

UDC 543.422.3-76 : 541.49

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SUBSTITUENT AND ENVIRONMENT INFLUENCE ON ANALYTICAL PROPERTIES OF ASSOCIATES OF XANTHENE DYES WITH POLYHEXAMETHYLENEGUANIDINE CHLORIDE

The interaction of 5 anionic xanthene dyes – 9-R-2,3,7-trihydroxy-6-fluorones (TOF) with cationic polyelectrolyte (PE) – polyhexamethyleneguanidine chloride (PHMG) has been studied by the optical spectroscopy in a concentration range where PHMG has a polyelectrolyte effect. Hammett σ -constants were calculated. The correlations between structure of TOF and shift of protolytic equilibrium in aqueous-polyelectrolyte solutions were established. Influence of pH, concentration of the ethanol, components ratio in the system PHMG-TOF on the character of the interaction of cationic PE with TOF and value of the analytical signal were studied based on absorption spectra. The results were compared to those obtained in water solutions.

Keywords: trioxofluorone; spectrophotometry; polyhexamethyleneguanidine chloride; polyelectrolyte; ionisation constant; aggregation.

Introduction. The application of dyes is frequently connected with the definition of PE [1-7]. 9-R-2,3,7-Trihydroxy-6-fluorones are the most widely studied and used. The degree of PE influence on ionic equilibria in the dye solutions depends on numerous factors involved in the process of PE-dye interaction. The effect is caused by capability of PE to change property of the substances in solubilized condition that is connected with the change of medium properties in a microenvironment [8; 9]. The solubilized substance passes from aqueous to aqueous-polyelectrolyte microphase. Thus the competitive interactions between polymeric molecules and dye, solvent and components of the system are possible. The number of trapped ions of dye depends on the number and conformation of PE molecules in the solution [10; 13]. The formation of associates «PE-dye» is possible by means of a hydrogen bridging, electrostatic and hydrophobic interactions and depends on the concentration ratio of the components. The change of chemical-analytical properties of dyes in the presence of PE was described earlier: phenylfluorone with a nonionic PE poly(vinylpyrrolidone) [11], bromphenol red and chlorphenol red with PHMG [8; 9]. The purpose of the present work is to study the optical, protolytic properties, as well as specifics of associate formation between TOF with various substituents in 9 position of xanthene core and cationic PE – PHMG ($M_r \approx 1,0 \times 10^4$ and $6,4 \times 10^3$) in aqueous and aqueous-alcoholic solutions.

Experimental

Materials and methods. Structural formulae of TOF (fig. 1) are shown in a table 1.

Starting solutions of PhF and SF C = 1×10^{-3} mol/L were prepared on the day of the experiment by dissolving the sample in 25 ml of twice-distilled water with addition of several drops of concentrated NaOH solution. Initial alcoholic solutions of o-NPhF, DSPhF and NF were prepared according to recommendations [12]: 1 ml HCl (6 mol/L) and 80-85 ml of 96% ethanol were added to the sample of dye and carefully heated until

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dissolved, after that solution was poured to a measuring flask (100 ml) with 96% ethanol added to marking. Working solutions were prepared by dilution of the initial alcoholic solutions on the day of the experiment. Working concentration of TOF were 1×10^{-6} mol/L and 5×10^{-6} mol/L.

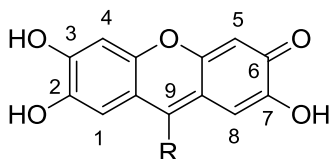


Fig. 1. Structural formula of 9-R-2,3,7-trihydroxy-6-fluorone

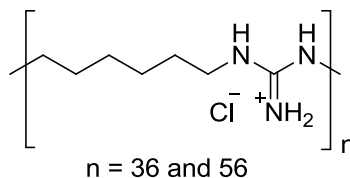


Fig. 2. Formula of PHMG unit

Table 1

Formulas of trioxyfluorones				
Trioxyfluorone	Abbreviation	R_1	R_2	R_3
Phenylfluorone	PhF		H	H
Salicylfluorone	SF		OH	H
o-Nitrophenylfluorone	o-NPhF		NO ₂	H
2,4-Disulfophenylfluorone	DSPhF		SO ₃ ⁻	SO ₃ ⁻
Nonylfluorone	NF	-C ₉ H ₁₉	-	-

