DOI 10.1007/s10812-020-01015-0
*Journal of Applied Spectroscopy, Vol. 87, No. 3, July, 2020 (Russian Original Vol. 87, No. 3, May–June, 2020)*

# COLORIMETRIC DETERMINATION OF WATER IN DMSO USING 4-HYDROXYSTYRYL DYES

**D. V. Snigur,**[a*] **Yu. P. Zhukova,**[b] **Ya. I. Studenyak,**[b]
**and A. N. Chebotarev**[a]

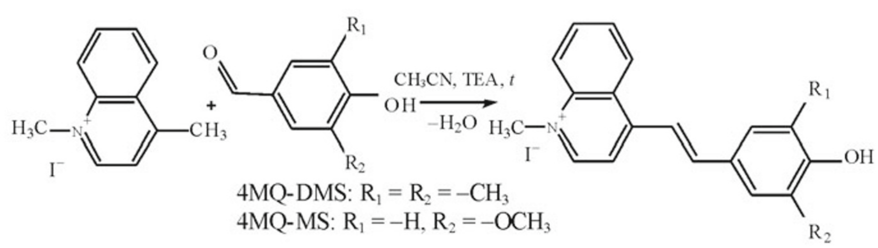
UDC 543.42.062:543.3

*The acid–base properties of two novel 4-hydroxystyryl dyes were studied using colorimetric and spectrophotometric methods. The corresponding ionization and hydroxylation constants were determined. Changes of the water:DMSO ratio was shown to cause significant changes of the dye absorption spectra and the corresponding colorimetric functions. Use of the yellowness index allowed moderate water contents (1–30%) in DMSO to be determined. It was advisable to use the color saturation function for analyzing such mixtures in the entire range of possible contents because it was linear over a wider concentration range (0–99%).*

***Keywords:*** *4-hydroxystyryl dyes, colorimetry, spectrophotometry, acid–base properties, water determination.*

**Introduction.** Water possesses unique physicochemical properties so that even traces of it can sharply affect the properties and behavior of other compounds and solvents. Water is an unwanted impurity in organic synthesis and high-purity semiconducting and other functional materials technology [1–3]. Nevertheless, water can exist in various forms in analytes (crystallization, constitutional, adsorption). The issue in most instances consists of establishing the total water content. The Fisher method is the main technique for determining the water content [4, 5]. Other methods, e.g., gas chromatography [6, 7], conductometry [8], and IR spectroscopy [9] are also used. Various tests for determining water in organic solvents have been developed, e.g., those based on measuring the solution acidity produced by adding citric acid or sodium hydrogen sulfide to organic solvents using indicator test strips containing Congo red [10]. Recently, highly sensitive fluorescent probes [11–15] and spectrophotometric methods using solvatochromic dyes [16, 17] were developed to determine water. It is noteworthy that a colorimetric method that was highly acclaimed for studying the acid–base properties of dyes [18–21] and to develop quantitative and semi-quantitative determinations of various analytes [22] has not been used to determine water contents. Merocyanine dyes with high molar absorption coefficients and unique solvatochromic properties are of interest as reagents sensitive to changes of medium solvation characteristics [23, 24]. The possibility in principle of using several 4-hydroxystyryl dyes based on 1-octylpyridine for spectrophotometric determination of the compositions of aqueous organic mixtures was demonstrated [25]. The present work reports the development of a colorimetric method for determining water in organic solvents using solvatochromic 4-hydroxystyryl dyes.

**Experimental.** The 4-hydroxystyryl dyes (4MQ-MS and 4MQ-DMS) were synthesized by reacting equivalent amounts of 1-methylquinolinium iodide and the corresponding 4-hydroxybenzaldehyde derivatives in refluxing MeCN in the presence of catalytic amounts of $Et_3N$ (TEA):



---

[*] To whom correspondence should be addressed.

[a] I. I. Mechnikov Odessa National University, Odessa, 65082, Ukraine; email: denis270892@yandex.ru; [b] Uzhgorod National University, Uzhgorod, 88000, Ukraine; email: yulyazhukova@i.ua. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 87, No. 3, pp. 362–367, May–June, 2020. Original article submitted September 26, 2019.

