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Tristimulus Colorimetric and Spectrophotometric Study of the State of 4-Hydroxystyryl Dyes in Aqueous Solutions

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Abstract—Acid-base properties of 4-hydroxystyryl dyes in aqueous solution have been studied by means of chemical tristimulus colorimetry and spectrophotometry. Ionization and hydroxylation constants of the dyes have been determined using chromaticity functions of specific and CIE color difference. It has been shown that aggregation processes in the solution of 4-hydroxystyryl dyes can be observed by means of tristimulus colorimetry. A scheme of acid-base transformations of the studied dyes in the solution has been suggested, and selected spectrophotometric parameters of the equilibrium ionic and molecular forms have been determined.

Keywords: 4-hydroxystyryl dye, chemical tristimulus colorimetry, spectrophotometry, ionization constant, hydroxylation constant

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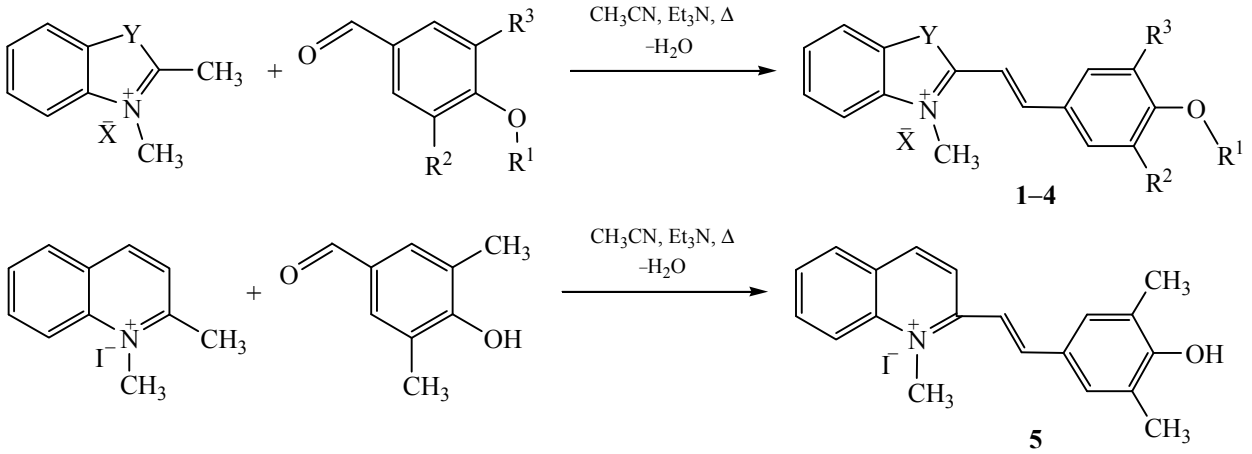
Merocyanine dyes have attracted much attention due to the unique properties, primarily the color changes upon various chemical transformations: protolytic, solvation, aggregation, and others. High molar absorptivity values and (in certain cases) strong fluorescence allow visual observation of such transformations with nanomoles of the dyes in the sample. Merocyanine dyes have been applied in the development of novel optoelectronic materials as well as fluorescent probes in biological and medical studies [1, 2].

The hydroxystyryl derivatives of nitrogen-containing heterocycles are among the most peculiar merocyanine dyes. In particular, the Brooker merocyanine has been investigated in view of the unique solvatochromic properties [3], whereas certain 2-hydroxystyryl and 2-hydroxyarylazomethine dyes are interesting due to the reversible formation of colorless *spiro* forms [4]. Recently, 4-hydroxystyryl dyes have become popular objects, since they are capable of generation of THz range [5] and exhibit nonlinear optical [6], sensor [7–11], and perichromic [12, 13] properties. For instance, ethyl(hydroxyethyl)cellulose modified with the Brooker merocyanine has been used as highly selective chromogenic and fluorogenic chemosensor for determination of cyanides in water at concentration of 1.0×10^{-7} to 1.9×10^{-5} mol/L [14]. Biosensors and biomarkers for certain target compounds in living cells have been developed on the basis of hydroxystyryl dyes [15]. However, practical application of such dyes in chemical analysis has been limited due to controversial and sometimes lacking data on their synthesis methods and the state in the solution over wide range of pH [16, 17].

Ionization constants (pK) are routinely determined by means of spectrophotometry, potentiometry, and tristimulus conductometry. Tristimulus colorimetry [18–21] has been recognized as a promising method of investigation of acid-base equilibriums. This method is based on calculation of color coordinates of equilibrium pH-dependent forms from the absorption spectra, thus distinguishing spectrally similar forms of compounds. It is advantageous over the conventional physico-chemical methods of investigation of protolytic equilibriums in a solution. For example, pK values of six functional groups of quercetin and morin have been determined by tristimulus colorimetry [20, 22]; that has been impossible using spectrophotometry and potentiometry methods.

