THE STATE AND CHEMICAL-ANALYTICAL PROPERTIES OF CERTAIN POLYMETHINE DYES IN AQUEOUS SOLUTIONS

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Abstract

The state of certain indocyanine derivatives symmetric carbocyanines and asymmetric styryls dyes, in aqueous solutions has been studied. The dyes exist as reactive single-charged forms in a wide acidity range. The spectrophotometric characteristics, protonation and hydrolysis constant has been estimated. The charge distribution in the dyes has been evaluated by quantum-chemical calculations. Protonation mechanism is discussed based on the data UV-, VIS- and NMR-^{1}H - spectroscopy. The results suggest the applicability of the dyes as effective analytical reactants.

Introduction

The polymethine dyes group includes organic compounds, which are characterized by the presence of the conjugate bonds chain, consisted of methine groups with the electron-donor and -acceptor radicals of the general formula $[R^1-(CH=)_n-R^2]^+X^-$ (X^- - inorganic counterion; n = 2, 3). Such compounds have a set of original properties and are rather widespread in different fields of science and engineering. However, their application in analytical chemistry is limited, though recently a series of the publications testifying to the efficiency of their application in a photometry of inorganic and organic matters has appeared.[1-3] Such reactants in many cases surpass the basic dye commonly used in analytical practice - triphenylmethanes and rhodamines.[4,5]

To forecast reactivity and expediency of application of new dyes in analytical chemistry it is necessary to know their spectrophotometric and protolytic properties.

The objective of the present paper is to study a state of new derivatives of indocyanine having chains of different length: as symmetric carbocyanines and asymmetric styryls dyes in aqueous solutions.

Materials and methods

Synthesis of dyes was carried out according to the guidelines[6,7] by condensation of the respective aldehydes and quaternary salts in waterless acetyloxide. The styryls dyes were synthesized outgoing with 4-(dimethylamino)-benzaldehyde, carbocyanines - from Fisher aldehydes (or its derivative) and applicable quaternary salt.

The reaction mixture was boiled in a flask under reflux condenser for 1-5 minutes. The flask was cooled, then distilled water was added (for the hydrolysis of the rest of acetyloxide). The obtained dyes were precipitated by diethyl ether; salting out by saturated KCl solution was additionally used. Dye crystals were filtered, washed with diethyl ether, benzene and recrystallized from acetone or methanol.
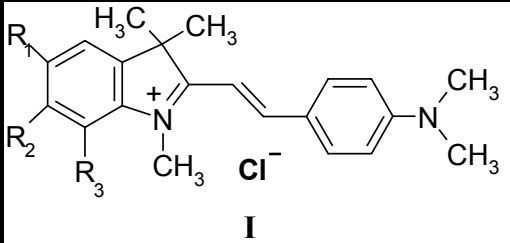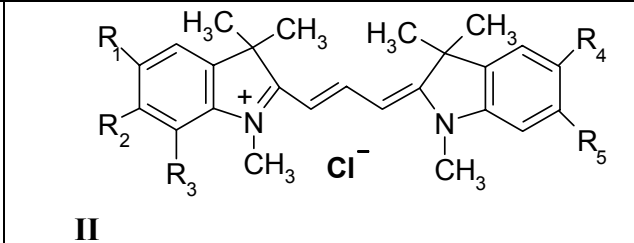
Purity of dyes was estimated by thin-layer chromatography on «Silufol UV-254» plates, using a mixture of butanol-1: acetic acid: water (4:1:5) as a mobile phase.

The dyes identified by the UV-, VIS-, IR- and ^{1}H NMR - spectroscopy. The structural formulas of studied dyes (styryls (I) and carbocyanines (II)), their full chemical names and abbreviated identifications are given in Table 1.

Stock aqueous solutions containing 10^{-3} mol•l^{-1} of dyes prepared by dissolution of their salts in water. The working solutions in smaller concentrations were prepared using the diluting the initial solutions.

