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ASSESSMENT OF THE COMPOSITION OF AQUEOUS-ORGANIC MIXTURES BY SOLVATOCHROMISM OF 4-[(OCTYLYLPYRIDINIUM)ETHENYL]PHENOLATE DYES

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Determination of the water content in organic solvents has attracted a number of researchers in many fields of science in view of its importance in various chemical processes. The presence of water is also monitored in industrial production lines, pharmaceutical manufacturing, food processing, paper production, biomedical and environmental monitoring [1, 2]. Water-organic systems are found in many extraction processes involving organic solvents, which are limited or unlimited mixed with water [3, 4]. Obtaining relevant data on their distribution in various extraction water-salt systems is rather time consuming and, to some extent, problematic because of high cost of consumable chromatographic materials. In addition, in the case of the analysis of corrosive and high-saline mediums, especially high alkaline ones, it is necessary to carry out a chromatographic analysis under special conditions that prevent damage of the stationary phases or equipment. The low water content in various substances such as common organic solvents, petroleum products and foods is determined by using standard instrumental methods such as Karl Fisher titration [5, 6]. In addition, there are some others methods for finding water content such as gas chromatography [7, 8], conductometry [9], infrared spectroscopy [10], chemical sensors [11] and others. For the last years a number of colorimetric or fluorescence methods became popular because they are more convenient than standard instrumental methods. Recent researches have been focused on developing highly sensitive fluorescent probes that can be made using simple synthesis and have potential applications in remote and in situ monitoring [11, 12]. Variety of probes has been developed

based on fluorophores and dyes. Tetraphenylpyrazine-triphenylamine (TPP-TPA) was used to detect water traces in organic solvents by monitoring the shift of the fluorescence peak wavelength. The use of optical fibers for the detection provides remote and field-deployable sensing ability [13]. Determinations of the water content have been successfully designed using hydroxynaphthalimide-based merocyanine dye [14], 1,8-naphthalimide [15], 8-hydroxyquinolines [16], 2,3-biphenil quinoxaline 6-amine [17], flavone derivatives [18], thioxanthone fluorophores [19] and 7H-indolo[1,2-a]quinolinium merocyanine[20]. Recently, chemosensors for water signaling have drawn considerable attention due to certain advantages [4]. Solvatochromic dyes became visual and spectrophotometric indicators of solvent polarity [21]. Merocyanine dyes and their derivatives exhibit reversible color changes upon exposure to light, heat, pH and polar solvents [22-26].

This work reports on the development of simple spectrophotometric probes on solvatochromic shift of two 4-hydroxystyryl dyes in its merocyanine forms for quantifying water content in organic solvents. As to 4-hydroxystyryl dyes, spectrophotometric, protolytic and solvatochromic properties of some derivatives of indolenine, benzotiazole, 4-pyridine, 2- and 4-quinoline were investigated previously [27-28]

Experimental part

The following commercially available chemicals (Aldrich, UOSlab) with the content of the main compound of at least 95-99% were used: 4-hydroxy-3,5-dimethylbenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, methanol,

ethanol, butanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO), triethylamine (TEA), toluene, tetrahydrofuran (THF) were used as received. For finding acidity constants were used universal buffer solutions [29].

The 4-hydroxystyryl N-octylpyridinium bromides dyes the namely are 4-[2-(4-hydroxy-3-methoxyphenyl) ethenyl]-1-octylpyridinium bromide (OP-MS) and 4-[2-(4-hydroxy-3,5-dimethylphenyl) ethenyl]-1-octylpyridinium bromide (OP-DMS). (Fig 1.) synthesized as describe previously for a similar scheme [27], from 0.5–2.0 mmol of the corresponding salts of the heterocyclic bases and a stoichiometric amount of the appropriate benzaldehydes in the presence of 0.02–0.05 mL of TEA in 2–5 mL of boiling acetonitrile (30–120 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.

