

# A novel probe for determination of electrical surface potential of surfactant micelles: *N,N'*-di-*n*-octadecylrhodamine

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**ABSTRACT:** The peculiarities of the structure of the fluorescent dye *N,N'*-di-*n*-octadecylrhodamine advantage its using as an interfacial acid–base probe in aqueous micellar solution of colloidal surfactants. Two long hydrocarbon tails of the dye provide similar orientation of both cation and zwitterion on the micelle/water interface, with the ionizing group COOH exposed to the Stern region in all the systems studied. Further, the charge type of the acid–base couple,  $A^+B^\pm$ , ensures similar values of the ‘intrinsic’ contribution,  $pK_a^i$ , to the ‘apparent’  $pK_a^a$  value in micelles of different surfactants. This makes the indicator suitable for determination of electrical surface potentials,  $\Psi$ . The  $pK_a^a$ s have been obtained in cationic, anionic, zwitterionic, and nonionic surfactant systems, at various salt background. In total 17 systems were studied. At bulk counterion concentration of ca. 0.05 M, the  $pK_a^a$  values vary from  $2.14 \pm 0.07$  in  $n\text{-C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  micelles to  $5.48 \pm 0.06$  in  $n\text{-C}_{16}\text{H}_{33}\text{OSO}_3^-\text{Na}^+$  micelles. The  $\Psi$  values, corresponding to the Stern region of micelles, have been evaluated as  $\Psi = 59.16 (pK_a^i - pK_a^a)$  for  $T = 298.15$  K. The  $pK_a^i$  parameter was equated to the average value of 4.23 in nonionic surfactants (4.12–4.32, depending on the surfactant type). For cetyltrimethylammonium bromide and sodium *n*-dodecylsulfate micelles, the  $\Psi$  values ( $\pm(7\text{--}11)$  mV) appeared to be +118 mV and at bulk  $\text{Br}^-$  concentration 0.019 M and  $-76$  mV at bulk  $\text{Na}^+$  concentration 0.020 M, respectively. This satisfactorily agrees with the theoretical values +111 and  $-84$  mV, estimated using the Oshima, Healy, and White equation for these well-defined colloidal systems. Finally, not only absorption, but also fluorescence spectra display the same response to changes in bulk pH. Copyright © 2007 John Wiley & Sons, Ltd. *Supplementary electronic material for this paper is available in Wiley InterScience at <http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/v20.html>*

**KEYWORDS:** surfactant micelles; *N,N'*-di-*n*-octadecylrhodamine; vis absorption; fluorescence; apparent ionization constant; electrical surface potential

## INTRODUCTION

The aim of this study is to involve the fluorescent dye *N,N'*-di-*n*-octadecylrhodamine into the set of presently used lipophilic interfacial acid–base indicators, to apply this substance to  $\Psi$  determinations, and to compare the results with the data obtained with common indicators.

The interfacial reactivity and photophysics of different substances is often connected with the problem of interfacial acidity.<sup>1</sup> The latter term can be understood both as interfacial pH values and as acid–base properties of substances located on the surface. The simplest, though somewhat reduced models of interfacial regions as media for protolytic conversions are the surfaces of surfactant

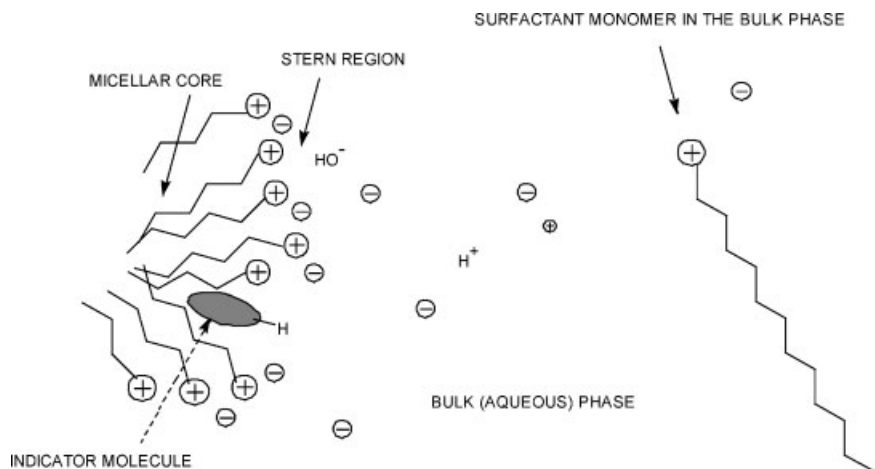
micelles. A touchstone for understanding the problem is the study of the behavior of acid–base indicators, including fluorescing dyes.<sup>1c–g,2</sup>

The key characteristic of the acid–base indicator couple completely bound by a micelle (Chart 1) is the so-called ‘apparent’ ionization constant,  $K_a^a$ , of the acid–base indicator HR ( $pK_a^a \equiv -\log K_a^a$ ):<sup>1c,d,2a–d</sup>

$$\begin{aligned} pK_a^a &= pK_a^w + \log \frac{\gamma_R}{\gamma_{HR}} - \frac{\Psi F}{RT \ln 10} \\ &= pK_a^i - \frac{\Psi F}{RT \ln 10} \end{aligned} \quad (1)$$