PHMG with apparent molecular weight $M_r \approx 1 \times 10^4$ ($n = 56$) and $M_r \approx 6.4 \times 10^3$ ($n = 36$) was. It had been refined by reprecipitation from 50% water solution to 25 % NaCl, since monomers and oligomers of PHMG with $[\eta] < 0.02$ dl/g are well soluble in concentrated solution of NaCl. Weight loss during reprecipitation of a technical product was 7%. An initial solution with concentration of 2.5×10^{-5} mol/L was obtained by dissolving PHMG sample in 100 ml twice-distilled water. More diluted solutions were received by dilution of the initial solution directly before the use.

The concentration of PHMG in the measurement unit [base-mol/L] was calculated using the formula: $C = C_M \cdot n$, where C_M – the molar concentration of PHMG, [mol/L]; n – the number of PE units.

Solutions of HCl, NaOH and acetate buffer solution were used to adjust pH. The acetate buffer solutions were prepared from 0.1 mol/L CH₃COOH and 0.1 mol/L CH₃COONa. All used reagents were analytically pure.

An aliquot of the TOF solution was added to a volumetric flask ($V = 25$ ml), the necessary acidity was created by adding HCl and NaOH solutions or 1 ml acetate buffer solution, then 15 ml twice-distilled water, aliquot of the PHMG solution. Water was added to marking. The solution was stirred. In 2 hours values of pH were checked on universal ionometer EV-74 with an glass indicator electrode and silver-chlorine half-cell; optical density was measured on spectrophotometer Specord M-40 (Germany, $\pm 0,001$) and Spectro Flex 6100 (Germany, $\pm 0,001$). A reference solution in all measurements was twice-distilled water. Ionisation constants of TOF and their associates with PHMG were defined by a method of isobestic points [13].

Results and discussions

Absorption Spectra. TOF in the solutions can be in 5 forms depending on acidity of a medium: protonated on carbonyl, molecular and three anionic forms. We used TOF with two types of substituents in xanthone core: an alkyl radical -C₉H₁₉ in case of NF and a phenyl radical (PhF) with the substituted hydrogen atoms in 2 and 4 positions (SF, DSPhF and o-NPhF). According to classification of substituents and heteroatoms in

organic molecules [14] hydrocarbon substituents of TOF under investigation have π -electronic system coinciding with π -systems of ethylene or benzol. Guanidine group of PHMG has a lone-electron pair and supplies two π -electrons. Dissociation of auxochromes of TOF in the presence of PHMG is accompanied by red shift of absorption bands of a reagent that corresponds to formation of associates between TOF and PHMG. The interactions «dye–polycation» are controlled by electrostatic forces. The influence of pH on efficiency of association between PHMG and TOF was investigated. PHMG is amphiphilic substance and at the same time it can exist in the cationic and neutral form ($pK_a \approx 11$). The increase in pH results in reduced number of protonated guanidine groups of PHMG being capable to interact with anionic form of a dye. Therefore the maximal red shift $\Delta\lambda$ of absorption bands is observed at pH = 4–6, when PHMG is in its cationic form. There are three forms of dye observed in a spectrum: protonated, molecular and monoanion (fig. 3). The change of polycation properties with the growth of pH can be used in order to interpret spectrophotometric characteristics of TOF in the absence and the presence of PHMG (table 2). Spectral shift λ_{max} is caused by the nature of substituent in the benzene core [15]. For PhF and o-NPhF the greatest red shift λ_{max} is observed and reaches as much as of 40 nm.