The crystalline precipitate that formed after cooling the reaction mixture was filtered off, rinsed with $Et_2O$, and dried. If a crystalline precipitate did not form, the excess of solvent was distilled off. The solid was rinsed with $Et_2O$ and recrystallized from MeOH. The purities of the obtained dyes were evaluated using TLC. Their structures were confirmed using PMR spectrometry (400 MHz, DMSO-$d_6$, δ, ppm); for 4MQ-MS: 9.86 (br.s, 1H), 9.25 (d, 1H, 6.4 Hz), 9.03 (d, 1H, 8.4 Hz), 8.41 (d, 1H, 6.8 Hz), 8.39 (d, 1H, 8.4 Hz), 8.23 (t, 1H, 8 Hz), 8.06–8.15 (dd, 2H, 16.4 Hz),* 8.02 (t, 1H, 7.6 Hz), 7.61 (s, 1H), 7.38 (d, 1H, 8 Hz), 6.87 (d, 1H, 8.4 Hz), 4.49 (s, 3H), 3.91 (s, 3H); for 4MQ-DMS: 9.23 (d, 1H, 6.4 Hz), 9.09 (br.s, 1H), 9.03 (d, 1H, 8.8 Hz), 8.39 (dd, 2H, 6.8 Hz/8.4 Hz), 8.24 (t, 1H, 7.5 Hz), 8.10–8.05 (dd, 2H, 16.5 Hz),* 8.02 (t, 1H, 8 Hz), 7.63 (s, 2H), 4.49 (s, 3H), 2.24 (s, 6H).

Stock solutions of 4MQ-MS and 4MQ-DMS of concentration $1 \cdot 10^{-3}$ M were prepared by dissolving weighed portions in distilled $H_2O$. Solutions with lower concentrations were prepared by the appropriate dilution of the stock solutions immediately before use. The acidity was adjusted using a universal buffer solution or addition of $H_2SO_4$ and KOH solutions. The reagents were at least analytical grade.

Electronic absorption spectra were recorded in 1-cm quartz cuvettes thermostatted at 25°C on UV-2600 (Shimadzu) and SF-56 spectrometers in the range 380–780 nm. The solution acidity was monitored using an ESL-63-07 glass electrode in combination with an EVL-1M3 AgCl reference electrode on an I-160 ion-meter calibrated using a standard buffer solution.

The following colorimetric functions were used: *L*, *A*, *B*, color coordinates in the CIELAB system; yellowness index ($Y_I$); color saturation (*S*); and specific color difference (SCD). Color coordinates *X*, *Y*, *Z* and *L*, *A*, *B* were calculated based on the recorded visible absorption spectra (380–780 nm) using the SF-56 software. The quantities *S*, SCD, and $Y_I$ were determined using the formulas:

$$S^2 = A^2 + B^2 , \tag{1}$$

$$\mathrm{SCD} = \Delta S / \Delta \mathrm{pH} , \tag{2}$$

where $\Delta\mathrm{pH} = \mathrm{pH}_1 - \mathrm{pH}_2$; $\Delta S = |S_1 - S_2|$; $S_1$ and $S_2$, color saturations of the studied solutions at $\mathrm{pH}_1$ and $\mathrm{pH}_2$;

$$Y_I = \frac{100(1.28X - 1.06Z)}{Y} , \tag{3}$$

where *X*, *Y*, *Z* are the color coordinates.

The p*K* constants were determined by colorimetry in a series of 25-mL volumetric flasks by adding dye solution (5 mL) of concentration $1 \cdot 10^{-4}$ M, adjusting the solution acidity in the range pH 2–14 (ΔpH 0.1), and diluting to the mark with an aqueous solution of the corresponding acidity.

The possibility of determining the compositions of aqueous organic mixtures was studied by preparing $H_2O$–DMSO solutions with dye concentration $2 \cdot 10^{-5}$ M after dilution and varying the $H_2O$ content from 0 to 99%. Absorption spectra of the solutions were recorded. The color saturation and yellowness indices were calculated.

**Results and Discussion.** Figure 1 shows absorption spectra of aqueous solutions of the studied dyes. In general, the changes in the absorption spectra of 4MQ-MS and 4MQ-DMS were observed to be similar. The dyes transitioned gradually from the cationic form into the electrically neutral form as the solution pH increased. This was accompanied by a bathochromic shift (~150 nm) of the absorption band (AB) with an isosbestic point at ~450 nm. The absorption intensity in basic solution decreased. This was seen most clearly for 4MQ-MS (Fig. 1a) and was most probably caused by hydroxylation of the dye.

Ionization ($\mathrm{p}K_\mathrm{a}$) and hydroxylation constants ($\mathrm{p}K_\mathrm{h}$) (Table 1) of the studied dyes were determined by processing the initially obtained spectrophotometric data using the equilibrium shift method. The slopes of the obtained curves were close to unity, indicating that one proton and one hydroxyl were involved in the acid–base transformations. The changes of SCD were calculated as a function of pH (Fig. 2). An analysis of Fig. 2 led to the conclusion that the acid–base properties of 4MQ-MS and 4MQ-DMS were similar and enabled the corresponding ionization and hydroxylation constants to be determined. Table 1 shows that the $\mathrm{p}K_\mathrm{a}$ and $\mathrm{p}K_\mathrm{h}$ values of the 4-hydroxystyryl dyes in aqueous solutions that were obtained using colorimetric and spectrophotometric methods were similar, which indicated that they were accurate.