The absorption spectra were recorded on SF-2000 and SF-46 spectrophotometers. The pH values of solution were controlled by a pH-121 potentiometer with a glass electrode. ^{1}H NMR spectra were obtained using VARIAN VXR-300 spectrometer with TMS as an internal standard. The quantum-chemical calculations were carried out using semi-empirical method MNDO (AM1 and PM3). Light absorption of dye solutions was studied in a broad acidity interval: from pH=14 to 18 mol•l^{-1} H$_2$SO$_4$. The stability of coloring of solutions of dyes in time and the reversibility of transition of the different forms of dyes preliminarily were studied according to guidelines in Ref.[8]

Table 1: The structural formulas of studied dyes, their full chemical names and abbreviated identifications

I	II

2-(4'-dimethylaminostyryl)-1,3,3-trimethylindolinium chloride, **BBR** (R_1, R_2, R_3: -H); 2-(4'-dimethyl-aminostyryl)-1,3,3-trimethyl-5-nitro-indolinium chloride, **5NIS** (R_1: -NO_2; R_2, R_3: -H); 2-(4'-dimethylamino-styryl)-1,3,3-trimethyl-6-nitro-indolinium chloride, **6NIS** (R_1, R_3: -H; R_2: -NO_2); 2-(4'-dimethylamino-styryl)-1,3,3-trimethyl-5,7-dibromo-indolinium chloride, **BIS** (R_1, R_3: -Br; R_2: -H); 2-(4'-dimethyl-aminostyryl)-1,3,3-trimethyl-5-thiocyanato-indolinium chloride, **TIS** (R_1: -SCN; R_2, R_3: -H); 2-(4'-dimethylamino-styryl)-1,3,3-trimethyl-5-phenyl-idolinium chloride, **PIS** (R_1: -C_6H_5; R_2, R_3: -H)	1,1',3,3,3',3'-hexamethyldiindocarbocyanine chloride, **DIC** (R_1, R_2, R_3, R_4, R_5: -H); 1,1',3,3,3',3'-hexamethyl-6-nitro-diindocarbo-cyanine chloride, **6NIC** (R_1, R_3, R_4, R_5: -H: R_2: -NO_2); 1,1',3,3,3',3'-hexamethyl-5-nitro-di-indo-carbocyanine chloride, **5NIC** (R_1: -NO_2; R_2, R_3, R_4, R_5: -H); 1,1',3,3,3',3'-hexamethyl-5,7-dibrom-diindocarbocyanine chloride, **BIC** (R_1, R_3: -Br; R_2, R_4, R_5: -H); 1,1',3,3,3',3'-hexa-methyl-5-phenyl-diindocarbocyanine chloride, **PIC** (R_1: -C_6H_5; R_2, R_3, R_4, R_5: -H); 1,1',3,3,3',3'-hexamethyl-5,7-dibrom-6'-nitro-diindocarbocyanine chloride, **6NBIC** (R_1, R_3: -Br; R_2, R_4: -H; R_5: -NO_2); 1,1',3,3,3',3'-hexa-methyl-5,7-dibrom-5'-nitro-diindocarbo-cyanine chloride, **5NBIC** (R_1, R_3: -Br; R_2, R_5: -H; R_4: -NO_2); 1,1',3,3,3',3'-hexamethyl-5,7-dibrom-5'-phenyl-diindocarbocyanine chloride, **PBIC** (R_1, R_3: -Br; R_2, R_5: -H; R_4: -NO_2); 1,1',3,3,3',3'-hexamethyl-6,6'-dinitro-diindocarbocyanine chloride, **6NICS** (R_1, R_3, R_4: -H; R_2, R_5: -NO_2); 1,1',3,3,3',3'-hexamethyl-5,5'-dinitro-diindo-carbocyanine chloride, **5NICS** (R_1, R_4: -NO_2; R_2, R_3, R_5: -H); 1,1',3,3,3',3'-hexamethyl-5,5'-dithiocyanato-diindocarbocyanine chloride, **TICS** (R_1, R_4: -SCN; R_2, R_3, R_5: -H).