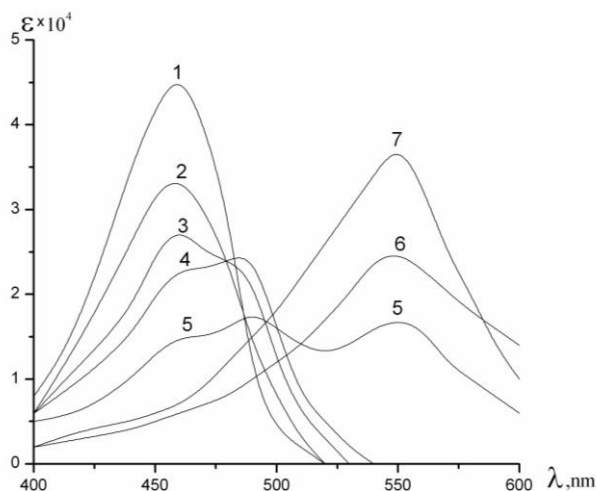


Fig. 3. Absorption spectra of o-NPhF in the presence of PHMG. $C_{o-NPhF}=C_{PHMG}=1 \times 10^{-6}$ M. pH: 1 – 1.0; 2 – 2.0; 3 – 3.0; 4 – 3.8; 5 – 4.8; 6 – 5.1; 7 – 5.8

Ionisation constants. The structure of reagent and external conditions (temperature, ionic strength, nature and composition of solvent) influence ionisation constants of reagents. At the concentration of 5×10^{-6} M PHMG has its maximal effect on a state of TOF in solution. When the concentration is decreased, PHMG does not cause any changes in absorption spectra and position of acid-base equilibriums of TOF in water solutions. The effect is due to conformational and steric difficulties which appear in collisions between PE and dye molecules. At concentration below 1×10^{-6} M PHMG displays polyelectrolyte effect [16–18]. Numerical values of ionization constants pK_a of dyes and pK_a^{app} (the apparent constant, it is showing the value of pH when deionization of dye form occurs in half) are given in table 3. Equilibrium involving formation of monoanion (H_2R^-) and dianion (HR^{2-}) forms of TOF in the presence of PHMG takes place in the subacidic and subalkali environment. The bridging of ionisation steps is observed for H_3R^0 and H_2R^- -forms. Definition of $pK_a^{app(1)}$ on the first stage was made by graphic

method using extreme areas of acidity [13; 17].

Table 2

Spectrophotometric characteristics of TOF in aqueous and aqueous-polyelectrolyte solutions

Dye	Form	λ_{\max} , nm (pH)				
		Without PHMG	With PHMG (n=56)	$\Delta\lambda$	With PHMG (n=36)	$\Delta\lambda$
PhF	H ₄ R ⁺	462 (<1.2)	462 (<1.0)	-	457-458 (<1.0)	-5
	H ₃ R ⁰	462, 490 (4.8-5.2)	462, 482 (1.5-3.0)	-8	462; 490 (2.0-5.7)	0
	H ₂ R ⁻	514 (8.4-9.0)	547 (3.0-8.5)	33	530 (5.7-9.5)	16
	HR ²⁻	532-538 (11.4-12.0)	564 (8.5-11.0)	26	547 (9.5-10.5)	15
	R ³⁻	556-558 (>13.0)	580 (>11.0)	22	572-573 (>11.0)	16
SF	H ₄ R ⁺	465 (<3.0)	460-465 (<2.5)	-	460 (<2.5)	-
	H ₃ R ⁰	462, 492 (3.0-6.0)	460, 490-495(3.0-5.5)	3	462; 491 (2.5-5.5)	3
	H ₂ R ⁻	506 (6.0-7.5)	537 (5.0-7.0)	31	534 (5.5-7.0)	31
	H ₂ R ⁻	512-514 (7.5-10.0)	515-520 (7.0-9.5)	8	513 (7.0-10.0)	8
	HR ²⁻	523 (10.0-12.5)	550-553 (9.5-11.5)	30	535 (10.0-12.0)	25
	R ³⁻	546 (>12.5)	560-565 (>11.5)	19	559 (>12.0)	19
o-NPhF	H ₄ R ⁺	463 (<2.5)	463 (<1.5)	-	463 (<2.0)	0
	H ₃ R ⁰	463, 491 (2.5-6.0)	463, 489 (1.5-5.0)	-2	463; 490 (2.0-5.0)	-2
	H ₂ R ⁻	515 (6.0-10.5)	555 (5.0-8.0)	40	520-523 (5.0-9.0)	8
	HR ²⁻	530 (10.5-12.5)	565 (8.0-11.0)	35	558-560 (9.0-11.0)	30
	R ³⁻	550 (>12.5)	577 (>11.0)	27	570 (>11.5)	20
DSPhF*	H ₄ R ⁺	448 (<2.0)	448 (<1.0)	-	448 (<1.5)	0
	H ₃ R ⁰	452, 475 (2.5-5.3)	452, 484 (2.5-5.0)	9	475-478 (2.5-5.5)	-3
	H ₂ R ⁻	502 (5.3-11.5)	530 (5.5-9.0)	28	497 (5.5-10.0)	-5
	HR ²⁻	523 (11.5-13.0)	545 (9.0-11.0)	22	535 (10.0-12.0)	12
	R ³⁻	535 (>13.0)	558 (>11.0)	23	544-547 (>12.0)	12
NF*	H ₄ R ⁺	446-450 (<2.0)	450 (<2.5)	-	447-448 (<3.0)	1
	H ₃ R ⁰	450, 478-480 (2.5-6.0)	450, 480 (2.5-5.0)	2	450; 477 (3.0-6.0)	4; -3
	H ₂ R ⁻	494-498 (6.0-11.0)	530 (5.0-9.5)	36	497-500 (6.0-10.0)	3
	HR ²⁻	510-516 (11.0-12.5)	545 (9.5-11.5)	40	521 (10.0-11.5)	11
	R ³⁻	536 (>12.5)	556 (>11.5)	20	550 (>11.5)	14

