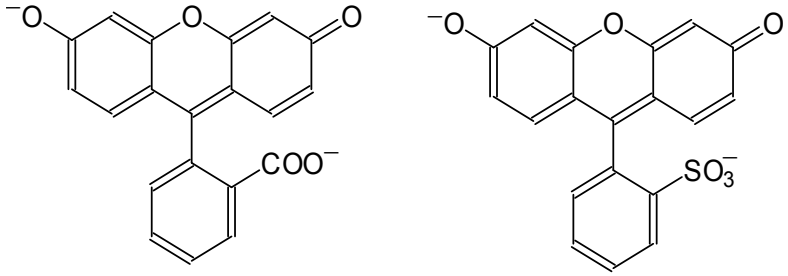
In this paper, the nitration of a hydroxyxanthene dye sulfonefluorescein is reported. The orange dyes thus obtained are identified as 4,5-dinitro and (probably) 2,4,5,7-tetranitro sulfonefluoresceins. The spectral and acid-base properties, interaction with lysozyme, and behavior in surfactant solutions are examined using visible spectroscopy, LDI-ToF, and MALDI-ToF. The xanthene moiety of the dyes is stable against protonation, whereas at high pH values created by NaOH, the rupture of the pyrone cycle readily occurs. Further nucleophilic attack on the central carbon atom results in formation of the carbinolic structure.

Key words: Nitro derivatives of sulfonefluorescein, nucleophilic attack, absorption spectra, LDI-ToF, MALDI-ToF, lysozyme, reversed microemulsions.

Fluorescein dyes are widely used in many fields of chemistry and related areas. This concerns, first of all, the mother compound, fluorescein, and its numerous halogen derivatives. Though the synthesis of tetranitro fluorescein was already reported by Adolf von Baeyer as early as 1876 [1], the nitro derivatives of fluorescein have been practically unexplored within decades, with few exceptions [2–4]. The situation changed after a set of papers devoted to synthesis, spectral, and protolytic properties of the nitro fluorescein dyes [5–9].

Meanwhile, another interesting dye from the fluorescein series is sulfonefluorescein. The synthesis of this compound has been described by Orndorff and Vose [10] and by other authors, whereas the study of the acid-base properties was published later [11, 12]. The structures of fluorescein and sulfonefluorescein in the form of dianions are given below.



However, to the best of the author's knowledge the nitro derivatives of sulfonefluorescein have not been described yet. The present study was undertaken in order to fill this gap.

Experimental

Synthesis of sulfonefluorescein. 14 g of P_4O_{10} was carefully added to 10 mL of 85 mass % aqueous phosphoric acid. The stirred mixture was heated to 100˚C to give transparent solution. 5.0 g of ammonium salt of the 2-sulfobenzoic acid was slowly dissolved in the reaction mixture at 150 ˚C. Then 5.0 g resorcinol was gradually added, and the formed dark red product was heated to 170–190 ˚C for 3 h. Along with the progress of reaction, the target product precipitates in the form of small glossy purple crystals, and the mass becomes more viscous. The reaction mixture was cooled to 80–90 ˚C and diluted with 150 mL ethanol–water mixture (50 vol %). After filtering off, washing with ethanol (95.6 mass %) and drying, 6.29 g of unpurified precipitate was obtained. As sulfonefluorescein is relatively poor soluble in the most of readily accessible solvents, the recrystallization was carried thought conversion of the compound into its soluble disodium salt and subsequent acidification of the solution by HCl [10]. The solution of the disodium salt (1 g) in 1000 mL of water was heated to boiling, then acidified by appropriate amount of HCl, and slowly cooled. This results in the precipitating of sulfonefluorescein in the form of large purple crystals. The ethanol–water mixture (50 vol %) could also be used as a solvent instead of water (1 g of salt per 50–100 mL). ^{1}H-NMR ($(CD_3)_2S=O$) δ/ppm: 7.99

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(1H, d, *J*=7.4, 3^1-H), 7.68 (1H, t, *J*=7.4, 5^1-H), 7.58 (1H, t, *J*=7.4, 4^1-H), 7.37 (2H, d, *J*=8.8, 1,8-H), 7.31-7.21 (3H, m, 6^1,4,5-H), 7.13 (2H, d, *J*=8.8, 2,7-H).

Synthesis of 4,5-dinitro sulfonefluorescein. 0.74 g of sulfonefluorescein was dissolved in 2 mL of 96 % sulfuric acid on heating (80 °C) and permanent stirring. The solution was cooled by ice, and the nitrating mixture (2 mL of sulfuric acid + 0.2 mL of nitric acid) was added under intense mixing. After 5 h of stirring at 20 °C, the solution was poured in 20 mL (not more!) of water with intense mixing. After heating, the deposit transforms into the mustard-yellow heavy powder, which was separated via decantation. The raw product was diluted on heating with aqueous acetonitrile (10 mL CH_3CN + 4 mL H_2O) and filtrated. To thus-obtained dark-brown transparent solution, 10 mL of conc. HCl was added. After 1 min, the small needle-shaped yellow-orange crystals began to deposit. After 1 h, the crystals were filtrated, washed by 4 mL of acetonitrile + 1 mL conc. HCl, and dried for 1 h at 125 °C. The product was light-brown. The yield was 0.70 g (75 %). ^{1}H-NMR ($(CD_3)_2S=O$) δ/ppm: ^{1}H-NMR ($(CD_3)_2S=O$) δ/ppm: 7.96 (1H, d, *J*=7.1, 3^1-H); 7.62 (1H, t, *J*=7.1, 5^1-H); 7.55 (1H, t, *J*=7.1, 4^1-H); 7.23 (1H, d, *J*=7.1, 6^1-H); 7.02 (2H, d, *J*=9.5, 1,8-H); 6.82 (2H, d, *J*=9.5, 2,7-H). The NMR spectra are given in Figures 1 and 2. The ^{1}H NMR spectra were recorded on Mercury Varian VX-200 spectrometer at 200 MHz.

Synthesis of 2,4,5,7-tetranitro sulfonefluorescein. 0.37 g of sulfonefluorescein was put into the 5 mL flask, and after adding 1 mL of conc. H_2SO_4 was heated with stirring until the solid was completely dissolved and a dark-brown solution appeared. The flask was cooled by ice, and the nitrating mixture (1 mL of sulfuric acid + 0.33 mL of nitric acid) was dropped under stirring. The spectrophotometric control demonstrated that the formation of the dinitro derivative takes place practically immediately. Further nitration, however, occurs very hard. After adding the whole amount of the nitration mixture, the flask was heated during 10 h at 55 °C under constant stirring. Slight scumming and liberation of brown vapors was observed. The cooled mixture was dropped into the solution of sodium acetate in methanol (8 g and 30 mL respectively). The abundant white sediment was separated by decantation. The transparent rich-rose filtrate was evaporated, and the dry residue was dispergated in 25 mL of acetonitrile. After filtration and evaporation, the garnet red substance was formed. The target dye was difficult to isolate. Its content was about 20–30 %, as roughly estimated by dissolving in water and determining the absorbance at 513 nm in aqueous solution. Despite the low content of the target substance, the sample thus obtained hereafter will be called tetranitro sulfonefluorescein.