Scheme 1.



$R^1 = R^2 = R^3 = H$, X = Br, Y = $CH(CH_3)_2$ (**1**); $R^1 = R^3 = H$, $R^2 = CH_3$, X = Br, Y = $CH(CH_3)_2$ (**2**); $R^1 = R^3 = H$, $R^2 = CH_3$, X = I, Y = S (**3**); R^1, $R^2 = OCH_2CH_2O$, $R^3 = H$, X = Br, Y = $CH(CH_3)_2$ (**4**).

In view of the above, this study aimed to investigate the state of a series of 4-hydroxystyryl dyes (derivatives of indole, quinoline, and benzothiazole) in aqueous solutions over wide pH range by means of chemical tristimulus colorimetry and spectrophotometry and to determine the corresponding constants of ionization and hydroxylation.

The studies 4-hydroxystyryl dyes were synthesized according to Scheme 1. In moderately acidic medium, compounds **1–3** and **5** existed in the RH^+ form, and compound **4** existed in the R^+ form.

Optical absorbance spectra of dyes **1–5** were recorded over wide range of the medium acidity; the spectra of the most structurally different dyes are shown in Figs. 1 and 2. The spectra (350–650 nm) of compound **4** with no functional groups capable of proteolysis contained a single absorption band at around 440 nm. Its weakening with the increase in pH (Fig. 1a) was probably due to hydroxylation.

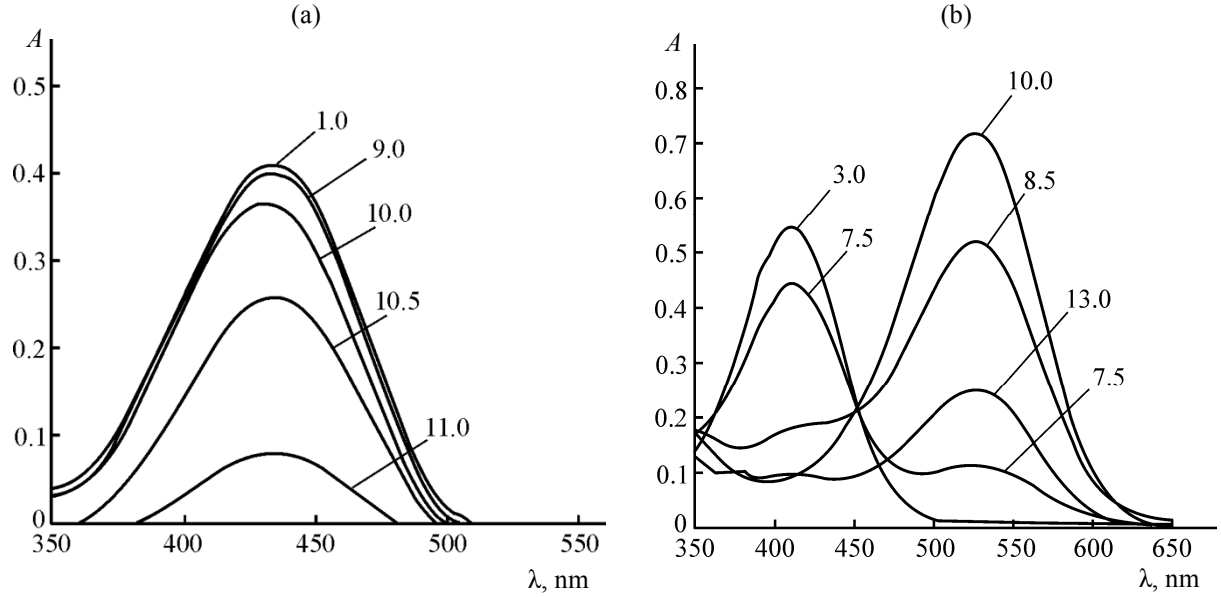


Fig. 1. Absorbance spectra of $2 \cdot 10^{-5}$ mol/L aqueous solutions of 4-hydroxystyryl dyes **4** (a) and **5** (b) (numbers at curves show the pH value).