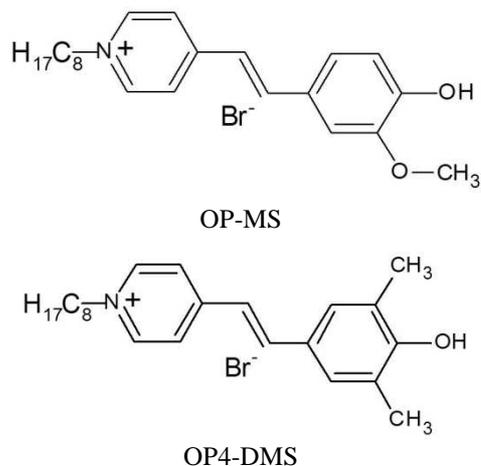


Fig. 1. Molecular structure of dyes in its salting (protonated) forms.

The purity of the dyes was checked by thin layer chromatography (TLC) on Sorbfil plates (Russia) using an ethanol–dioxane–toluene–acetic acid (2 : 1 : 1 : 0.2) as eluent. Structure of the dyes is confirmed by ^1H NMR-spectrometry using Varian Gemini 400 NMR spectrometer:

OP-MS: ^1H NMR (400 MHz, DMSO- d_6), 8.87 (d, 2H), 8.13 (d, 2H), 7.94 (d, $J = 16$ Hz, 1H), 7.32–7.36 (d, $J = 16$ Hz, 2H), 7.18 (d, 1H), 6.86 (d, 1H), 4.448 (t, 2H), 3.847 (s, 3H), 1.88 (m, 2H), 1.25 (m, 10H), 0.843 (t, 3H).

OP-DMS: ^1H NMR (400 MHz, DMSO- d_6) δ 8.90 (d, $J = 6.5$ Hz, 2H), 8.15 (d, $J = 6.4$ Hz, 2H), 7.90 (d, $J = 16.2$ Hz, 1H), 7.37 (s, 2H), 7.29 (d, $J = 16.2$ Hz, 1H), 4.47 (t, $J = 7.4$ Hz, 2H), 2.21 (s, 6H), 1.89 (q, $J = 7.1$ Hz, 2H), 1.58 – 0.97 (m, 10H), 0.84 (t, $J = 6.6$ Hz, 3H).

Electronic absorption spectra were recorded using SF-10 and SHIMADZU UV-1800 spectrophotometers in 1 cm quartz cells at 220/400–750 nm. The acidity medium was monitored by potentiometry with pH-glass electrode calibrated using standard buffer solutions.

The stock solutions of the dyes (10^{-3}M) in ethanol or in distillate water were prepared from the weighed sample of dye. The solutions with lower concentrations were prepared diluting the stock solutions by appropriate solvent or distillate water obviously. The medium acidity was adjusted by universal buffer solutions. Merocyanine forms of dyes were generated in situ by the introduction of excess amount of bases (TEA, Na_2CO_3 or KOH).

Results and discussion

Acidity constant (pK_a) and λ_{max} of light absorption of the protonated (RH^+) and merocyanine (R^0) forms of the investigated dyes were found by the spectrophotometric method [30] (Fig. 2, Table 1).

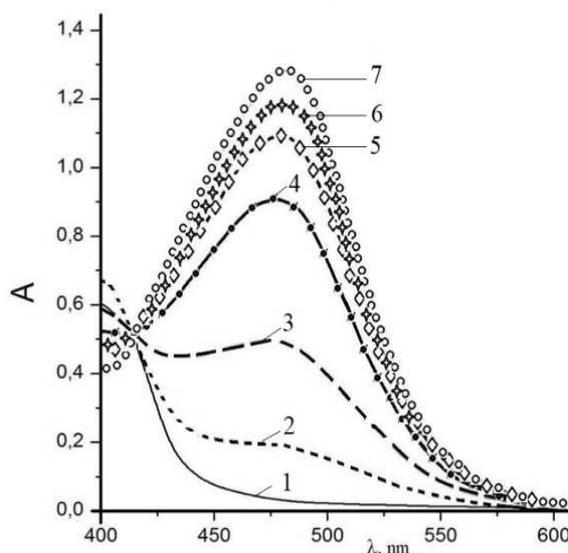


Fig. 2. Light absorption of OP-DMS in aqueous solutions at different pH: (1- $\text{pH}=6,09$; 2- $\text{pH}=8,00$; 3- $\text{pH}=8,55$; 4- $\text{pH}=9,08$; 5- $\text{pH}=9,51$; 6- $\text{pH}=9,98$; 7- $\text{pH}=11,04-12,0$)