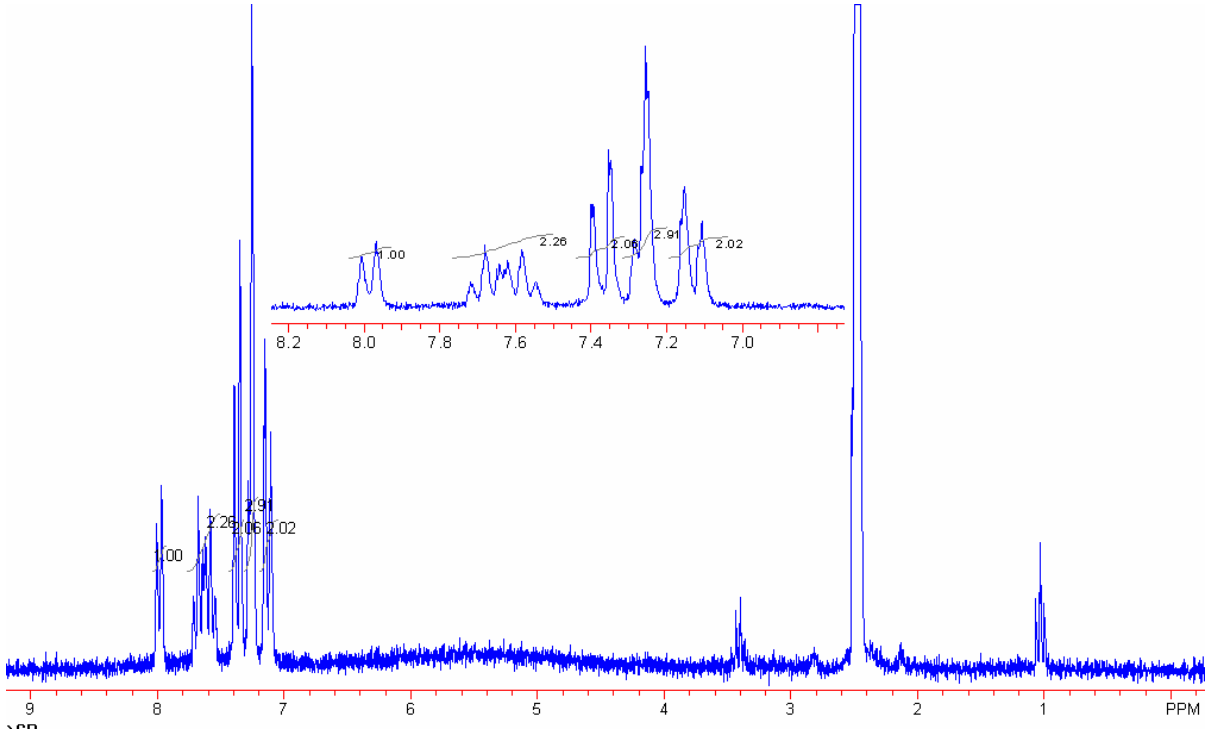


Figure 1. The 1H-NMR spectrum of sulfonefluorescein.

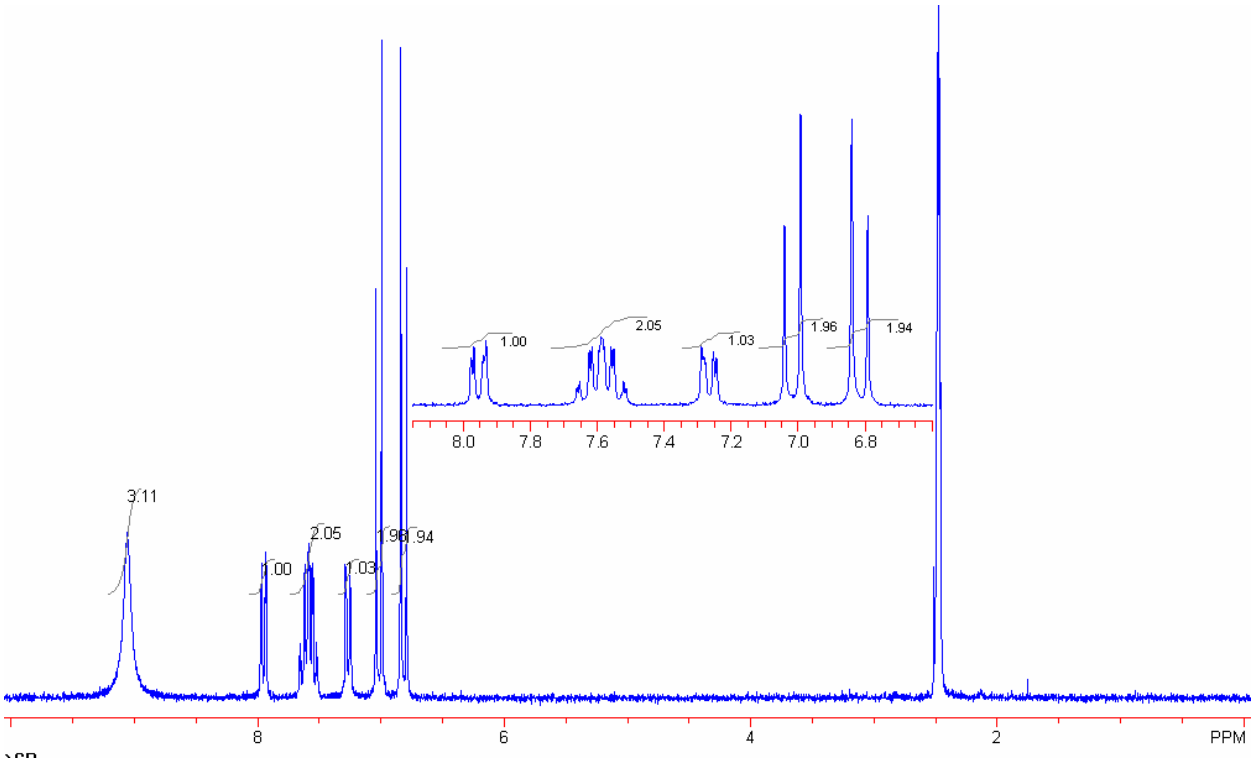


Figure 2. The 1H-NMR spectrum of 4,5-dinitro sulfonefluorescein.

LDI-ToF and MALDI-ToF Mass Spectra. The mass spectrometry is one of very few analytical techniques capable to give an insight into the structure of molecules. The Laser Desorption/Ionization Time-of-Flight (LDI-ToF) and Matrix-Assisted Laser Desorption Ionization – Time of Flight (MALDI-ToF) mass spectrometry was performed using an Autoflex II LRF 20 Bruker Daltonics instrument, equipped with a pulsed nitrogen laser (λ =337 nm; pulse width of 3 ns). Both liquid samples and samples in matrix were deposited onto a standard steel target and dried under ambient conditions. Each mass spectrum presented in this report is a sum of 70 spectra in LDI-ToF and 600 spectra in MALDI-ToF methods. Positive or negative ions were extracted in linear mode. The studies were conducted in the range of 4 to 100 m/z (MALDI-ToF) and 20 to 3000 m/z in LDI-ToF methods. The matrixes for the MALDI-ToF mass spectrometric studies were prepared by standard procedures: 12 mg of sinapic acid (Fluka) was dissolved in 1 mL of water–acetonitrile 1 : 1 mixture, with addition of 1 μL of trifluoroacetic acid.