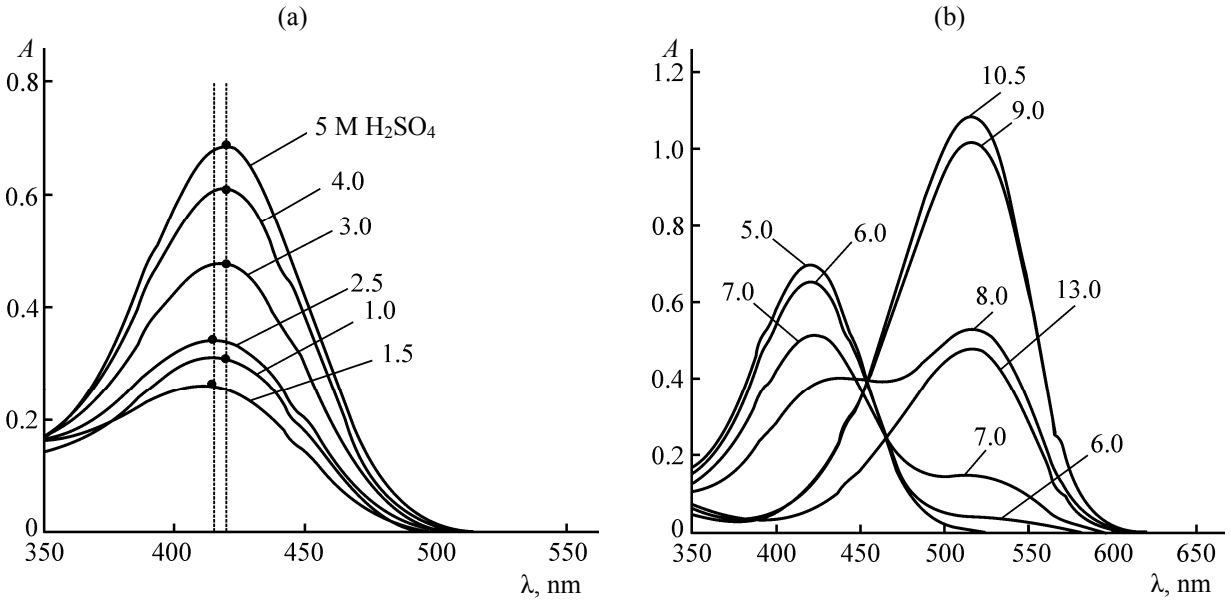


Fig. 2. Absorbance spectra of 2×10^{-5} mol/L aqueous solutions of compound **3** at the acidity range of 5 mol/L H_2SO_4–pH 4 (a) and pH 5.0–12.0 (b) (the numbers at curves show the pH value).

The spectra of structurally similar compounds **1**, **2**, and **5** were marginally different; those of compound **5** are given in Fig. 1b for the purpose of discussion. The increase in the medium pH led to the steady transformation of the cationic form of the dye (with the absorption maximum around 420 nm) into the merocyanine one (about 540 nm); the transition was marked by a bathochromic shift of the absorption band and the presence of an isosbestic point. In strongly alkaline medium (pH > 11), the absorption band of the merocyanine form was somewhat weakened (Fig. 1b), similarly to compound **4**.

Absorption spectra of compound **3** (Fig. 2) deserve special attention. The shape of the spectra evidenced the presence of several equilibrium forms of dye **3** in the probed pH range. In strongly acidic medium (5 mol/L H_2SO_4), the sulfur atom of the benzothiazole fragment was protonated to form the doubly charged RH_2^{2+} form with the absorption maximum at about 419 nm (Fig. 2a). The change in the medium acidity to pH 1 resulted in the weakening of the band at 419 nm. Further increase in pH led to slight (4 nm) hypsochromic shift of the band, to 415 nm. It should be noted that the spectra of compound **3** contained shoulders at 385–390 and 440–450 nm, most prominent at pH 2–4 (Fig. 2a). In weakly acidic medium (pH 4–6), the absorption band was shifted to 420 nm due to the formation of the RH^+ form with spectrophotometric parameters very close to those of the RH_2^{2+} form (Fig. 2). In alkaline medium (Fig. 2b), the band assigned to the singly charged RH^+ form at about 420 nm was weakened, and the absorbance at 535 nm became stronger. The presence of the isosbestic point at 455 nm evidenced the equilibrium between the cationic RH^+ (420 nm) and merocyanine R^0 (535 nm) forms of the dye. At pH > 11, the absorption band at 535 nm was weakened (Fig. 2b), likely due to the dye hydroxylation and the increase in the fraction of the ROH form.