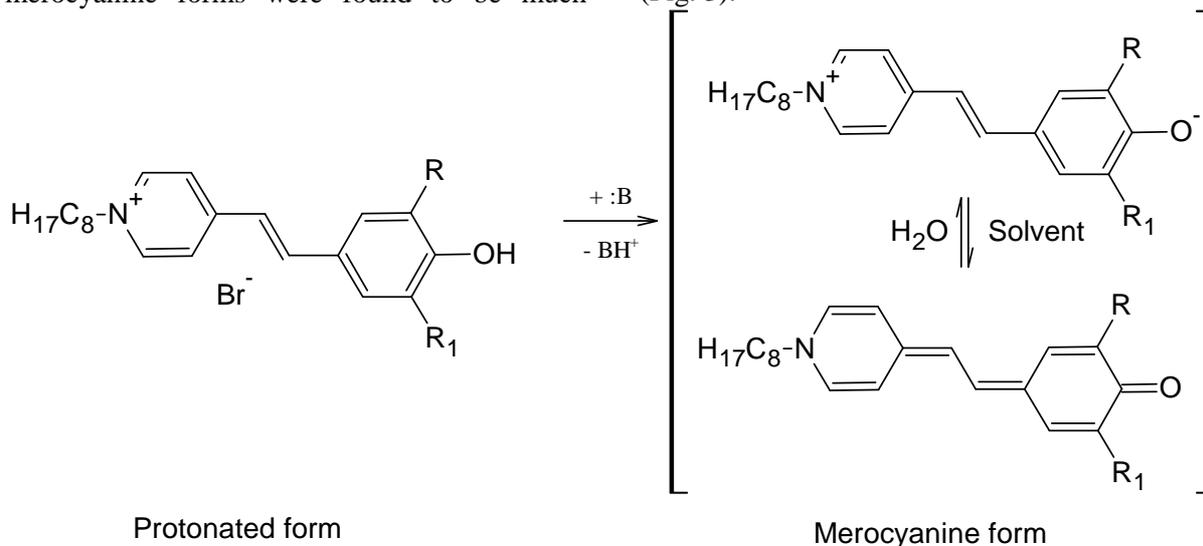
Table 1. Spectrophotometric and protolytic characteristics of dyes in aqueous solution

Dye	λ_{HR}^+ , nm	$\epsilon \times 10^{-4}$	λ_R^0 , nm	$\epsilon \times 10^{-4}$	$\Delta\lambda$, nm	pK _a
OP-MS	385	1,45	471	2,80	86	8,45
OP-DMS	383	1,70	480	3,30	97	8,83

The molar absorption coefficients of the merocyanine forms were found to be much

higher than those of the protonated forms in aqueous solutions. The acidity constants (pK_a) of the investigated dyes lay in the range 8-9. The transformation from the protonated to merocyanine form is accompanied by bathochromic shift near 86 nm for OP-MS and 97 nm for OP-DMS. These data indicate a high contrast of the reaction.

The investigated dyes can exist in two resonance forms (protonated and merocyanine): (Fig. 3).

**Fig. 3.** Transformation process of dyes.

For investigation of solvatochromic behaviors (Table 2) of the merocyanine dye forms, the following steps were used: 0.2 ml of 10^{-4} M dye was added to 5 ml of solvent; then, to the solution obtained, 1 drop of TEA was added in order to make a merocyanine dye form. Absorption maximums of merocyanine forms in different solvents has been determined by spectrophotometric method.