Results and discussion

The investigation of the state of the obtained dyes in aqueous solutions shows what they have intensive coloring with a maximum of absorption at 535-565 nm in neutral and low acidity media. The coloring of the dyes fades in high acidity or alkalinity of media. Such transformations are caused by protolysis processes that can be expressed as:

$$
\begin{array}{cc}
\textbf{H}_2\textbf{O} & \textbf{H}_2\textbf{O} \\[2pt]
\textbf{RH}^{2+} \Leftrightarrow \textbf{R}^+ \Leftrightarrow \textbf{ROH} \\[2pt]
\textbf{H}_3\textbf{O}^+ & \textbf{H}_3\textbf{O}^+
\end{array}
\tag{1}
$$

Applicable protolysis constants equal:

$$
K_1 = \frac{\left[R^+\right]\cdot\left[H_3O^+\right]}{\left[RH^{+2}\right]}
\tag{2}
$$

$$
K_2 = \frac{\left[ROH\right]\cdot\left[H_3O^+\right]}{\left[R^+\right]}
\tag{3}
$$

Protolysis constants were determined by spectrophotometry method. Samples with different serial acidity of medium were prepared. The Figure 1 shows what light absorption of PIS solutions depends on the media acidity. Three maximums correspond to the different forms of a dye - ionic (R^+, HR^{2+}) and hydrolyzed (ROH). The R^+ form dominates in an interval pH from 3 up to 10 and gives rise to the absorption maximum at 548 nm. Wile increasing the acidity, the single-charged R^+ is protolysed.
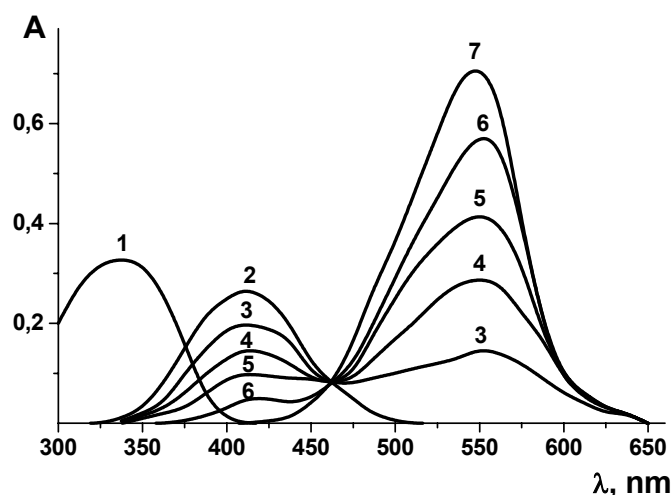

Figure 1: The absorption spectrum of $1\cdot10^{-5}$ mol•l^{-1} solution of PIS vs. on an acidity of media: 1 - pH 12.0; 2 - pH 0.5; 3 - pH 1.4; 4 - pH 1.8; 5 - pH 2.2; 6 - pH 2.6; 7 – pH 3.0 - 10.0.

This process is accompanied by the shift of the absorption maximum to 410 nm. In alkaline media at pH > 10, the (Scheme 1) equilibrium is shifted to the hydrolyzed form,

which is characterized by low-intensity absorption. The absorption maximum of the hydrolyzed form is shifted to a short-wave range (λ_{max} = 330 nm). The isobestic point at 463 nm indicates that in pH interval from 0.5 to 3.0 PIS exists in two equilibrium forms. The spectrophotometric characteristics of the different forms of dyes and their protolysis constants are listed in Table 2. The absence of other forms of dyes in dilute aqueous solutions and validity of the selected protolysis mechanism are also confirmed the following considerations. On pH = f(lg(A/(A_{max}-A))) graphs the quantity of connected protons can be evaluated from the slope of the straight lines (n = tg α). For dyes, that protolysed in high-acidity media (carbocyanines), Hammet acidity function H_0 was used instead of pH. As shown in Figure 2, the tangent of slope angle for all carbocyanines dyes is close to 1. The similar data were obtained for styryls, indicating the similar mechanism of protolytic transformations of the studied polymethine dyes in solutions.