The obtained dataset of absorption spectra of dyes **1**–**5** was processed by tristimulus colorimetry methods. The values of chromaticity functions were plotted as functions of the medium pH. They are exemplified by the data for compounds **3**–**5** in Fig. 3. The presence of several maximums in the plots revealed the existence of several equilibrium acid-base forms of the dyes, the pH values of the maximums corresponding to the pK values of the respective acid-base equilibriums of the functional groups (Table 1). In the case of dye **4**, containing no functional groups capable of dissociation, a single maximum at pH about 10.5 (Fig. 3, curve *1*) was assigned to its hydroxylation (pK_h). Introduction of the functional groups involved in the protolytic transformations (dyes **1**–**3**, **5**) resulted in the appearance of new maximums in the tristimulus colorimetric curves. For example, the SCD = f(pH) and ΔE_{76} = f(pH) plots for compound **5** (Fig. 3, curve *2*) contained two maximums. The first one (pH about 8)

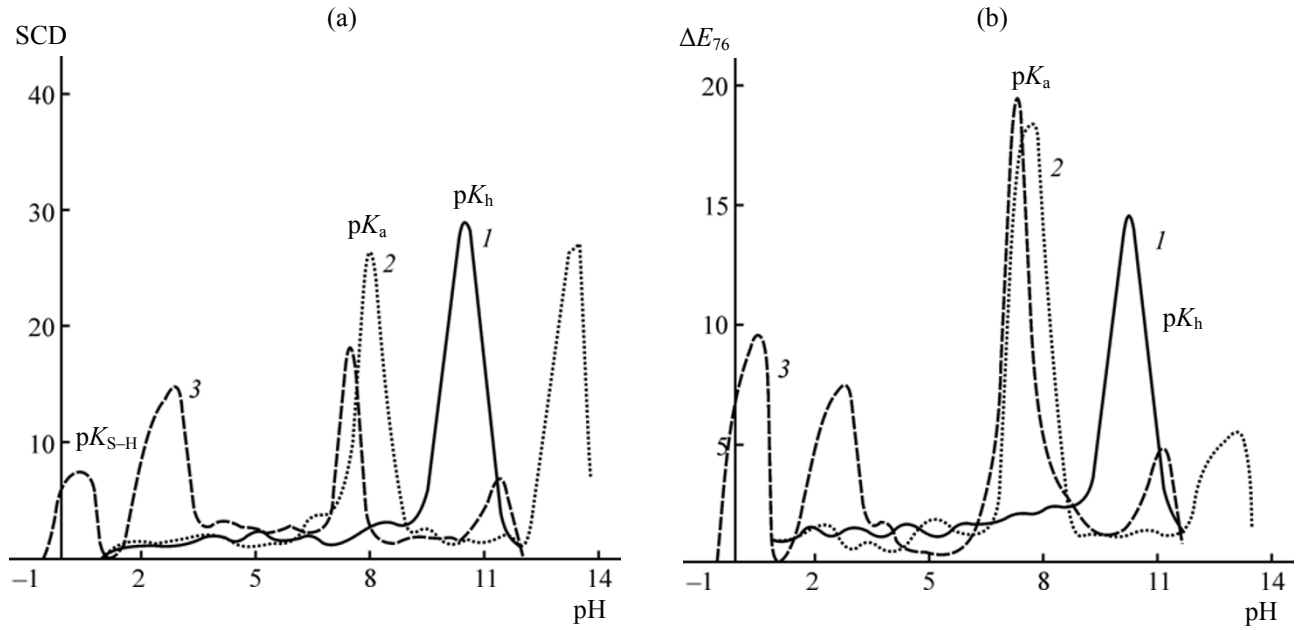


Fig. 3. Chromaticity functions of the solutions of 4-hydroxystyryl dyes **4** (*1*), **2** (*2*), and **3** (*3*) as functions of pH. (a) Specific color difference SCD and (b) CIE color difference ΔE_{76}.

was assigned to dissociation of the phenolic hydroxyl (pK_a), whereas the second one (pH about 13) corresponded to the dye hydroxylation. The respective plots for dyes **1** and **2** were similar. Other processes occurring in the studied systems (such as specific aggregation, protonation of heteroatoms, etc.) could result in the more complex shape of the curves. For instance, four maximums were observed in the plots for compound **3** in the probed pH range (Fig. 3, curve *3*). The maximum at pH 0.5–1.0 was due to protonation of the sulfur atom to afford the RH_2^{2+} form, and the maximum at pH 2.5–3.0 was likely due to the specific aggregation, typical of certain merocyanine dyes [23, 24]. That was confirmed by hypsochromic shift of the absorption band from 420 nm to 415 nm and the appearance of a shoulder at 440–450 nm in the spectra of compound **3** (Fig. 2a), typical of the H-aggregation of the polymethine dyes [23, 24]. From the pK_{S-H} and pK_a values for dye **3** it was concluded that the RH^+ form containing a deprotonated sulfur atom and a hydroxyl group (thus favoring the aggregation) was the predominant form at pH 2–4 (90–99%). The maximums at pH 7.5–8.0 and 12.0 (Fig. 3, curve *3*) were assigned to dissociation of the phenolic hydroxyl and to the dye hydroxylation, respectively.