Table 2. Maximums of absorption of merocyanine forms of dyes in various solvents (λ_R^0), nm

Dye	Water	Methanol	Ethanol	Butanol-1	DMSO	DMF
OP-MS	471	525	524	566	602	610
OP-DMS	480	538	563	583	612	619

In the transition from aqueous to DMF solutions, for both dyes the same maximum solvatochromic shift ($\Delta\lambda_{max}$) is equal to 139 nm. But the greatest difference in the displacements for dyes (30 nm) was observed for the ethanol solutions, which indicates the specificity of the solvation of phenoxyl groups in such solutions. Due to the largest solvatochromic shift of dyes observed in aqueous-DMF solution, it was decided to investigate the system "water-DMF" in order to develop a method for evaluating their composition. The series of solutions with different content of solvent has been prepared in the presence of the same amount of dye and its VIS-spectra were registered (Fig. 3-4).

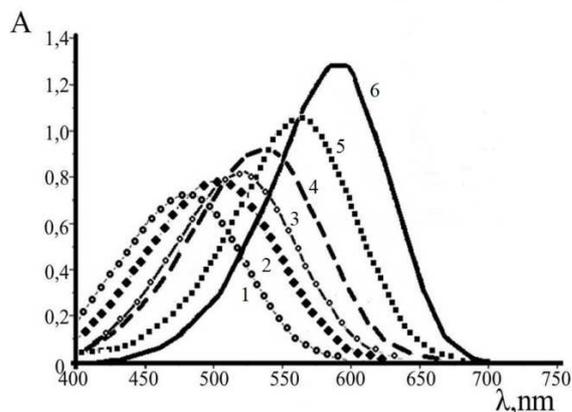


Fig. 3. Absorption spectrum of OP-MS dye in binary water-DMF solutions of different composition: φ(water), % v/v: 1- 99; 2-80; 3-60; 4-40; 5-20; 6 - <1.

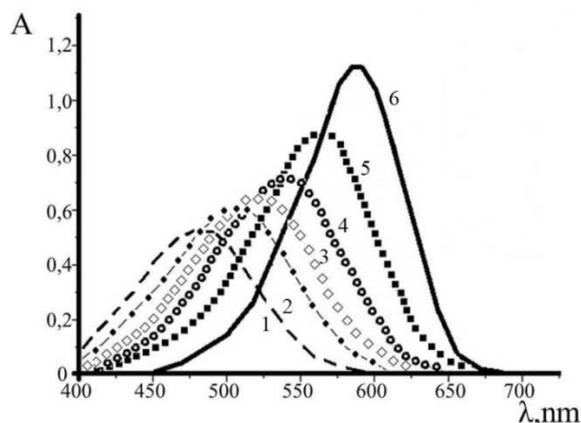


Fig. 4. Absorption spectrum of OP-DMS dye in water-DMF solutions in various composition. φ(water), % v/v: 1-99; 2-80; 3-60; 4-40; 5-20; 6 - <1.

Determination of mixtures composition in "Water - DMF" systems by solvatochromic shifts of dyes.

A number of data processing algorithms are used to select the best quantitative parameter that binds the composition of the mixtures (water content) with solvatochromic shifts of the dyes, namely: (1) the value of the maximum light absorption (λ_{max}); (2) the value of the wavelength at half the height of the long-wave area of spectrum ($\lambda_{1/2}$); (3) the ratiometric parameter as a relative ratio of absorbtion at fixed wavelengths corresponding to the maximum absorption of dyes in pure water and DMF solutions ($A_{\lambda 1}/A_{\lambda 2}$) and others. Some of the spectral data processing results obtained and their linearization are given in the Tables 3-4.

Table 3. Selection of functions for determination composition of mixtures "water-DMF" by solvatochromic shifts of OP-DMS dye in solutions

Nº	Function*	Equations	R ²	C _{H2O} , %v/v
1	$C_w=f(\lambda_{1/2})$	$y = -1,0779x + 621,79$	0,9942	0-50
2	$C_w=f(A_{480})$	$y = 0,0061x + 0,0744$	0,9925	0-60
3	$C_w=f(A_{585})$	$y = -0,0192x + 1,09$	0,9794	0-50
4	$C_w=f(\lg(A_{480}/A_{585}))$	$y = 0,0302x - 1,1654$	0,9938	0-50

* Ratiometric functions type of $C_w=f(A_{480}/A_{585})$ and $C_w=f(A_{585}/A_{480})$ were not linear.