In a particular case of tetranitro sulfonefluorescein, we were able to obtain good-quality mass spectra of both negative and positive ions, which are shown in Figure 3.

In the representative (both positive and negative ion) spectra, one can clearly identify a number of fragmentation products. For this sample, a sharp intense molecular peak was not observed due to cleaving off the nitro groups and other fragments of molecules addends. For tetranitro sulfonefluorescein, the calculated molecular masses for the fragments of molecules are in good agreement with experimental result. Indeed, the negative ion mass spectrum (Figure 3a) shows the presence of fragments at m/z 546 $(M\text{-}2H)^-$, m/z 346 ($M\text{-}4NO_2$ and -OH groups)$^-$, m/z 330 ($M\text{-}4NO_2$ and -2OH)$^-$, m/z 175 ($M\text{-}4NO_2$, 2-OH and $C_6H_4SO_3H$-fragment)$^-$, m/z 345 ($M\text{-}C_6H_4SO_3H$-fragment)$^-$, as well as a number of fragments at the high m/z, higher than M^-, such as m/z 569 $(M + Ca)^-$ and m/z 585 $(M + K)^-$. The positive ion mass spectrum is not so rich in fragments. We observed the calculated molecular masses for the fragments at m/z 501 $(M\text{-}NO_2)^+$, m/z 468 ($M\text{-}NO_2$,-O,-OH)$^+$, m/z 455 $(M\text{-}2NO_2)^+$, m/z 454 $(M\text{-}2NO_2)^+$, and m/z 438 ($M\text{-}2NO_2$ and -OH groups)$^+$.

As for the mass spectra of the dinitro sulfonefluorescein, they are more informative (Figure 4). We observed the molecular ion of the compound at m/z 456 (negative mode) and at m/z 459 $(M+3H)^+$ under positive mode. In the latter, we also detected a series of peaks, confirming the fragmentation of the molecule, namely, at m/z 414 $(M\text{-}NO_2)^+$, m/z 367 $(M\text{-}2NO_2)^+$, m/z 442 $(M\text{-}OH)^+$, m/z 298 ($M\text{-}C_6H_4SO_3H$-fragment)$^+$, and adducts with K^+ and Na^+ (at m/z 497 and m/z 481). In negative mode,

similar fragments were revealed: m/z 457 $(M+H)^-$ m/z 440 $(M-O)^-$, m/z 426 $(M-O_2)^-$, m/z 411 $(M-NO_2)^-$, m/z 365 $(M-2NO_2)^-$, m/z 375 $(M-SO_3H)^-$, and m/z 501 $(M+NO_2)^-$.

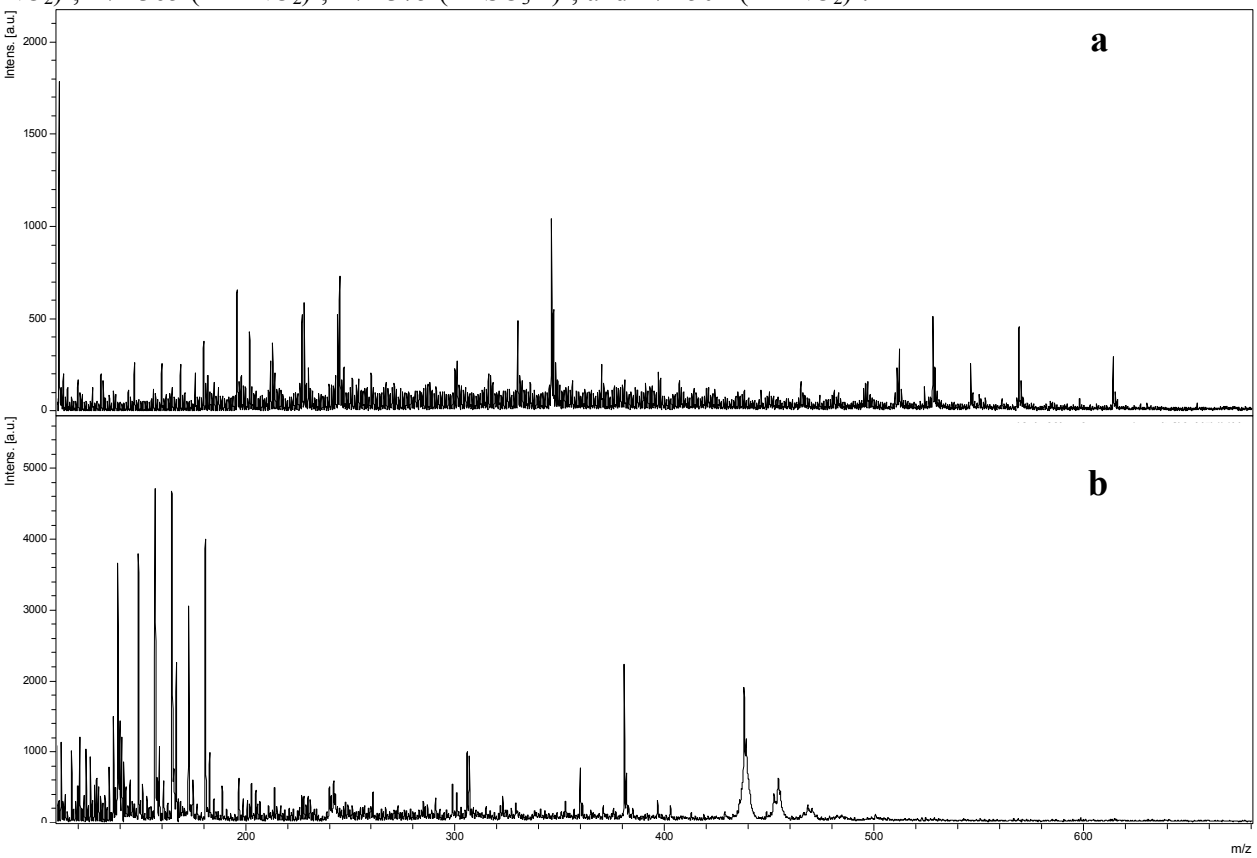


Figure 3. Representative negative (a) and positive ions (b) of LDI-ToF mass spectra of tetranitro sulfofluorescein.