Table 2: The spectrophotometric and protolytic characteristics of the polymethine dyes

| Dye	$\lambda_{max.}$			$\varepsilon \cdot 10^{-4}$			pK_1	pK_2
	R^+	HR^{2+}	ROH	R^+	HR^{2+}	ROH		
BBR	537	382	290	6.6	2.6	1.9	1.43	12.20
6NIS	556	371	-	10.0	3.3	-	0.70	11.85
5NIS	580	380	-	9.9	3.4	-	0.31	11.80
BIS	550	375	350	8.3	2.4	4.0	1.75	11.10
PIS	548	410	330	7.1	2.5	3.2	1.75	10.10
TIS	568	375	349	7.7	2.3	2.8	1.10	11.70
DIC	538	325	345	14.3	3.2	2.9	-1.81	13.60
6NIC	536	-	-	15.6	-	-	-3.46	11.80
5NIC	560	-	-	10.0	-	-	-3.48	11.80
BIC	544	323	343	14.7	2.7	-	-2.63	12.95
PIC	549	350	348	9.2	2.0	2.5	-2.49	12.80
TIC	551	338	325	15.1	2.3	1.4	-2.74	11.60
6NBIC	541	320	-	12.6	2.6	-	-3.42	11.45
5NBIC	563	333	-	9.7	2.4	-	-3.95	12.05
PBIC	557	338	340	12.2	2.1	2.7	-2.86	12.40
6NICS	533	336	340	17.4	3.1	3.1	-4.46	12.00
5NICS	575	320	-	15.6	-	-	-4.90	11.25
TICS	550	333	-	15.5	-	-	-3.49	11.30
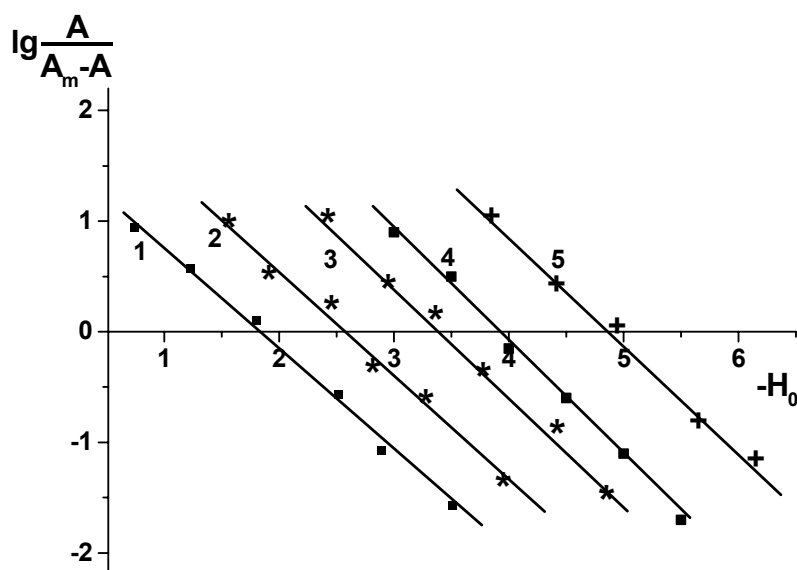
Figure 2: Determination of number of protons taking part in protonation of the polymethine dyes: 1 - DIC; 2 - BIC; 3 – 5NIC; 4 – 5NBIC; 5 –5NICS.

Table 3: A local charge distribution on chains $N - N$ in molecules of polymethine dyes

Dye	For styryl:								
	N_1	C_1	C_2	C_3	C_4	C_5	C_6	C_7	N_2
BBR	0.380	0.024	-0.318	0.165	-0.229	0.028	-0.205	0.062	0.091
5NIS	0.304	0.044	-0.330	0.183	-0.248	0.051	-0.222	0.077	0.141
6NIS	0.340	0.034	-0.328	0.178	-0.242	0.043	-0.214	0.072	0.122
BIS	0.381	0.026	-0.324	0.172	-0.233	0.033	-0.208	0.066	0.098
TIS	0.362	0.029	-0.322	0.172	-0.235	0.036	-0.210	0.068	0.102
PIS	0.396	0.017	-0.314	0.160	-0.226	0.024	-0.202	0.058	0.085
	For carbocyanines:							
	N_1	C_1	C_2	C_3	C_4	C_5	N_2
DIC	0.305	0.024	-0.324	0.127	-0.324	0.024	0.305
BIC	0.299	0.021	-0.320	0.126	-0.319	0.023	0.324
5NIC	0.245	0.028	-0.312	0.123	-0.309	0.019	0.355
TIC	0.284	0.024	-0.321	0.127	-0.324	0.023	0.326
PIC	0.322	0.019	-0.323	0.125	-0.325	0.024	0.296
PBIC	0.294	0.022	-0.325	0.125	-0.318	0.017	0.338
5NBIC	0.350	0.020	-0.311	0.128	-0.313	0.030	0.259
5NICS	0.288	0.034	-0.312	0.134	-0.312	0.034	0.288
6NBIC	0.405	-0.072	-0.216	0.025	-0.222	-0.064	0.317