---

*A doubled doublet of the dimethine chain with significantly distorted intensities of the components was observed, i.e., overlap of doublet components, that increased significantly the intensities of the component band and decreased significantly the intensities of the separate (not overlapping) parts of the doublets.

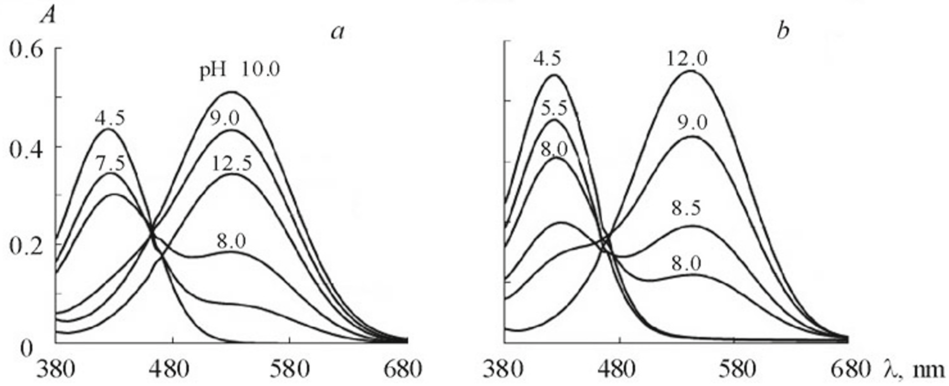


Fig. 1. Absorption spectra of 4MQ-MS (a) and 4MQ-DMS (b) at various solution acidities; $C = 2 \cdot 10^{-5}$ M, $l = 1$ cm.

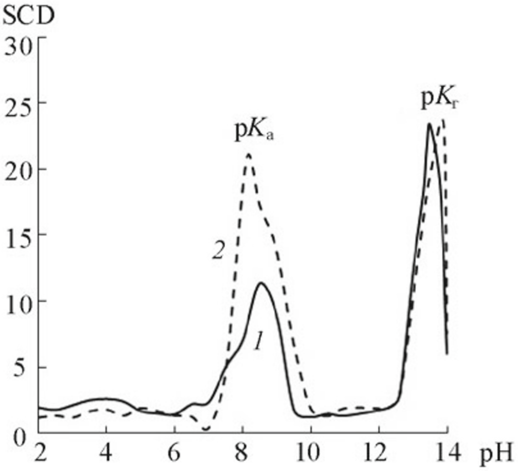


Fig. 2. Dependence of specific color difference of 4MQ-MS (1) and 4MQ-DMS solutions (2) on solution acidity.

TABLE 1. Ionization ($pK_a$) and Hydroxylation Constants ($pK_h$) of 4-Hydroxystyryl Dyes in Aqueous Solutions ($n$ = 3, $P$ = 0.95)

| Dye | $pK_a^*$ | $pK_a^{**}$ | $pK_h^*$ | $pK_h^{**}$ |
|---|---|---|---|---|
| 4MQ-MS | 8.4 ± 0.2 | 8.3 ± 0.1 | 13.5 ± 0.2 | 13.3 ± 0.2 |
| 4MQ-DMS | 8.6 ± 0.2 | 8.7 ± 0.1 | 13.9 ± 0.2 | 13.8 ± 0.2 |

*Determined by colorimetry.

**Determined by spectrophotometry.

Because the changes in the absorption spectra and colorimetric functions were similar, the influence on them of the $H_2O$–DMSO ratio was demonstrated using 4MQ-DMS as an example. Figure 3a (water content <50%) shows that the absorption spectrum of 4MQ-DMS in DMSO showed an AB component with maxima at 625 and 690 nm, the intensities of which fell with increasing water content in the system. A new AB with a maximum at ~440 nm appeared. Its intensity increased with increasing water content. It is noteworthy that the long-wavelength AB component disappeared with water content >50% whereas the short-wavelength AB increased in intensity and shifted bathochromically (Fig. 3b).