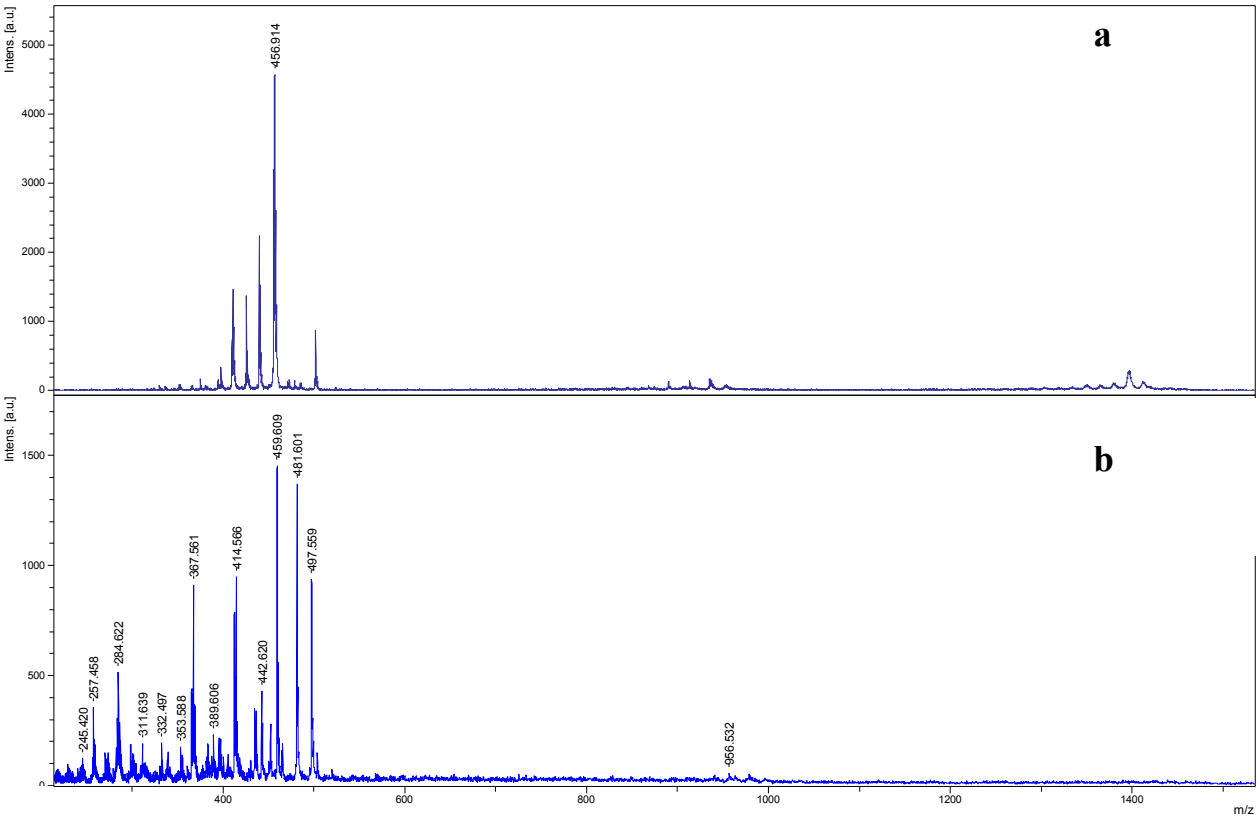


Figure 4. Representative negative (a) and positive ions (b) of LDI-ToF mass spectra of dinitro sulfofluorescein.

For this dye, unlike the tetranitro compound, the structures formed by two molecules of the dye and Na^+ (m/z 936 in negative mode) or K^+ (m/z 953 in negative mode) are characteristic, accompanied by the next series of peaks at m/z1412 $(3M+2Na)^-$ and at m/z 1442 $(3M+2K)^-$. The peaks corresponding to the 1 : 1 composition for $M + Me^+$ were not detected.

Concluding, the LDI-ToF mass spectra confirm the composition of both synthesized compounds.

Results and Discussion

The absorption spectra of sulfonefluorescein and its dinitro derivative in aqueous solutions at different pH values are presented in Figure 5. In the case of the unsubstituted dye, taking into account the thermodynamic values of pK_{a1} = 3.23 and pK_{a2} = 6.76 in water [11], the attribution of the spectra to the corresponding molecular (in fact, zwitter-ionic) and ionic forms is understandable.

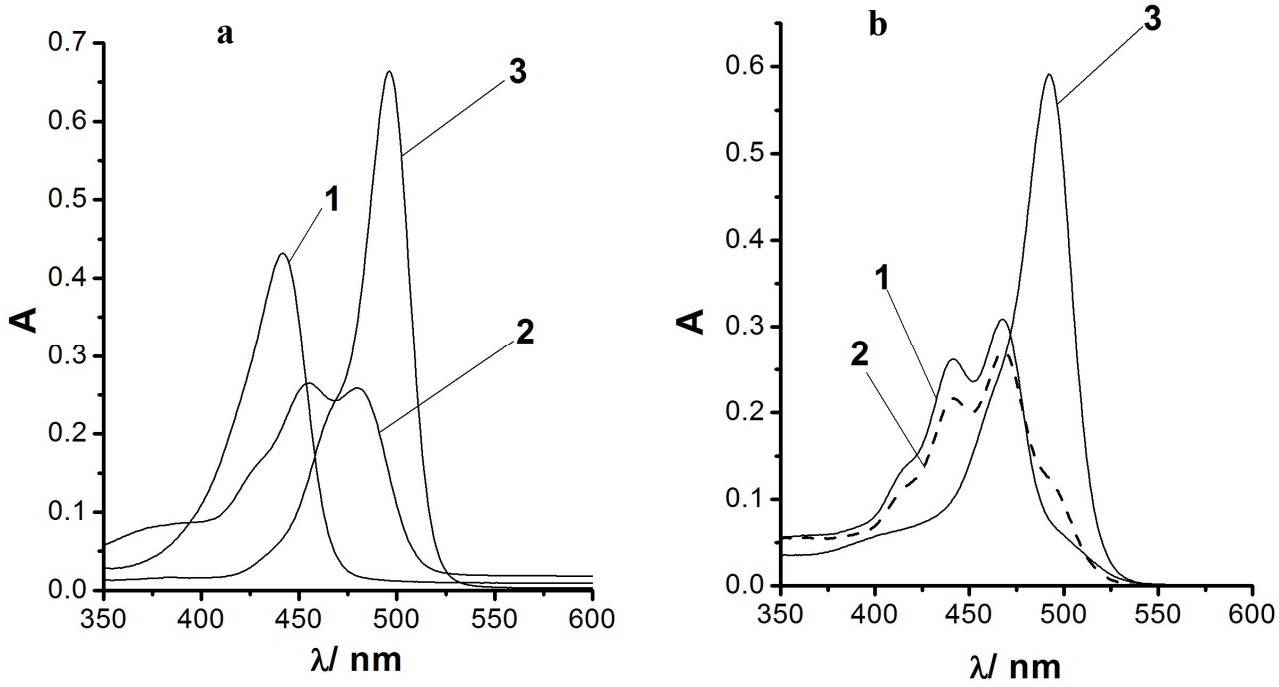
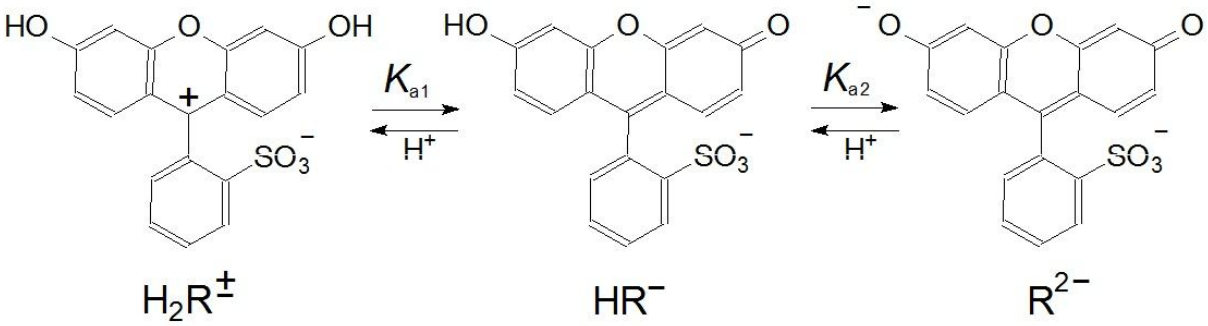
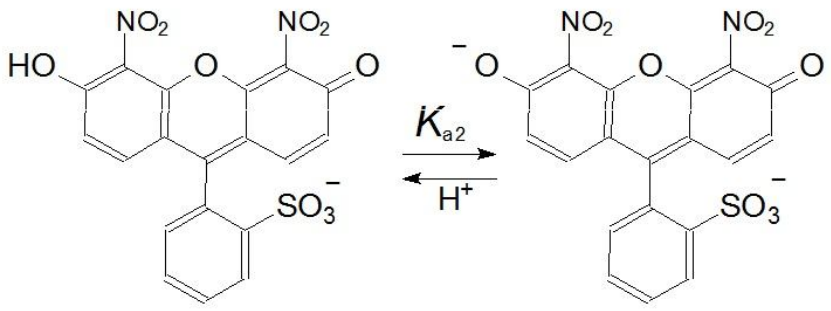


