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Absorption, fluorescence, and acid-base equilibria of rhodamines in micellar media of sodium dodecyl sulfate

Elena N. Obukhova [a], Nikolay O. Mchedlov-Petrossyan [b,*], Natalya A. Vodolazkaya [b], Leonid D. Patsenker [a], Andrey O. Doroshenko [b], Andriy I. Marynin [c], Boris M. Krasovitskii [a,1]

[a] Scientific-Technological Complex 'Institute for Single Crystals' of the National Academy of Sciences of Ukraine, Kharkov 61001, Ukraine
[b] Kharkov V.N. Karazin National University, Kharkov 61022, Ukraine
[c] National University of Food Technologies, Kiev 01601, Ukraine

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ABSTRACT

Rhodamine dyes are widely used as molecular probes in different fields of science. The aim of this paper was to ascertain to what extent the structural peculiarities of the compounds influence their absorption, emission, and acid-base properties under unified conditions. The acid-base dissociation ($HR^+ \rightleftarrows R + H^+$) of a series of rhodamine dyes was studied in sodium *n*-dodecylsulfate micellar solutions. In this media, the form R exists as a zwitterion $R^{\pm}$. The indices of apparent ionization constants of fifteen rhodamine cations HR^+ with different substituents in the xanthene moiety vary within the range of $pK_a^{app} = 5.04$ to 5.53. The distinct dependence of emission of rhodamines bound to micelles on pH of bulk water opens the possibility of using them as fluorescent interfacial acid–base indicators.

1. Introduction

In this paper, we report new data on the absorption, fluorescence, and the acid ionization constants of a series of rhodamine dyes in micellar solutions of sodium *n*-dodecylsulfate, SDS.

Due to their unmatched fluorescent properties, rhodamine dyes are constantly and widely used in various branches of chemistry and related sciences. Several reviews reflect the further progress in application of these compounds and creating new rhodamines and some relative dyes [1–4]. Recently, a new class of highly emissive and rather unusual rhodamine dyes has been proposed by Kamino et al. [5,6].

Within the past decade, rhodamine dyes have been used for studying polyelectrolyte solutions [7–9] and reverse micelles [10], as components of the polyamido acid-based Langmuir–Blodgett films [11], and as interfacial indicators for the liquid-liquid interface [12]. Rhodamines have been also used to create pH-sensitive hydrogels [13] and mercury(II) chemosensors [14], for DNA recognition [9] and monitoring of the mitochondrial membrane potential [15], and as molecular thermometer for nanoparticles for optical hyperthermia [16], and for creating the fluorescent images of core-shell magnetic nanoparticles used in hyperthermia therapy [17].

The above references are only few examples of versatile utilizations of rhodamines. Some other applications have been mentioned in our previous paper, where the behavior of rhodamine B (**1**) in micellar media has been studied [18]. This dye is a representative of rhodamines with the free COOH group, which dissociates in aqueous solutions with $pK_a^w = 3.22$ [18].

$$HR^+ \rightleftarrows R + H^+ \quad (1)$$

Such dyes may exist as cation, HR^+, zwitterion, $R^{\pm}$ (both colored and fluorescent), and γ-lactone, R^0 (colorless, non-fluorescent), depending on pH and solvent nature. The structures are presented in Scheme 1.

The lactonic tautomer R^0 of the neutral form is stabilized and predominates in aprotic (or, more precise, not hydrogen bond donor) solvents [3,19,20]. In water, the fraction of R^0 species of rhodamine B is too small to be registered experimentally; indirect estimates lead to the value of $[R^0] / [R^{\pm}] \approx 0.005–0.01$ [20].

Importantly, both absorption and excitation spectra of the species $R^{\pm}$ and HR^+ in water and water-rich mixed solvents are rather similar. In pure water, the $\lambda_{max}{}^{abs}$ values are 553 nm and 557 nm respectively, whereas the molar absorptivities practically coincide (108×10^3 mol^{-1} L cm^{-1}). The formation of the colorless tautomer is much more expressed for the lactams, which cationic form possesses the group CONHZ instead of COOH [14,21,22]. Naturally, if the carboxylic group of rhodamines is esterified, the lactonization becomes impossible.

The state of protolytic equilibrium of rhodamines with free (non-esterified) carboxylic function is important for their behavior in various media. For instance, it is of key significance for light emission processes [3,5,16,22], for behavior of the dyes in polyelectrolyte and DNA

* Corresponding author.
E-mail address: mchedlov@univer.kharkov.ua (N.O. Mchedlov-Petrossyan).
[1] Deceased.