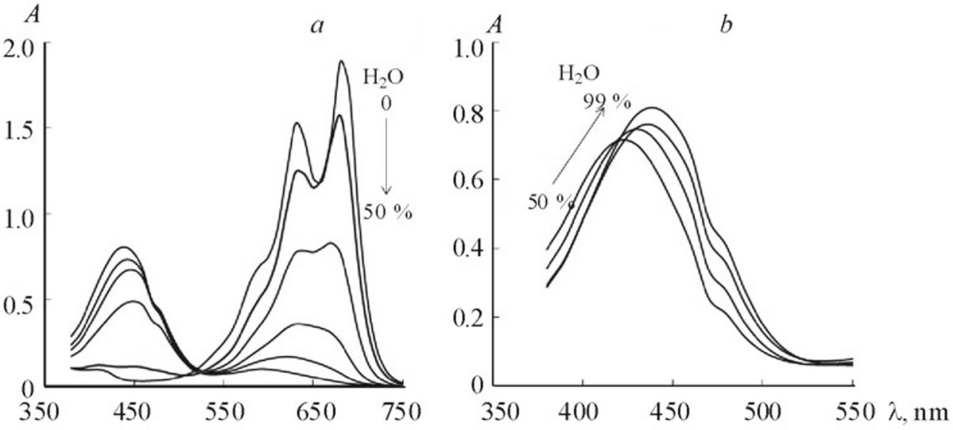


Fig. 3. Absorption spectra of 4MQ-DMS in $H_2O$–DMSO solutions: $H_2O$ content <50 (a) and >50 vol.% (b); $C = 2\cdot10^{-5}$ M, $l = 1$ cm.

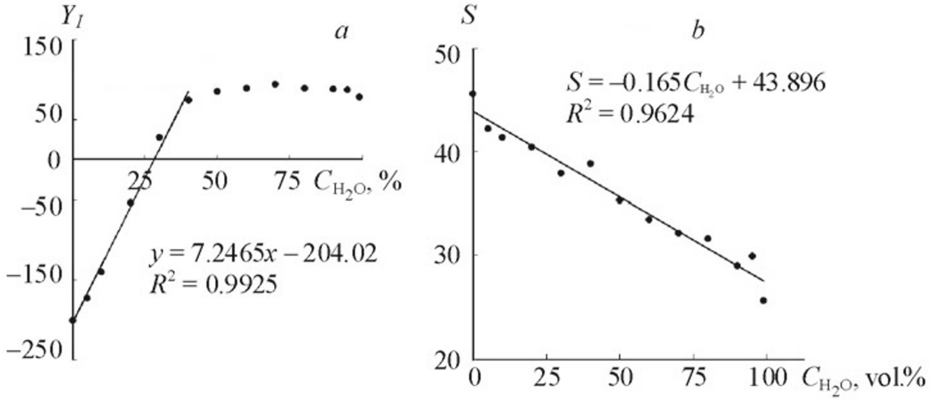


Fig. 4. Dependence of colorimetric functions of yellowness index (a) and color saturation (b) of 4MQ-DMS solutions on $H_2O$ content; $C = 2\cdot10^{-5}$ M, $l = 1$ cm.

Figure 4 shows the changes of colorimetric functions yellowness index and saturation of 4MQ-DMS as functions of water content (vol.%). The yellowness index at low water contents increased practically linearly ($R^2 = 0.9925$) with increasing water content (<40% $H_2O$) and appeared as a saturation curve. In turn, the color saturation (Fig. 4b) of the solutions decreased with increasing water content and obeyed a linear equation ($R^2 = 0.9624$). Use of the yellowness index enabled moderate water contents (1–30%) in DMSO to be determined. However, the color saturation function, which was linear over a wider concentration range (0–99%), was advisable for such mixtures over the whole range of possible contents.

**Conclusions.** The acid–base properties of two novel 4-hydroxystyryl dyes were studied by spectrophotometry and colorimetry. The corresponding ionization and hydroxylation constants were found. Changes of the $H_2O$–DMSO ratio were shown to cause substantial changes of the electronic absorption spectra and corresponding colorimetric functions of these dyes. The yellowness index increased and the color saturation decreased with increasing water content in the system. Equations describing adequately the relationships of the colorimetric functions and the water content were proposed.

## REFERENCES

1. T. A. Blank and L. P. Eksperiandova, *Visn. Kharkiv. Nats. Univ., Khim.*, **16**, 27–38 (2008).
2. L. P. Eksperiandova, *Nontraditional Approaches to the Analysis of Functional Materials and Environmental Samples* [in Russian], Institute of Single Crystals, Kharkov (2011), pp. 179–215.