Figure 5. The absorption spectra of sulfonefluorescein (a): at pH 1.0 (1, HCl solution, the H_2R form); at pH 5.0 (2, acetate buffer solution, the HR^- form); and at pH 10.0 (3, NaOH dilute solution, the R^{2-} form) (a). The absorption spectra of dinitro sulfonefluorescein (b): at pH 1.0 (1, HCl solution); pH 1.7 (2, in HCl solution); and in water without additives (3, the R^{2-} form). The optical path length was 1.00 cm.

The structural formulae of sulfonefluorescein species are as follows:



Accordingly, it becomes evident that in the case of dinitro sulfonefluorescein the spectrum in pure water should be ascribed to the dianion R^{2-}, whereas the absorption at pH = 1.0 may correspond to the monoanion HR^-:



HR^- R^{2-}

Such difference between the two dyes is evidently caused by the influence of the nitro groups. Indeed, the pK_{a2} value of the dinitro substituted dye is ca. 4 units lower as compared with pK_{a2} = 6.76 of the sulfonefluorescein. This conclusion may be easily made basing on the spectra in solutions of different acidity (Figure 6). However, the absence of a distinct isosbestic point allows supposing the overlapping of the second equilibrium.

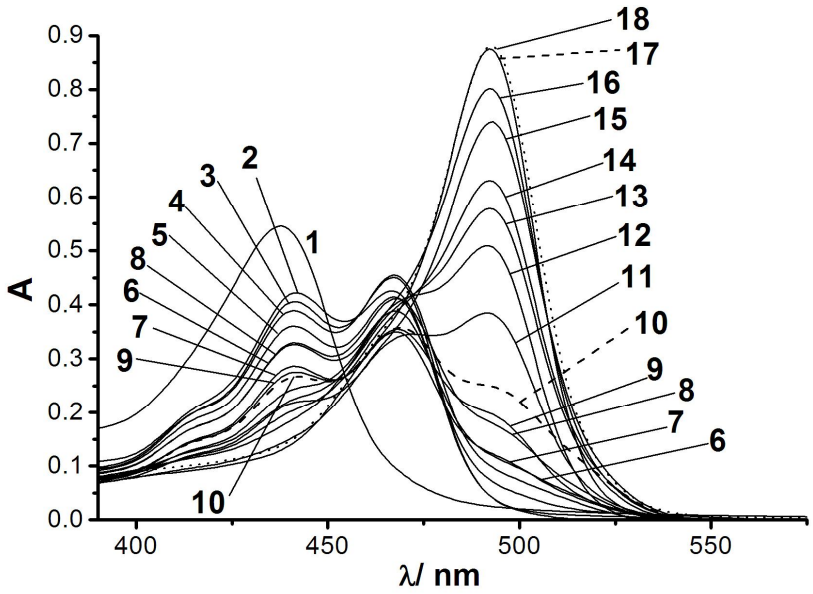
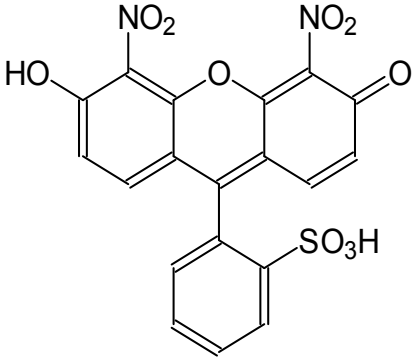


Figure 6. The absorption spectra of 4,5-dinitro sulfonefluorescein in solutions with 8.8 M H_2SO_4 (1), 1.68 HBr (2); in HBr solutions with the pH values in the concentration scale, pH_c, of 0.14 (3) and 0.8 (4); in HCl solutions at pH_c 1.0 (5), 1.3 (6), 1.5 (7), 1.7 (8), and 1.9 (9); in HCl solutions with pH in activity scale, as determined using the glass electrode, pH = 1.94 (10), 2.59 (11), 2.54 (12), 2.81 (13), 2.86 (14), 3.10 (15), and 3.30 (16); in entire water (17); and in diluted NaOH solution, pH 11 (18). Dye concentration: 8.73×10^{-6} M. The maximal R^{2-} molar absorptivity is 100.3×10^{-3} M^{-1} cm^{-1} at 492 nm.

Hence, the neutral form may appear, possessing the quinonoid structure:



It is reasonable assuming that the absorption spectrum of these species in the visible region is similar to those of the monoanion with the SO_3^- group, but not absolutely equal. The small differences cause the blur isosbestic point. It should be noted, however, that the pK_a of *p*-toluenesulfonic and benzenesulpfonic acids are with –(1.06–1.34) and –2.8 extremely low [13, 14]. Otherwise, the spectra may be effected by the inconstancy of the ionic strength.

The acidity range of the predominance of the cationic form is shifted towards the concentrated sulfuric acid solutions.

The tetranitro derivative is even more stable against protonation. Even in 1 M HCl solution, the spectrum of the R^{2-} dianion stays unchanged. As it is clearly seen in Figure 7, the protonation of the tetranitroxanthene chromophore takes place in much more acidic media.