* C_{TOF}=5×10⁻⁶M. C_{PHMG}, base-mol/L (M_r): 2.8×10⁻⁴(10⁴) and 1.8×10⁻⁴(6,4×10³).0.4% vol. ethanol

Table 3

The influence of PHMG on pK_a^{app} of TOF

Ionised forms transferrin	H ₄ R ⁺ ↔ H ₃ R ⁰			H ₃ R ⁰ ↔ H ₂ R ⁻			H ₂ R ⁻ ↔ HR ²⁻			HR ²⁻ → R ³⁻			
PHMG	The number of links, n												
Dye	Ionisation constant	n=36		n=56		n=36		n=56		n=36		n=56	
		pK ₀	pK _a ^{app} ₍₀₎	pK ₁	pK _a ^{app} ₍₁₎	pK ₂	pK _a ^{app} ₍₂₎	pK ₃	pK _a ^{app} ₍₃₎				
PhF	2.20	2.10	2.05	6.89	5.80	5.30	9.85	9.65	8.80	11.40	10.05	10.20	
SF	3.56	2.80	2.88	6.09	5.85	5.32	10.05	9.70	9.08	11.10	11.60	10.10	
o-NPhF*	2.71	2.90	2.18	6.30	5.00	4.92	9.45	9.00	7.63	11.81	10.75	10.83	
DSPhF*	2.78	2.70	2.65	6.26	5.40	5.28	10.60	10.10	9.81	11.39	12.10	10.45	
NF*	2.52	3.30	2.90	6.40	6.30	4.80	10.87	10.00	10.05	12.20	11.10	11.21	

* C_{TOF}=5×10⁻⁶M. C_{PHMG}, base-mol/L: 2.8×10⁻⁴(n = 56) and 1.8×10⁻⁴(n = 36). 0.4% vol. ethanol.

Specificity of interaction of PHMG with the TOF molecules is caused by hydrophilicity of macromolecule. Change of substituent in xanthene core defines features of effect only in the case of deprotonation of TOF at transferring forms: H₄R⁺ ↔ H₃R⁰. In the presence of PHMG (n = 56) the pK_a^{app}₍₀₎ for NF is shifted to alkaline region for 0.38 pH units; in the presence of PHMG (n = 36) – for 0.78 pH units. This is due to the hydrophobic interaction of alkyl radical of NF with PHMG. pK_a^{app} of protonated form in polyelectrolyte medium is shifted to acidity region pK_a in PHMG free solution.