According to the protolysis affinity of hetarylderivatives styryls dyes can be arranged in a series 5NIS < 6NIS < TIS < BBR < BIS < PIS (Table 2). The introduction of the electron-acceptor radicals (-NO$_2$, -SCN) in indolinyum nucleus as a results in the decreasing basicity of dyes, and their greater stability to proton attack. At the same time, an introduction of such electron-donor radicals, as the phenyl group, results in the increasing of basicity of PIS dye as opposed to basic styryl - BBR.

The carbocyanines dyes are not easily protolysed (pK$_1$ = -1.8 ÷ -4.9). The protolysis rate decreases from DIC to NO$_2$- derivation 5NICS and 6NICS. The difference in hydrolysis capability in dyes feebly marked. Both styryls and carbocyanines are hydrolyzed at rather high pH values of solution (see Table 2). The explanation of essential differences in protolytic properties of two groups of dyes of the same class requires more in-depth research of the mechanism of protolytic transformations. It is known that the charge of polymethine dyes is distributed nonuniformly, being localized on nuclear of end-groups or in polymethine chain.[9] The carbocyanines have much greater symmetry of molecules comparing with the styryls. Therefore, the bonds of

Table 4: ^{1}H NMR spectra of BBR and PIS dyes

Dye	Solvent	The signals of the protons, δ (ppm)
BBR	DMSO-D6	1.75 s (6H, 2CH$_3$); 3.17 s (6H, 2CH$_3$); 3.98 s (3H, NCH$_3$); 6.89, 8.09 2d (4H, C$_6$H$_4$NMe$_2$, 9.0); 7.28 d (1H, CH=, 16.2); 7.45 – 7.58 m (2H, C$_6$H$_4$); 7.71, 7.78 2d (2H, C$_6$H$_4$, 7.2); 8.31 d (1H, CH=, 15.9)
	CF$_3$COOD	1.92 s (6H, 2CH$_3$); 3.54 s (6H, 2CH$_3$); 4.29 s (3H, NCH$_3$); 7.64 – 7.82 m (5H, CH=, C$_6$H$_4$); 7.93, 8.18 2m (4H, C$_6$H$_4$NMe$_2$, 9.0); 8.37 d (1H, CH=, 18.0)
PIS	DMSO-D6	1.82 s (6H, 2CH$_3$); 3.17 s (6H, N(CH$_3$)$_2$); 4.00 s (3H, NCH$_3$); 6.89, 8.09 2d (4H, C$_6$H$_4$NMe$_2$, 13.5); 7.28 d (1H, CH=, 23.4); 7.46 s (1H, C$_6$H$_3$); 7.42 – 7.56, 7.75 – 7.89 2m (1H, C$_6$H$_3$; 5H, C$_6$H$_5$); 8.13 m (1H, C$_6$H$_3$); 8.34 m (1H, CH=, 23.4).
	CF$_3$COOD	1.98 s (6H, 2CH$_3$); 3.56 s (6H, N(CH$_3$)$_2$); 4.32 s (3H, NCH$_3$); 7.62 – 7.99 m (8H, C$_6$H$_5$, C$_6$H$_3$; 2H, C$_6$H$_4$NMe$_2$; 1H, CH=); 8.20 d (2H, C$_6$H$_4$NMe$_2$, 13.2); 8.39 d (1H, CH=, 24.9)

polymethine chain are adjusted and are close to semipolar in carbocyanines. For non-symmetrical dyes the alternation of bonds should have are expected, one half of the

bonds close to single, the other half - to double. For such dyes, the positive charges to electron-donating nuclear are shifted.[9,10]