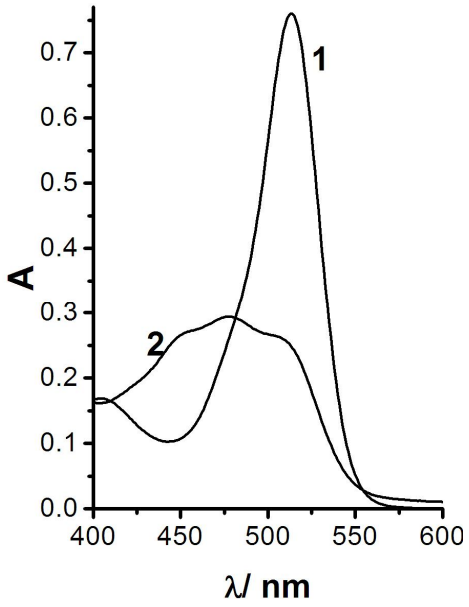
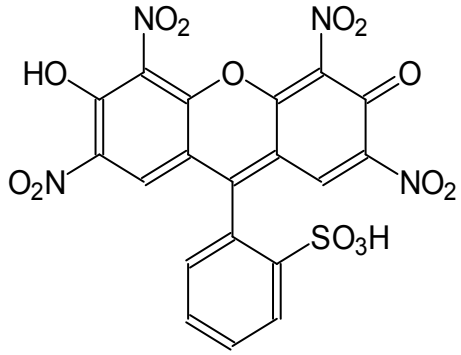


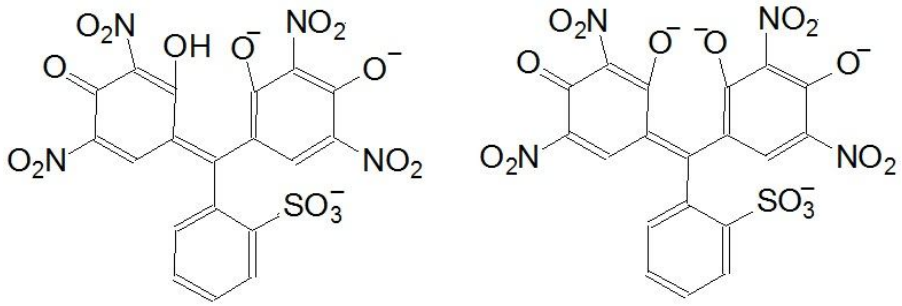
Figure 7. The absorption spectra of the tetranitro sulfonefluorescein in water (1, the R^{2-} form) and in 8.8 M H_2SO_4 solution (2).

As the SO_3^- group is probably protonated under such hard conditions, the dye species existing in 8.8 M sulfuric acid should be depicted as a neutral molecule:

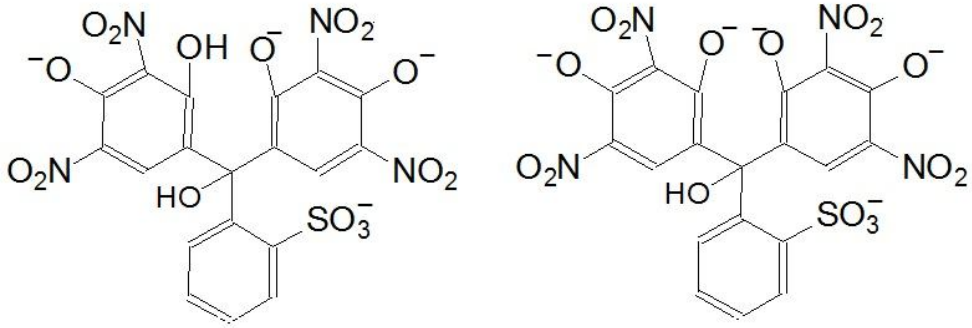


Further protonation and formation of the $-SO_3H_2^+$ group may take place in more acidic media, at $H_o < -6$ [13].

However, at high pH values created by NaOH, the change of the dianionic spectrum occurs readily. The rupture of the pyrone cycle results in formation of the triphenylmethane dye with the following probable structures:



This alkaline product manifests itself in a distinct bathochromic shift of the band up to λ_{max} in the region of 600 nm, in accordance with the data for nitrofluorescein dyes [7]. Simultaneously, the absorption near 400 nm increases, which should be ascribed to the nucleophilic attack on the central carbon atom with carbinol formation:



In the case of dinitro sulfonefluorescein, these processes are not so expressed (Figure 8). In any case, the appearance of these new species is accompanied by the decrease of the initial dianionic absorption band. Hence, the electron-attracting properties of nitro groups manifest itself distinctly.

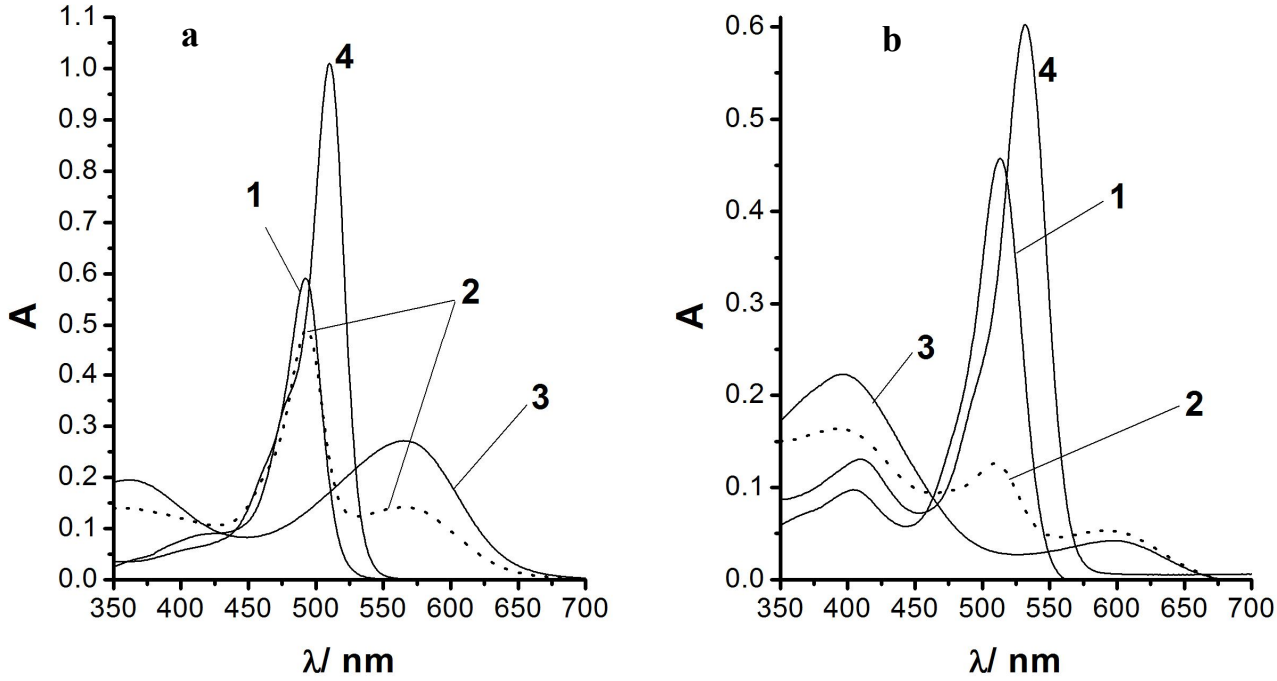
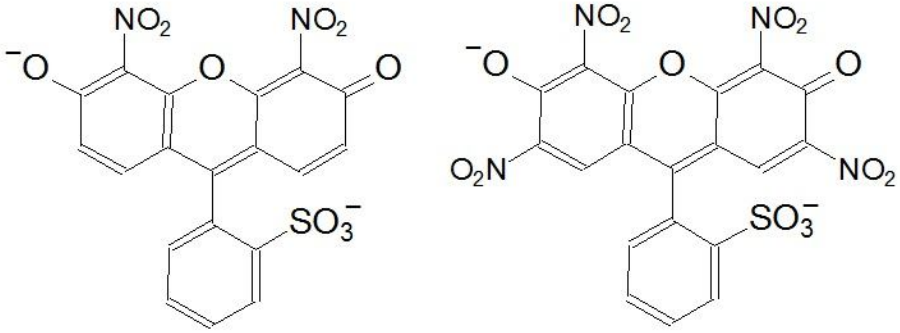


Figure 8. The absorption spectra of the dinitro sulfonefluorescein (a): in water solution in pure water (1); at pH 12.9 (2, in NaOH solution, measured immediately); at pH 12.9 (3, in NaOH solution after 4 hours); and in 0.01M CTAB solutions (4). The absorption spectra of tetranitro sulfonefluorescein (b): in water (1); at pH 12.0 (2, in NaOH solution, measured immediately); at pH 12.9 (3, in NaOH solution, measured immediately); and in 0.01M CTAB solutions (4).