The influence of the substituent can be calculated using objective parameters such as ionization constant. We calculated the Hammett σ -constants for different stages of ionisation to make correct correlation with the nature of substituent [19]. σ -Constants serve as a semiquantitative measure of electronic and other effects of substituents. σ -Constants connect the change of ionisation constants of TOF at association with PHMG and constants of substituents defined using ionisation constants of substituted TOF:

$$\sigma_R = \lg \frac{K_R}{K_0},$$

where K_0 – ionisation constant of PhF, K_R – ionisation constants of substituted TOF (SF, o-NPhF, DSPhF).

The change of Hammett σ -constants for different ionisation stages is observed for TOF with various substituents in ortho-position of phenyl ring. Independent correlations $\Delta pK_a^{app} - \sigma$ were established. They are described by the general equation:

$$\Delta pK_a^{app} = \Delta pK_a^{app*} + \rho \times \sigma_R,$$

where ΔpK_a^{app*} is the shift of apparent ionisation constant of PhF in aqueous-polyelectrolyte environment; ρ – reaction constant, which is typical for this series of TOF; σ_R – Hammett constant of substituent R.

The linear dependence (fig. 4) with a high correlation coefficient is observed for the monoanion formation in the presence of PHMG:

$$\text{PHMG (n = 36):} \quad \Delta pK_a^{app(1)} = 0.32 + 1.25 \times \sigma_R \quad (R^2 = 0.996)$$

$$\Delta pK_a^{app(3)} = 1.91 + 1.37 \times \sigma_R \quad (R^2 = 0.930)$$

$$\text{PHMG (n = 56):} \quad \Delta pK_a^{app(1)} = 0.87 + 1.36 \times \sigma_R \quad (R^2 = 0.937)$$

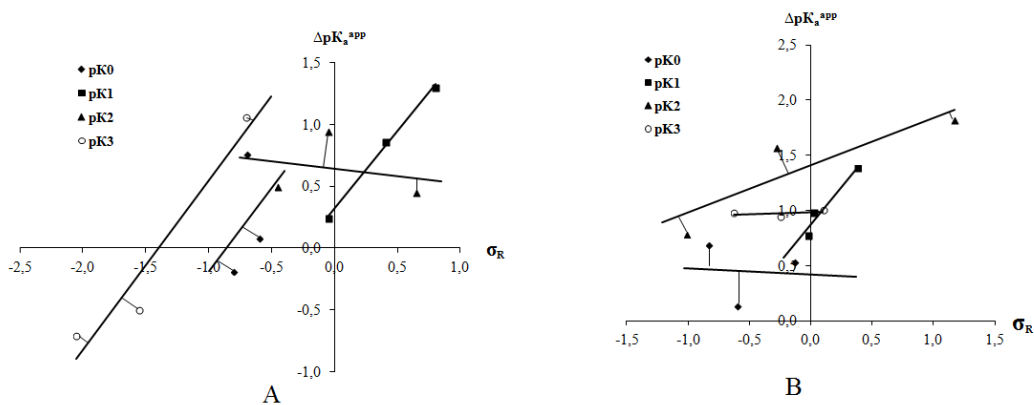


Fig. 4. The correlation of the shift of ΔpK_a^{app} by σ -constants for TOF-PHMG.

$C_{\text{PHMG (n=36)}} = 1.8 \times 10^{-4}$ base-mol/L (A), $C_{\text{PHMG (n=56)}} = 2.8 \times 10^{-4}$ base-mol/L (B)

In the series of SF–DSPhF–o-NPhF with PHMG (n=36) present $\Delta pK_a^{app(1)}$ values for monoanion formation have respective values of 0.24–0.86–1.30.

Correlation curves of ΔpK_a^{app} as a function of substituent σ -constant in the presence of PHMG are shown on fig. 4. It has to be noted that correlation deviates from linear as concentration of PHMG increases.