To verify the values of pK_a and pK_h determined by tristimulus colorimetry, the absorbance spectra were

Table 1. Ionization constants (pK_a and pK_{S-H}) and hydroxylation constants (pK_h) of the 4-hydroxystyryl dyes in aqueous solutions (n = 3, P 0.95)[a]

Dye	pK_{S-H}	pK_a	pK_a[b]	pK_h	pK_h[b]	ΔpH[c]
1	–	7.2±0.2	7.2±0.1	12.8±0.1	13.1±0.2	5.8
2	–	6.9±0.1	6.9±0.2	13.0±0.1	13.2±0.1	6.2
3	0.8±0.1	7.5±0.2	7.8±0.1	11.9±0.2	12.1±0.1	4.3
4	–	–	–	10.5±0.2	10.4±0.1	–
5	–	8.1±0.2	8.3±0.1	13.5±0.2	13.5±0.2	5.3

[a] n, Data set volume; P, probability. [b] Determined by spectrophotometry. [c] ΔpH, The width of pH range of the merocyanine form predominance.

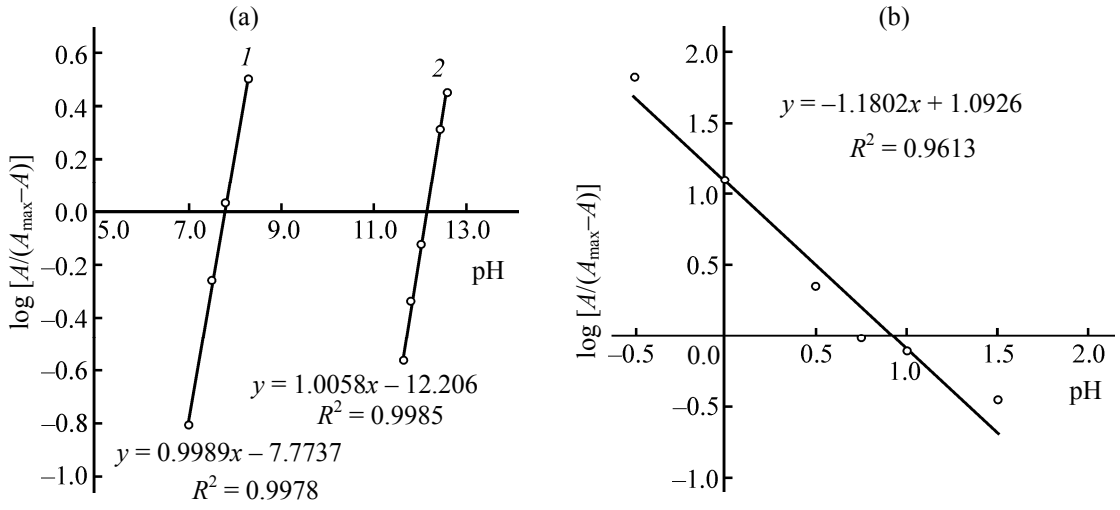


Fig. 4. Graphical determination of the pK_a and pK_h (a) and p$K_{S–H}$ (b) values.

further processed using the equilibrium shift method (the results for dye **3** are given in Fig. 4). The slope of curve *1* was close to unity, evidencing the release of a single proton per the dye molecule during deprotonation of compound **3**. The determined pK_a values were close to those determined by means of tristimulus colorimetry (Table 1). Hydroxylation of dye **3**, similarly to other hydroxystyryl dyes, involved the addition of a single OH group per the dye molecule (Fig. 4a, curve *2*); the corresponding pK_h values are collected in Table 1. The similarly determined protonation constant of the sulfur atom in compound **3** (Fig. 4b) equaled p$K_{S–H}$ 0.9±0.1 ($\varepsilon_{419} = 3.4\times10^4$ L mol^{-1} cm^{-1}).

The data in Table 1 revealed the good coincidence of the tristimulus colorimetry and spectrophotometry results. Moreover, the correlation between the pK_a values determined independently confirmed excellent inter-laboratory reproducibility of the method. The pK_a values (Table 1) were in good agreement with the data for other hydroxystyryl dyes obtained earlier by means of spectrophotometry [25, 26], increasing with the increase in the basicity of the heterocyclic fragment.