To the best of the authors' knowledge, the two dyes reported here have not been described anywhere. Thus, they may be named as 'Kharkov Orange 1' and 'Kharkov Orange 2' respectively.

The next step was to utilize these dyes for examining some lyophilic colloid systems. On going from water to micellar solutions of cetyltrimethylammonium bromide (CTAB), the absorption bands of R^{2-} undergo bathochromic shift and marked increase in intensity (Figures 8a and 8b, curves 4). Such bathochromic shifts are typical for the binding of the negatively charged hydroxyxanthene dye species by cationic interfaces:



Another system studied using the nitro sulfonefluoresceins was the solution of the lysozyme protein (Aldrich, M.m. $\approx 14.2\times10^3$). In lysozyme solution, spectra of the dyes are slightly shifted towards the red against the absorption bands in pure water (Figure 9). This gives evidence for binding of the dianions R^{2-} by the protein macromolecule.

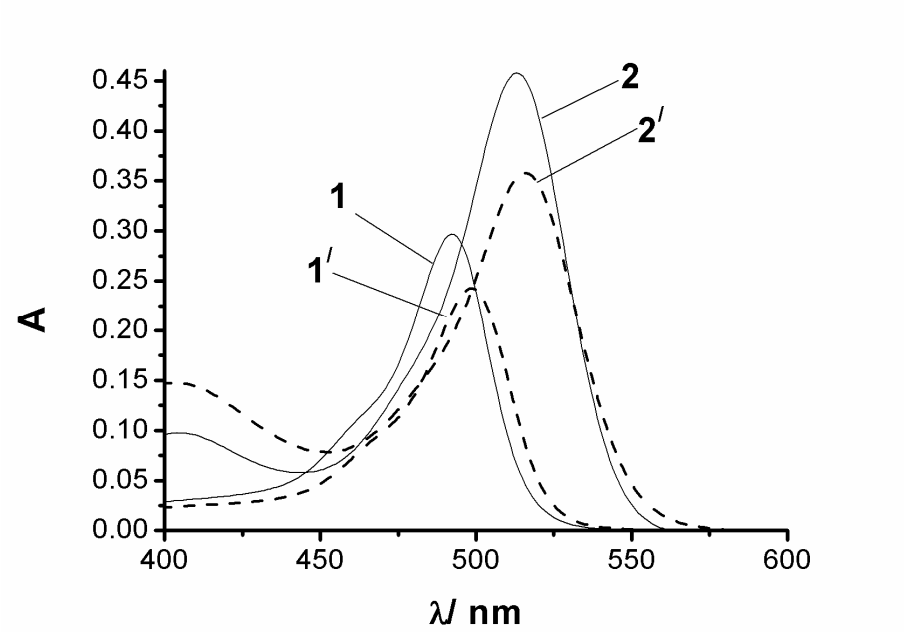


Figure 9. The absorption spectra of the dinitro sulfonefluorescein (1) and tetranitro sulfonefluorescein (2) in pure water and with adding of the lysozyme ($1^{/}$) and ($2^{/}$), correspondingly. The dye concentrations are 2.96×10^{-6} and about 6×10^{-6} M respectively, the protein concentration equals to 0.45 g per L.

The study of these interactions was furthered by using the MALDI-ToF technique. The protein lysozyme and tetranitro sulfonefluorescein were dissolved in water at concentration of 1 mg/mL and ca. 6×10^{-5} M (as calculated using the conventional maximal molar absorptivity of 80×10^3 M^{-1} cm^{-1}) respectively. The lysozyme solution was mixed with a solution of tetranitro sulfonefluorescein in volume ratio 1:9. After incubation under ambient conditions for 2 h solutions were investigated by MALDI-ToF.

Figure 10a shows the mass spectra of the negative ions of the starting solution of lysozyme. The peaks should be ascribed to the mono-charged ions of monomers (14318 m/z), dimers (28635 m/z),

and trimers (42953 m/z) of lysozyme. For solutions of lysozyme with tetranitro sulfonefluorescein, the mass spectra of negative ions reflect the formation of protein–dye complexes with the stoichiometric ratio of 1:1. The peak at 14318 m/z refer to the lysozyme, whereas the new peak appearing at 14861 m/z refer to lysozyme complex with the tetranitro sulfonefluorescein (Δ m/z 543 is in satisfactory agreement with the mass of the dye). The peak at 28607 m/z corresponds to the lysozyme dimer and the new peak at m/z 29097 (Δ m/z is 490) should be ascribed to the 2 : 1 lysozyme–dye complex (Fig. 10b). Mass spectra of the positive ions were similar to those of negative ones. Experimentally obtained values of m/z of the structures correspond to the theoretically calculated ones within the limits of the measurement uncertainties. Hence, we observe the decrease in the propensity of lysozyme to oligomerization process after addition of tetranitro sulfonefluorescein.

Finally, an attempt was made to use the high reactivity of the dyes with alkali for revising the exchange processes between the aqueous nanodroplets stabilized by surfactants in chloroform. For this purpose, the reversed microemulsions H_2O–surfactant–$CHCl_3$ were utilized. The surfactant was the so-called gemini 16–4–16:

$$C_{16}H_{33}–N(CH_3)_2^+–(CH_2)_4–N(CH_3)_2^+–C_{16}H_{33}\ 2Br^-$$

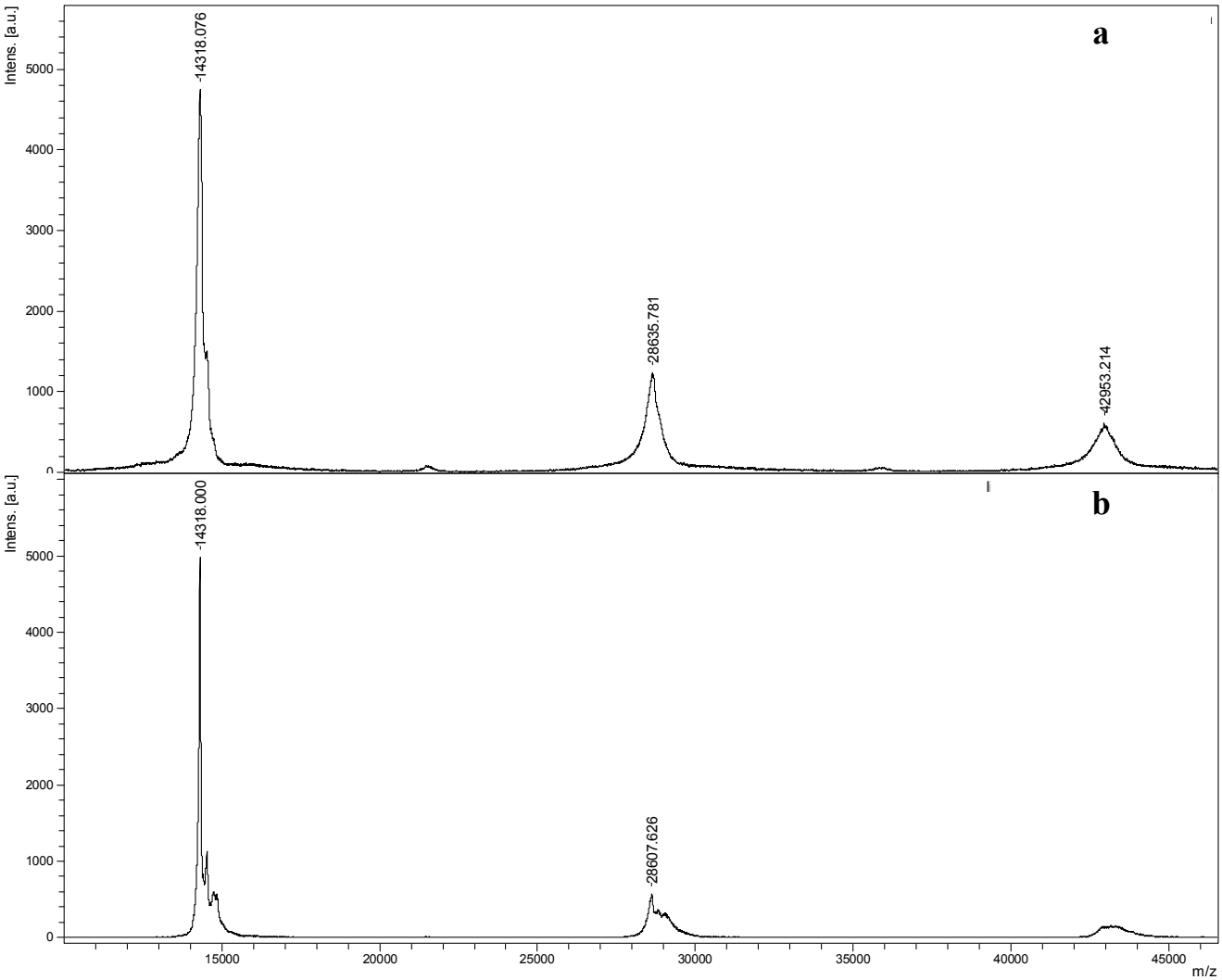


Figure 10. The MALDI-ToF mass spectra negative ions of lysozyme (a) incubated with tetranitro sulfonefluorescein in aqueous solution (b).

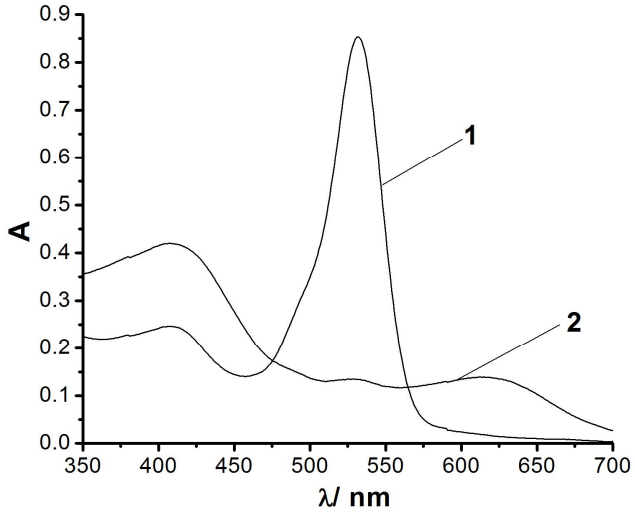


Figure 11. The absorption spectra of the tetranitro sulfonefluorescein in reversed microemulsions formed by gemini surfactant 16–4–16 in chloroform, with water : surfactant ratio of $W = 9.7$. The curve 1 refers to the dye in the system without alkali. The curve 2 is the absorption spectrum in the mixture of two equal volumes of reversed microemulsions; before mixing, one microemulsion contained the dye solution within the nanodroplets of solubilized water, whereas the second one contained the 4.0 M NaOH solution. The dye concentrations in (1) and (2) are equal.

The concentrations of the working solutions in chloroform were 0.172 M for 16–4–16 and 1.67 M for water. Equal volumes of two microemulsions, one containing the dye dissolved in the aqueous droplets ('water pools') and another containing 4.0 M of alkali were carefully mixed. The spectrum of the tetranitro derivative changes practically immediately (Figure 11), whereas the alterations of the absorption spectra of dinitro sulfonefluorescein were rather insignificant and became observable only within four days.

Similar results have been obtained with some other cationic surfactants. These findings allow concluding that the exchange between water droplets certainly takes place. It occurs, however, not so easy and complete as in the case of mixing of homogeneous aqueous solutions.

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С. В. Шеховцов, Н. О. Мчедлов-Петросян, Н. Н. Камнева, Т. Ю. Громовой. Новые оранжевые красители: нитропроизводные сульфофлуоресцеина.

В работе сообщается о нитровании гидроксиксантенового красителя сульфофлуоресцеина. Полученные красители идентифицированы как 4,5-динитро и (вероятно) 2,4,5,7-тетранитросульфофлуоресцеины. Спектральные и кислотно-основные свойства, взаимодействие с лизоцимом, а также поведение в растворах ПАВ изучены с помощью электронной спектроскопии и методов LDI-ToF и MALDI-ToF. В то время как ксантеновая часть красителей устойчива по отношению к протонированию, пироновый цикл легко размыкается при высоких значениях pH, создаваемых при помощи NaOH. Последующая нуклеофильная атака на центральный углеродный атом приводит к образованию карбинольной структуры.

Ключевые слова: Нитропроизводные сульфофлуоресцеина, нуклеофильная атака, спектры поглощения, LDI-ToF, MALDI-ToF, лизоцим, обращенные микроэмульсии.

С. В. Шеховцов, М. О. Мчедлов-Петросян, Н. М. Камнєва, Т. Ю. Громовий. Нові оранжеві барвники: нітропохідні сульфофлуоресцеїну.

У роботі доповідається про нітрування гідроксиксантенового барвника сульфофлуоресцеїну. Одержані барвники ідентифіковані як 4,5-динітро та (ймовірно) 2,4,5,7-тетранітросульфофлуоресцеїни. Спектральні та кислотно-основні властивості, взаємодію з лізоцимом, а також поведінку у розчинах ПАР вивчено за допомогою електронної спектроскопії та методів LDI-ToF і MALDI-ToF. У той час як ксантенова частина барвників стійка по відношенню до протонування, піроновий цикл легко розмикається при високих значеннях pH, створених за допомогою NaOH. Наступна нуклеофільна атака на центральний атом вуглецю приводить до створення карбінольної структури.

Ключові слова: Нітропохідні сульфофлуоресцеїну, нуклеофільна атака, спектри поглинання, LDI-ToF, MALDI-ToF, лізоцим, обернені мікроемульсії.