Aggregation TOF in aqueous-polyelectrolyte and aqueous-alcoholic solutions. Molecules of a dye in aqueous solution tend to aggregate that hinders their interaction with PE. Dimeric dye ions exist even in the diluted aqueous solutions. Spectral characteristics of aggregates and monomeric forms considerably different [20]. Dimer formation for neutral and ionic forms of xanthene dyes is observed. It can be detected by differential absorption spectroscopy. Van-der-Waals interactions of dye molecules appear

in both aqueous and non-aqueous solutions. In aqueous solutions dimeric form is predominant, whereas in organic solvents their fraction is negligible [21; 22].

Aggregation of the dye molecules increases with the growth of their concentration on a polymeric chain with high charge density [16]. The maximum yield of ionic associates at concentration of PHMG and TOF less than 5×10^{-6} M is observed (fig. 5). Aggregation efficiency depends on the concentration ratio of dye and PE.

The PE behavior in organic solvents and in aqueous solutions is essentially different. The interactions of the analytical reagents with PE in mixed solvents are more difficult compared to the processes occurring in individual solvents. Ability of the organic dye to form an ionic associate with PE depends strongly on the balance between polymer-dye, polymer-solvent and dye-solvent interactions. Besides, spectral characteristics of dyes are defined by polarity of a medium [23]. It is important to consider the influence of the composite constituents against each other and the contribution each of them to the process of dissolved substance solvation [24].

The influence of aqueous-organic environment was investigated using PHMG–*o*-NPhF system at pH 5.2. In aqueous-alcoholic solution with $C_{et} = 0.4\%$ vol. the dye was present in dimeric form (fig. 6, curve 6) with an absorption maximum at 490 nm ($\epsilon = 1.8 \times 10^4$). In a solution with $C_{et} = 95.2\%$ vol. molecular form of *o*-NPhF was predominant with intense absorption at 520 nm ($\epsilon = 4.3 \times 10^4$) (fig. 6, curve 7).

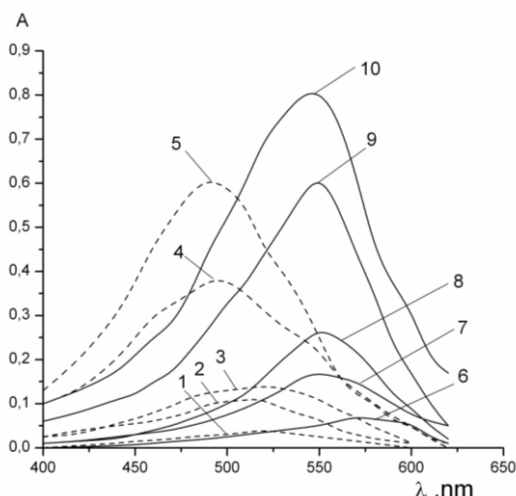


Fig. 5. Absorption spectra of *o*-NPhF (1-5) and system of *o*-NPhF-PHMG (6-10). $C_{o-NPhF} = C_{PHMG} \times 10^6$, mol/L: 0.4 (1, 6); 0.8 (2, 7); 1.2 (3, 8); 3 (4, 9); 5 (5, 10). pH 5.2. $l = 50$ mm