The obtained absorbance spectral data allowed calculation of molar absorptivities of equilibrium acid-base forms of compounds **1–5** (Table 2). It is to be seen that the studied compounds exhibited high values of molar absorptivity and wide pH range of the merocyanine form predominance (Table 1), opening the possibilities of their application as spectrophotometry reagents.

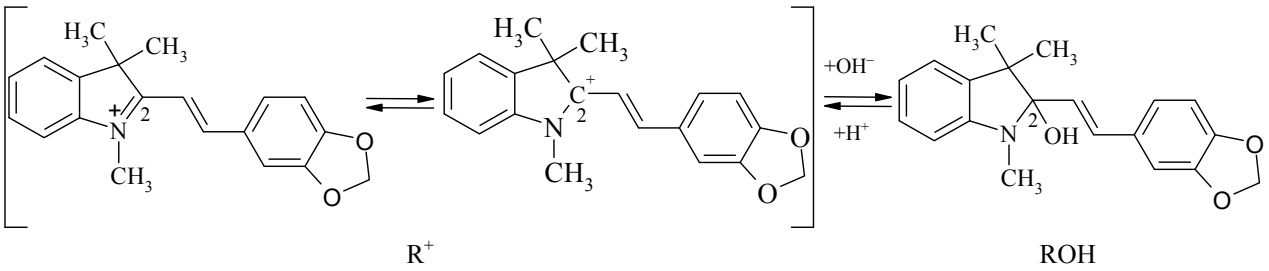
According to the obtained data, the behavior of the studied dyes over the probed pH range could be described as follows. Dye **4** was hydroxylated in alkaline pH range. The semi-empirical CNDO quantum-chemical simulation (HyperChem Pro 6 software) showed that the highest positive charge was localized at the C^2 atom of the heterocyclic fragment, and the formation of the ROH form could be expressed by Scheme 2.

It should be noted that the electrostatic interaction between the hydroxyl group and the positively charged nitrogen atom in compound **4** was unlikely, since the formation of such ionic associate would result in the solution discoloration.

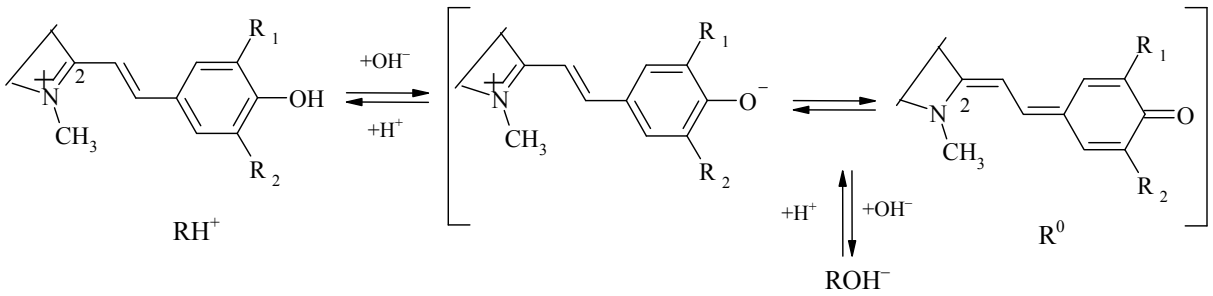
Table 2. Spectrophotometry parameters of the 4-hydroxystyryl dyes

Dye	λ_{max}, nm			$\varepsilon_\lambda\times10^{-4}$, L mol^{-1} cm^{-1}		
	RH^+	R^0	ROH	RH^+	R^0	ROH
1	416	516	290	3.6	6.7	2.3
2	428	540	340	3.2	6.9	1.0
3	420	515	360	3.5	5.4	2.4
4	–	430	270	–	2.1	1.7
5	410	526	345	3.1	3.6	2.7

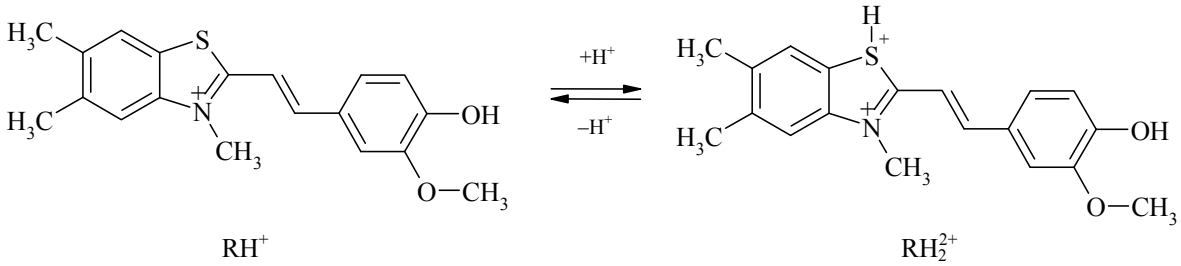
Scheme 2.