Table 4. Solvatochromic parameters of dyes in "Water-DMFA" solution

water, % v/v	OP-MS		OP-DMS	
	λ_{max} , nm	$\lambda_{1/2}$, nm	λ_{max} , nm	$\lambda_{1/2}$, nm
<1	585	623	575	619
10	575	610	565	608
20	562	600	550	597
30	550	588	540	584
40	537	578	528	573
50	527	568	516	565
60	517	562	508	555
70	513	555	500	548
80	505	547	495	543
90	493	537	488	532
99	475	521	485	518

The one from most suitable quantitative criterion for spectrophotometric analysis of the mixtures of interest was the $\lambda_{1/2}$ - the value of the wavelength, which corresponds to the long-wave branch of the spectrum at half of its height. An example of obtaining these values is shown in the Fig. 5. (The perpendicular was lowered to X from the most long-wave maximum. The next perpendicular was drawn from one half of high ($1/2$) spectra to the point of intersection with the spectrum from which the third perpendicular was lowered on the wavelength axis).

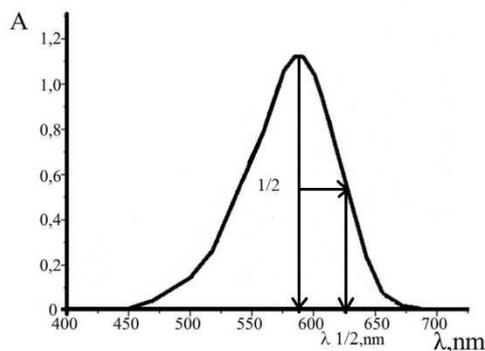


Fig. 5. Schematic image for measuring $\lambda_{1/2}$ long-wave branch.

The coefficients of sensitivity to water content are low and amount to 1.5-1.6 nm per volumetric fraction (%), however, it allows for the analysis of mixtures with significant content of the both components. A detailed examination of such interrelation in the entire range of the «water-DMF» mixtures indicated that there are no strict linear function between the $\lambda_{1/2}$ parameter and composition of the mixture, and, more simply, such correlation are described with the third-order polynomial, which can be used for the analysis (Fig. 6, 7).

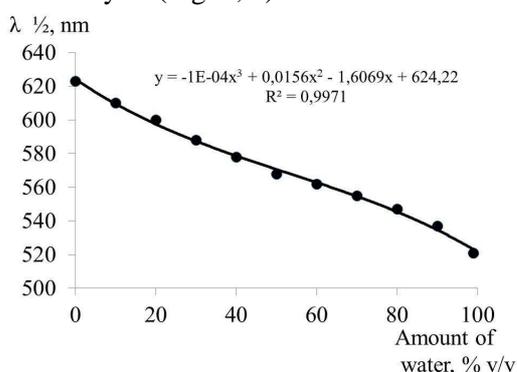


Fig. 6. Calibration plot for determination of water content in DMF by solvatochromic shifts of OP-MS.

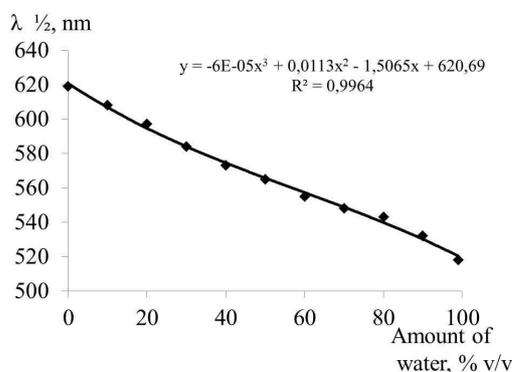


Fig. 7. Calibration plot for determination of water content in DMF by solvatochromic shifts of OP-DMS.