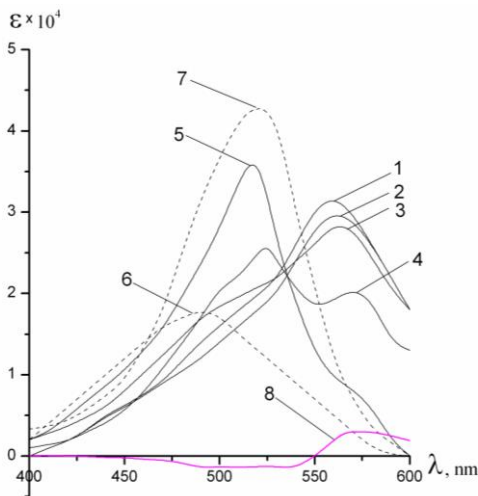


Fig. 6. Absorption spectra of *o*-NPhF-PHMG (1-5), *o*-NPhF (6-7) in aqueous-alcoholic solutions and differential spectrum of *o*-NPhF-PHMG at 96 % vol. ethanol (8). Concentration of ethanol, % vol.: 1.6 – 0.4; 2 – 20.0; 3 – 40.0; 4 – 60.0; 5, 7 – 95.2; 8 – 96.0. pH 5.2; $C_{PHMG} = 1 \times 10^{-6}$ mol/L; $C_{o-NPhF} \times 10^{-5}$ mol/L: 1×10^{-6} (1-7), 1×10^{-5} (8)

Influence of the substituent in xanthene core observes as deprotonation TOF in aqueous-polyelectrolyte medium. For NF with alkyl substituent shift $pK_a^{app(0)}$ in alkaline area was 0.78 pH units at injection of PHMG ($n = 36$). For other TOF with aryl substituents pK_a^{app} is displaced in acidic area on all ionisation steps. Maximum displacement $pK_a^{app(1)}$ was 1.59 for monoanion of PhF and $pK_a^{app(3)}$ was 1.82 for threanion of *o*-NPhF in the presence of PHMG. The results of research can be used in development of PHMG detection techniques using association with trioxyfluorone dyes in aqueous solutions, drugs and alcoholic surrogates.

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ВЛИЯНИЕ ЗАМЕСТИТЕЛЕЙ И ХАРАКТЕРА СРЕДЫ НА АНАЛИТИЧЕСКИЕ СВОЙСТВА АССОЦИАТОВ КСАНТЕНОВЫХ КРАСИТЕЛЕЙ С ПОЛИГЕКСАМЕТИЛЕНГУАНИДИНИЙ ХЛОРИДОМ

Взаимодействие 5 красителей ряда 9-R-2,3,7-тригидрокси-6-флуоронов (ТОФ) с полигексаметиленгуанидиний хлоридом (ПГМГ) в диапазоне концентраций полиэлектролитного эффекта ПГМГ изучено методом оптической спектроскопии. Рассчитаны σ -константы Гаммета и установлены корреляции между строением ТОФ и смещением протолитических равновесий в водно-полиэлектролитных растворах. На основании спектров поглощения изучено влияние pH, концентрации этанола, соотношения компонентов ПГМГ/ТОФ на величину аналитического сигнала и характер взаимодействий катионного полиэлектролита с ТОФ. Результаты сравниваются с результатами, полученными в водных растворах.

Ключевые слова: триоксифлуорон; спектрофотометрия; полигексаметиленгуанидиний хлорид; полиэлектролит; константа ионизации; агрегация.

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ВПЛИВ ЗАМІСНИКІВ ТА ХАРАКТЕРУ СЕРЕДОВИЩА НА АНАЛІТИЧНІ ВЛАСТИВОСТІ АСОЦІАТИВ КСАНТЕНОВИХ БАРВНИКІВ З ПОЛІГЕКСАМЕТИЛЕНГУАНІДИНИЙ ХЛОРИДОМ

Взаємодія 5 барвників ряду 9-R-2,3,7-тригидрокси-6-флуоронів (ТОФ) з катіонним поліелектролітом полігексаметиленгуанидиний хлоридом (ПГМГ) у діапазоні концентрацій поліелектролітного ефекту ПГМГ вивчена методом оптичної спектроскопії. Розраховані σ -константи Гамета та встановлені кореляції між будовою ТОФ і зсувом протолітичних рівноваг у водно-поліелектролітних розчинах. На основі спектрів поглинання було вивчено вплив pH, концентрації етанолу, співвідношення компонентів ПГМГ/ТОФ на величину аналітичного сигналу та характер взаємодій катіонного поліелектроліту з ТОФ. Результати порівнюються з результатами, отриманими у водних розчинах.

Ключові слова: триоксифлуорон; спектрофотометрія; полігексаметиленгуанидиний хлорид; поліелектроліт; константа іонізації; агрегація.

Надійшла до редколегії 16.05.13