Scheme 3.



Scheme 4.



Likewise, the acid-base equilibriums in the solution of dyes **1**, **2**, and **5** could be as shown in Scheme 3.

As follows from the scheme, the dyes existed in the singly charged cationic RH^+ form in acidic medium. The increase in pH resulted in dissociation of the oH group in position 4, leading to the formation of the neutral form; the equilibrium was shifted towards the merocyanine form R^0. In alkaline medium (pH = 10–14), the solutions color became weaker due to the dyes hydroxylation, disruption of the conjugation path, and formation of the ROH^- form.

The scheme of acid-base equilibriums in a solution of dye **3** was in general similar, differing in the possibility of protonation of sulfur atom of the benzothiazole fragment to yield the RH_2^{2+} form in strongly acidic medium (Scheme 4).

In summary, we investigated the acid-base properties of a series of novel 4-hydroxystyryl dyes over wide range of the medium acidity. Dye **4** contained no functional groups capable of protolysis and was thus involved exclusively in the hydroxylation equilibrium. Dyes **1**, **2**, and **5** were involved in the dissociation of the phenolic hydroxyls on top of the hydroxylation, and compound **3** additionally revealed the protonation equilibrium of sulfur atom of the benzothiazole fragment. The corresponding ionization and hydroxylation constants were determined by means of tristimulus colorimetry and spectrophotometry; major spectrophotometric parameters of the equilibrium ionic and molecular forms were obtained. Analysis of the obtained experimental data and the results of quantum-chemical simulation suggested the possible scheme of acid-base equilibriums in the solutions of the studied

dyes. In the case of dye **3**, aggregation processes were observed by means of tristimulus colorimetry, along with the acid-base equilibriums. Overall, the use of CIE color difference functions as the analytical signals gave the complete set of information on the occurring equilibriums over a wide range of medium acidity.

EXPERIMENTAL

The following commercially available chemicals (Aldrich, Sinbias Ukraine) with the content of the major compound of at least 95% were used: the Fischer bases as bromides 2-methylquinolinium and 2,5,6-trimethylbenzothiazolium quaternized with excess of iodomethane in acetonitrile into 1,2-dimethylquinolinium and 2,3,5,6-tetramethylbenzothiazolium iodide, respectively [27]; 4-hydroxybenzaldehyde, 4-hydroxy-3,5-dimethylbenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, and 1,3-benzodioxol-5-carbal-dehyde were used as received.

Electronic absorption spectra were recorded using Specord S 600 (Analytik Jena AG, Germany) and SF-56 (LOMO-Spektr) spectrophotometers in 1 cm quartz cells at 190–780 nm. The medium acidity was monitored using a glass electrode with a Thermo Orion 720A ionomer (Thermo Scientific, USA) calibrated with standard buffer solutions. ^{1}H NMR spectra were recorded using Varian Gemini 300 NMR and Bruker-500 spectrometers in DMSO-d_6. The dyes purity was determined via TLC on Sorbfil plates (Russia) using an ethanol–dioxane–toluene–acetic acid (2 : 1 : 1 : 0.2) as eluent.

The dyes were synthesized from 0.5–2.0 mmol of the corresponding salts of the heterocyclic bases and a stoichiometric amount of the benzaldehyde in the presence of 0.02–0.05 mL of triethylamine in 2–5 mL of boiling acetonitrile (3–30 min). After the reaction mixture cooling, the crystalline precipitate was filtered off, washed with diethyl ether, and dried. If the product did not precipitate, excess of the solvent was distilled off; the residue was washed with diethyl ether and recrystallized from methanol.

2-[2-(4-Hydroxystyryl)]-1,3,3-trimethyl-3*H*-indolium bromide (1). ^{1}H NMR spectrum, δ, ppm: 1.80 s (6H, CH_3), 4.13 s (3H, CH_3), 7.00 d (2H$_{arom}$, J = 7.1 Hz), 7.50 d (1H, HC=CH, J = 16.2 Hz), 7.56–7.65 m (2H$_{arom}$), 7.85–7.88 m (2H$_{arom}$), 8.18–8.15 m (2H$_{arom}$), 8.40 d (1H, HC=CH, J = 16.5 Hz).