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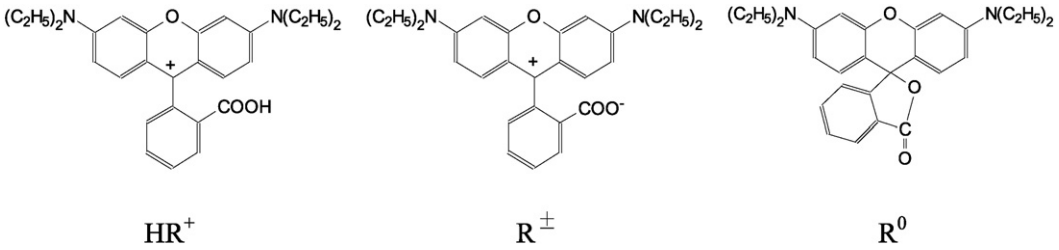


Scheme 1. Rhodamine B (**1**) cation HR^+ and the two tautomers of the neutral form R: $R^{\pm}$ and R^0.

solutions [7–9], in silicate layers [23], and on toluene–water interface [12], as well as for the control of the photocatalytic degradation of rhodamines on solid catalysts [24].

On the other hand, a huge number of rhodamines were synthesized and proposed for different applications in analytical chemistry, biochemistry, biomedicine, etc. [25,26]. Therefore, it is necessary to reveal to what degree the structural modification of the xanthene moiety affects the acidity of the COOH group in the phthalic acid residue.

Earlier we have studied the ionic equilibria of rhodamine B and several other rhodamines in aqueous [27] and organic [20] media, as well as in aqueous micellar solutions of surfactants [18,28–30]. The aim of this study was to reveal the peculiarities of photophysical and protolytic properties of a series of rhodamine dyes in micellar solutions of SDS, which can be regarded as (reduced) models of more complicated colloidal biomolecular solutions. Such micellar system, being a well-defined reaction medium, may serve for better understanding of the behavior of rhodamines at various charged interfaces.

2. Experimental

2.1. Synthesis

The cationic forms of the dyes are shown in Scheme 2.

Non-symmetrical rhodamine dyes **2**, **4**–**6** and **8**–**11** containing various substituents in 3 and 6 positions were synthesized by a condensation of hydroxyjulolidine-benzoylbenzoic acid or benzoylbenzoic acid derivatives with correspondent *m*-X_2N-phenol in 75–80% sulfuric acid. Symmetrical rhodamine dyes **3** and **7** were synthesized by fusion of phthalic acid anhydride with *m*-dimethylaminophenol, *m*-diethylaminophenol, or 8-hydroxyjulolidine followed by treatment of the resulted melt with concentrated hydrochloric acid. Further neutralization of the obtained solutions with 20% aqueous NaOH yielded crystalline products, which were column purified (Silica gel 60).

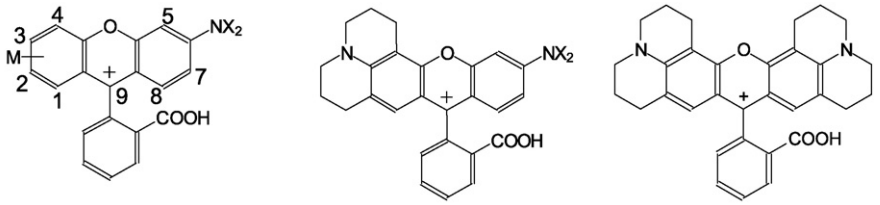
The purity of the dyes was verified by the synchronous fluorescence spectroscopy. More detailed synthetic protocols are given in Supplementary data. The dyes have been introduced into the solutions in molecular (zwitterionic or lactonic) forms. Only the solid samples of dyes **9** and **1** were almost colorless, i.e., mainly in the form of lactones, whereas other were colored.

2.2. Materials

Hydrochloric, acetic and phosphoric acids and borax were analytical-grade reagents. Sodium chloride was purified by re-crystallization from aqueous ethanol. The standard sodium hydroxide solution was prepared using CO_2-free water and was protected from the atmosphere. The sample of SDS (purity: 99%) purchased from Sigma-Aldrich was used without further purification.

2.3. Apparatus

The absorption spectra were measured using the SF-46 apparatus in 1 or (in rare instances) 5 cm cells at 25.0 ± 0.1 °C. The determination of pH was performed at 25.0 ± 0.1 °C using ESL-63-07 glass electrode and an Ag|AgCl reference electrode in a cell with liquid junction (1 mol L^{-1} KCl). A compensation scheme with P 37-1 potentiometer and pH-121 pH-meter as a nil instrument was used. Standard buffers with pH = 1.68, 4.01, 6.86, and 9.18 were used for cell calibration. The fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorometer. The fluorescence decay kinetics was measured on a nanosecond pulse fluorometer, see description of experimental setup and data treatment in ref. [31]. The particle size distribution was determined via dynamic light scattering (DLS) using Zetasizer Nano ZS Malvern Instruments, scattering angle 173°; each measurement was made by 42 runs and repeated 9 to 15 times. The zeta-potential values were determined at scattering angle 13°.



X = Et, M = 3-NEt_2 (**1**);
X = Et, M = 3-NMe_2 (**2**);
X = Me, M = 3-NMe_2 (**3**);
X = Et, M = 3-NH_2 (**4**);
X = Et, M = 3-NH_2-benzo[c] (**8**);
X = Et, M = 1.2-benzo (**9**);
X = Et, M = 2-NH_2 (**10**);
X = Et, M = 3-Cl (**11**).

X = Et (**5**); Me (**6**)

(**7**)

Scheme 2. The investigated rhodamines in their cationic forms.