Quantum-chemical calculations suggest (Table 3) that the maximum positives charge in both groups of dyes is accumulated at the 2-C atom of indolynyum group (0.126 – 0.194).
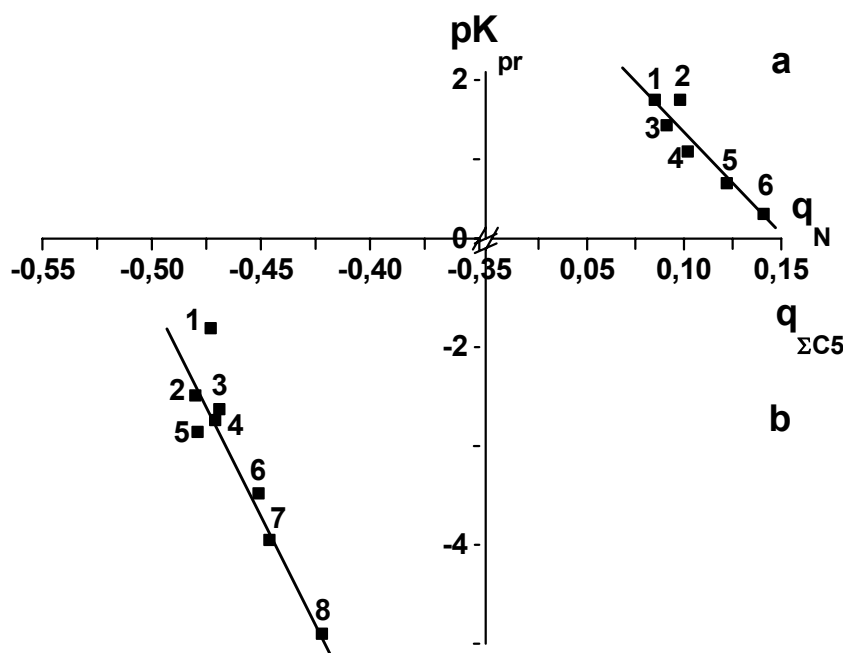

Figure 3: Dependence of protonation constants of polymethine dyes on the value of a charge: a) - on atom of Nitrogen of aminogroup (styryls): 1 - PIS; 2 – BIS; 3 - BBR; 4 - TIS; 5 – 6NIS; 6 - 5NIS; b) - general charge on atoms of Carbon of polymethine chain (carbocyanines): 1 - DIC; 2 - PIC; 3 - BIC; 4 - TIC; 5 - PBIC; 6 – 5NIC; 7 - 5NBIC; 8 – 5NICS.

Therefore, it is possible to expect that exactly this atom take part in hydrolysis (affixture of hydroxyl). The largest negative charge is accumulated on the Nitrogen atom of the aminogroup of styryls: - (0.226-0.246) and on the α-C atom of polymethine chain: -(0.222-0.324). These facts suggest a probable distinction in the protonation mechanism: styryls predominantly attack a positive proton on the nitrogen atom of aminogroup, carbocyanines – to the α-C atom of polymethine chain. The ^{1}H NMR-spectra of dyes in dimethylsulfoxide-d_6 and deuterotrifluoroacetic acid confirm these assumptions (Table 4). In dimethylsulfoxide-d_6 the BBR and PIS dyes are single-charged, in deuterotrifluoroacetic they are protonated. This is confirmed by difference in the

^{1}H NMR spectra (strong displacement of signals of CH_3 - group protons in the 3 position of indolynyum group, the differentiation of cleavages of protons in the α-position to atom nitrogen of aminogroup disappears, and is exhibited as a multiple) and the protolytic properties. The relation between the charge on reactive center of the dyes and the respective protolysis pK (Figure 3) also confirm the difference in protolysis mechanism.