2-[2-(4-Hydroxy-3-methoxystyryl)]-1,3,3-trimethyl-3*H*-indolium bromide (2). ^{1}H NMR spectrum, δ, ppm: 1.79 s (6H, CH_3), 3.93 s (3H, OCH_3), 4.12 s (3H, NCH_3), 6.99 d (1H$_{arom}$, J = 8.1 Hz), 7.49 d (1H, HC=CH, J = 15.9 Hz), 7.55–7.64 m (2H$_{arom}$), 7.76–7.86 m (4H$_{arom}$), 8.36 d (1H, HC=CH, J = 15.9 Hz).

2-[2-(4-Hydroxy-3-methoxystyryl)]-1,5,6-trimethylbenzothiazolium iodide (3). ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, CH_3), 2.46 s (3H, CH_3), 3.90 s (3H, OCH_3), 4.29 s (3H, NCH_3), 6.92 d (1H$_{arom}$, J = 8.2 Hz), 7.49 d (1H$_{arom}$, J = 7.4 Hz), 7.63 s (1H$_{arom}$), 7.77 d (1H, HC=CH, J = 15.9 Hz), 8.02 s (1H$_{arom}$), 8.05 d (1H, HC=CH, J = 15.6 Hz), 8.11 s (1H$_{arom}$), 10.22 br.s(1H).

2-(2-Benzo[1,3]dioxol-5-vinyl)-1,3,3-trimethyl-3*H*-indolium bromide (4). ^{1}H NMR spectrum, δ, ppm: 1.79 s (6H, CH_3), 4.14 s (3H, NCH_3), 6.23 s (2H, OCH_2O), 7.17 d (1H$_{arom}$, J = 7.8 Hz), 7.55 d (1H, HC=CH, J = 16.5 Hz), 7.61–7.64 m (2H$_{arom}$), 7.80 d (1H$_{arom}$, J = 8.1 Hz), 7.85–7.89 m (2H$_{arom}$), 8.00 s (1H$_{arom}$), 8.37 d (1H, HC=CH, J = 16.2 Hz).

2-[2-(3,5-Dimethyl-4-hydroxystyryl)]-1-methylquinolinium iodide (5). ^{1}H NMR spectrum, δ, ppm: 2.22 s (6H, CH_3), 4.50 s (3H, NCH_3), 7.61 s (2H$_{arom}$), 7.66 d (1H, HC=CH, J = 15.6 Hz), 7.89 t (1H$_{arom}$, J = 7.4 Hz), 8.11–8.14 m (2H, HC=CH, H$_{arom}$), 8.29 d (1H$_{arom}$, J = 7.7 Hz), 8.51 d (2H$_{arom}$, J = 9.1 Hz), 8.93 d (1H$_{arom}$, J = 8.8 Hz), 9.22 br.s(1H). Recrystallized in the form of solvate with a methanol molecule.

The stock solutions of the dyes (1 mmol/L) in distilled water were prepared from the weighed specimens prior to the experiment. The solutions with lower concentrations were prepared diluting the stock solutions. The medium acidity was adjusted by addition of sulfuric acid of potassium hydroxide (analytical pure grade).

To determine the pK values by means of tristimulus colorimetry, 5 mL of the 0.1 mmol/L solution of the dye was introduced in a 25 mL volumetric flask, the desired pH value was adjusted (in the 5 mol/L H_2SO_4–pH 14 range with a step of ΔpH 0.1), and the mixture was diluted with a solution with the corresponding pH to 25 mL.

The following chromaticity functions were used in the calculations: color coordinates in the CIELAB system (L, A, and B), CIE color difference (ΔE_{76}), color saturation (S), and specific color difference (SCD). The L, A, and B coordinates were calculated

from the recorded absorbance spectra at 380–780 nm. The S, SCD, and ΔE_{76} were determined using Eqs. (1)–(3).

$$S^2 = A^2 + B^2, \quad (1)$$

$$\text{SCD} = \Delta S/\Delta\text{pH}, \quad (2)$$

with $\Delta\text{pH} = \text{pH}_1 - \text{pH}_2$; $\Delta S = |S_1 - S_2|$; S_1 and S_2 – the color saturation at pH_1 and pH_2, respectively.

$$\Delta E_{76} = \sqrt{\Delta L^2 + \Delta A^2 + \Delta B^2}, \quad (3)$$

with $\Delta L = L_1 - L_2$, $\Delta A = A_1 - A_2$, and $\Delta B = B_1 - B_2$.

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