Another quantitative criterion suitable for assessing the moderate water content is the logarithmic values of the ratio of absorptivity measured at the maximum absorption of purely aqueous and DMF solutions (critical values of wavelengths of the merocyanine form), for example, for OP-DMS dye is the value of $\lg(A_{480}/A_{585})$. However, these values are only suitable for the assessment of moderate water content.

For other systems, the situation may vary considerably. For example, for “water-THF” solutions, although significant solvatochromic shift are observed (155 nm), however, light absorption of solutions decreases with the transition from water to THF solution.

Distribution and water content in extraction phases

The study of the distribution of dyes in some extraction systems by the classical extraction-spectrophotometric method has shown that these dyes are well extracted by polar organic solvents (alcohols, ketones, etc.) including systems with salting-out agent (Na_2CO_3) and solvents that are completely mixed with water (ethanol, isopropanol, acetone), with the corresponding values of the distribution coefficients larger than 10^2 . It is interesting to note that in the case of aromatic hydrocarbon extraction a significant difference in the distribution of the investigated dyes was observed. Thus, distribution coefficient (D) in the “toluene- H_2O ” system for OP-DMS equals 0.75 and for OP-MS is only <0.01 . The study of the distribution of 4-hydroxystyryl octylpyridinium dyes in their merocyanine form has shown that the values of dyes are most strongly determined by the nature of ortho-substituents in the 4-hydroxystyryl moiety. Moreover, the maximum contribution to the growth of D is made by two alkyl (methyl) groups, showing a strong “steric effect” on the hydration of the phenol group. Similar unsubstituted, o-methoxy and o,o-dimethoxy substituted dyes are practically not extracted by toluene in their merocyanine/zwitterionic forms.

Conclusions

Spectrophotometric, protolytic and solvatochromic properties of the OP-MS and OP-DMS dyes were investigated. The scheme of

ptolytic transformations has been proposed. The maxima of absorption of the merocyanine dye forms in various solvents have been investigated. The series of solutions with different content of the solvent has been studied in the presence of the same amount of the dye, and their VIS-spectra were registered. Ratiometric functions were investigated for the selection of the best quantitative parameter that binds the composition of the mixtures (water content) with solvatochromic shifts of the dyes. The correlation coefficients (R^2) are greater than 0.99. It is noted that the color of the merocyanine forms of dyes depends on the composition of water-organic solutions ranging from pink to blue in the transition from water to a pure solvent, which allows to set the composition of the mixtures. The possibilities of determining the composition of mixed solutions using colorimetric scales and by processing spectrophotometric data are discussed.

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ASSESSMENT OF THE COMPOSITION OF AQUEOUS-ORGANIC MIXTURES END EXTRACTION PHASES BY SOLVATOCHROMISM OF 4-[(OCTYLYLPYRIDINIUM)ETHENYL]PHENOLATE DYES

Yuliya Zhukova, Yaroslav Studenyak, Larisa Fetjko, Diana Pogan

This work deals with the investigation of assesment of the composition of aqueous dimethylformamide mixtures based on solvatochromic shift of some 4-hydroxystyryl dyes. The purity of the studied dyes was tested. Spectrophotometrical, protolytical and solvatochromic properties of the OP4-MS and OP4-DMS dyes were investigated. The transformation from the protonated to merocyanine form is accompanied by bathochromic shift. Absorption maxima of the cationic and merocyanine forms in aqueous solutions and acidity constants (pK_a) of the investigated dyes have been determined by spectrophotometric method. Ratiometric functions were investigated for the selection of the best quantitative parameter that binds the composition of the mixtures (water content) with solvatochromic shifts of the dyes. Correlation coefficients (R^2) are greater than 0.99. It is noted that the color of merocyanine forms of dyes depends on the composition of water-organic solutions ranging from pink to blue in the transition from water to a pure solvent, which allows to set the composition of the mixtures. The possibilities of determining the composition of mixed solutions using colorimetric scales and by processing spectrophotometric data are discussed.