3. J. Mitchell, Jr., and D. M. Smith, *Aquametry*, Interscience Publishers, New York, 1948, 444 pp. [Russian translation, Khimiya, Moscow (1952), pp. 165–224].
4. V. Kestens, P. Conneely, and A. Bernreuther, *Food Chem.*, **106**, 1454–1459 (2008).
5. K. Fischer, *Angew. Chem.*, **48**, 394–396 (1935).
6. W. K. O′Keefe, F. T. T. Ng, and G. L. Rempel, *J. Chromatogr. A*, **1182**, 113–118 (2008).
7. R. Nuβbaum, D. Lischke, H. Paxmann, and B. Wolf, *Chromatographia*, **51**, 119–121 (2000).
8. M. S. Ribeiro, L. Angnes, and F. R. P. Rocha, *J. Braz. Chem. Soc.*, **24**, 418–422 (2013).
9. S. Cho, H. Chung, Y.-A. Woo, and H.-J. Kim, *Bull. Korean Chem. Soc.*, **26**, 115–118 (2005).
10. V. G. Amelin, A. V. Tret′yakov, and T. A. Stepanova, *Zh. Anal. Khim.*, **65**, No. 3, 321–324 (2010) [V. G. Amelin, A. V. Tret′yakov, and T. A. Stepanova, *J. Anal. Chem.*, **65**, No. 3, 316–318 (2010)].
11. H. S. Jung, P. Verwilst, W. Y. Kim, and J. S. Kim, *Chem. Soc. Rev.*, **45**, 1242–1256 (2016).
12. K. H. Kim, W. J. Lee, J. N. Kim, and H. J. Kim, *Bull. Korean Chem. Soc.*, **34**, 2261–2266 (2013).
13. V. E. Gontcharenko, A. M. Lunev, I. V. Taydakov, V. M. Korshunov, A. A. Drozdov, and Y. A. Belousov, *IEEE Sens. J.*, **19**, 7365–7372 (2019).
14. J. S. Kim, M. G. Choi, Y. Huh, M. H. Kim, S. H. Kim, S. Y. Wang, and S.-K. Chang, *Bull. Korean Chem. Soc.*, **27**, 2058–2060 (2006).
15. K. P. Wang, Y. Lei, J. P. Chen, Z. H. Ge, W. Liu, Q. Zhang, and Z. Q. Hu, *Dyes Pigm.*, **151**, 233–237 (2018).
16. H. Park and S. Chang, *Dyes Pigm.*, **122**, 324–330 (2015).
17. P. R. Sahoo, K. Prakash, A. Kumar, and S. Kumar, *Chemistry Select*, **2**, No. 21, 5924–5932 (2017).
18. A. N. Chebotarev, D. V. Snigur, Yu. P. Zhukova, E. V. Bevzyuk, Ya. I. Studenyak, and Ya. R. Bazel′, *Zh. Obshch. Khim.*, **87**, No. 2, 216–224 (2017) [A. N. Chebotarev, D. V. Snigur, Yu. P. Zhukova, K. V. Bevziuk, Ya. I. Studenyak, and Ya. R. Bazel, *Russ. J. Gen. Chem.*, **87**, No. 2, 196–203 (2017)].
19. D. V. Snigur, A. N. Chebotarev, and E. V. Bevzyuk, *Zh. Prikl. Spektrosk.*, **85**, No. 1, 27–32 (2018) [D. V. Snigur, A. N. Chebotarev, and K. V. Bevziuk, *J. Appl. Spectrosc.*, **85**, No. 1, 21–26 (2018)].
20. A. Shokrollahi and E. Zare, *J. Mol. Liq.*, **219**, 1165–1171 (2016).
21. A. N. Chebotarev, D. V. Snigur, and E. V. Bevzyuk, *Metody Ob'ekty Khim. Anal.*, **12**, No. 2, 76–84 (2017).
22. V. M. Ivanov, O. V. Monogarova, and K. V. Oskolok, *Zh. Anal. Khim.*, **70**, No. 10, 1011–1025 (2015) [V. M. Ivanov, O. V. Monogarova, and K. V. Oskolok, *Russ. J. Anal. Chem.*, **70**, No. 10, 1165–1178 (2015)].
23. A. V. Kulinich and A. A. Ishchenko, *Usp. Khim.*, **78**, No. 2, 151–175 (2009) [A. V. Kulinich and A. A. Ishchenko, *Russ. Chem. Rev.*, **78**, No. 2, 141–164 (2009)].
24. Yu. P. Zhukova and Ya. I. Studenyak, *Nauk. Visn. Uzhgorod. Univ., Ser. Khim.*, **34**, No. 2, 40–44 (2015).
25. Yu. Zhukova, Ya. Studenyak, L. Fetjko, and D. Pogan, *Nauk. Visn. Uzhgorod. Univ., Ser. Khim.*, **39**, No. 1, 45–51 (2018).