According to the obtained data, the protolytic equilibrium of polymethine dyes in aqueous solution, can be presented in the following scheme:

For styryls dyes (Scheme 5):

(5)
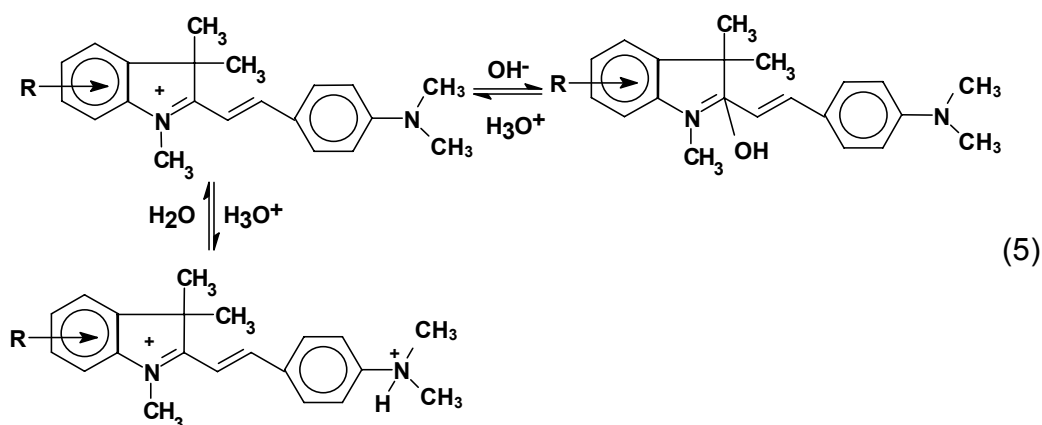
For carbocyanines dyes (Scheme 6):

(6)
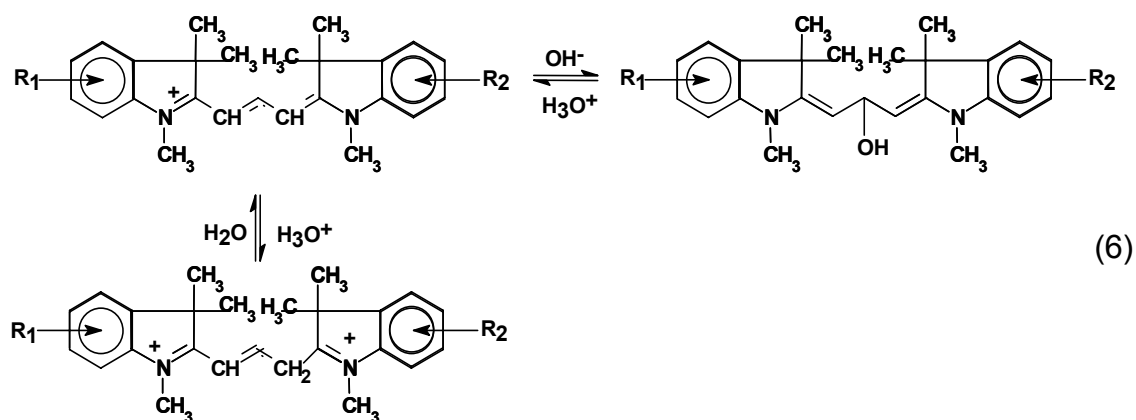
The absorption spectra of aqueous solutions of dyes at different concentration (10^{-4} - 10^{-6} mol·l^{-1}) identical, which indicates on the absence of significant changes in their form and intensity (at fixed value of product of dye concentration and thickness of an absorbing layer c·l). The spectra obtained after several days are identical to those of the

monomer forms in dilute solutions. Unlike dyes of other classes (triphenylmethanes, rhodamines), the processes of aggregation (dimerization etc.) are not typical for polymethine.[11] It allows to obtain of ion-pairs in media with a high saline background, and to use higher concentration of the solutions of dyes. Inasmuch as the single-charged form of dyes high-intensity coloring and its high stability to protolytic transformations ($\Delta pK = 8 \div 15$), it is possible to suggest the perspective of the application of the studied dyes as reactants for the spectrophotometric analysis.

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Povzetek

Štuidirali smo obnašanje nekaterih barvil v vodnih raztopinah. S spektrofotometričnimi metodami smo določili konstante protonacije in hidrolize. S kvantnomehanskimi izračuni smo ocenili porazdelitev naboja in na osnovi UV/Vis ter NMR spektroskopskih podatkov predlagamo mehanizem protonacije.