Here  $K_a^w$  is the ionization constant in water,  $K_a^i$  is the so-called ‘intrinsic’ ionization constant,  $\gamma$  are the activity coefficients of transfer of corresponding species from water to micellar pseudophase,  $\Psi$  is the electrical surface potential (as a rule, regarded as the potential of

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**Chart 1.** A schematic picture of micelle/water interface with an embedded indicator dye (cationic surfactant micelle is chosen as an example)

Stern layer),  $F$  is the Faraday constant,  $R$  is the gas constant,  $T$  is the absolute temperature. The common electrostatic model of acid–base indicators ionization in micelles, based on Eqn (1), is certainly adequate in outline.

Equation (1) can be derived, assuming that the partition of all the species  $i$  with charge  $z_i$  between the phases can be described by Eqn (2):<sup>1c,3</sup>

$$\frac{a_{i,m}}{a_{i,w}} = \gamma_i^{-1} \exp\left(\frac{-z_i \Psi F}{RT}\right) \quad (2)$$

Here  $a_i$  are activities, suffixes m and w denote micellar pseudophase and aqueous (bulk) phase, correspondingly. The  $\Psi$  value is supposed to be the same for both indicator species. To a first approximation,  $\Psi$  is the electrical potential of the Stern layer, and the  $\gamma_i$  values correspond to the transfer from the infinitely diluted solution in water to the Stern layer.

Having the  $\Psi$  value, it is possible to predict the difference between the pH value of the bulk (continuous, aqueous) phase and the interfacial value,  $\text{pH}_m \equiv -\log a_{\text{H}^+}^m$ :

$$\text{pH}_m = \text{pH} + \log \gamma_{\text{H}^+} + \frac{\Psi F}{RT \ln 10} \quad (3)$$

However, it must be kept in mind, that the activity coefficient of transfer of the hydrogen ion from water to micellar pseudophase,  $\gamma_{\text{H}^+}$ , is a quantity of extrathermodynamic character. Some authors omit the term  $\log \gamma_{\text{H}^+}$  at all.<sup>1d,2d,i</sup>

The  $\text{p}K_a^a$  values of indicators completely bound by ionic micelles, membranes, etc., may be used to monitor the electrical potential of the charged surface,  $\Psi$ , if correct evaluation of  $\text{p}K_a^i$  is possible.<sup>1c,d,2,3</sup> And really, from Eqn (1), it can be easily derived:  $\Psi = (RT \ln 10 / F)(\text{p}K_a^i - \text{p}K_a^a)$ . However, the more number of indicator dyes are involved into the determination of  $\Psi$ , the stronger discrepancies became evident.<sup>1c,d,2-4</sup> The main assumptions of the electrostatic model in its

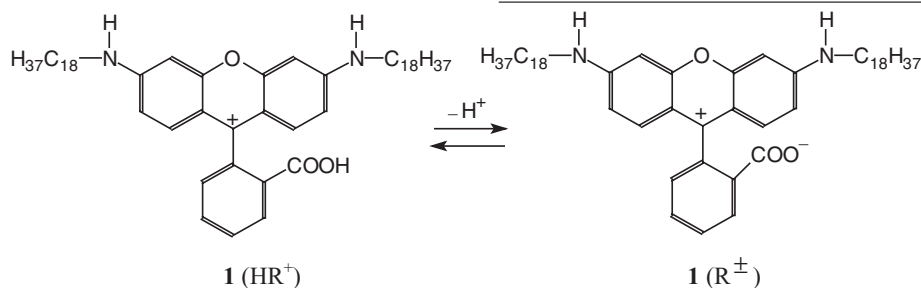
simple form are proved to be mostly justified only approximately and sometimes are even invalid. They are: (i) the constancy of the  $\text{p}K_a^i$  value of the given indicator in any micellar system and (ii) the constancy of the electrical potential of Stern layer  $\Psi$  of the given surface as obtained by using any indicator. The analysis of data demonstrates that the  $\Psi$  values in a fixed micellar system determined by using a set of indicator dyes can differ up to  $\approx 200 \text{ mV}$ .<sup>3a,c,5</sup>

Furthermore, we have demonstrated that the improvements of the model, for example, the methods of  $\text{p}K_a^i$  estimation, up to now proposed in literature, are rather arbitrary and open to criticism.<sup>3c,5</sup> The validity of the traditional electrostatic model [Eqn (1)] was tested using micellar solutions of over 20 colloidal surfactants as media for protolytic reactions.<sup>3c</sup> Powerful differentiating impact of micelles, caused first of all by the miscellaneous character of any micellar surface, seems to be the main hindrance to exact evaluations of the interfacial electrical potential of micelles by means of acid–base indicators.<sup>3a,c</sup> (In this context, the term ‘differentiating’ reflects non-equivalent changes in  $\text{p}K_a$  of an indicator on going from water to micelles.) Different character of location of indicator species in various micelle/water interfaces can contribute to the  $\text{p}K_a^i$  alteration.<sup>2c,h,3c-e</sup>

Recently we revealed that the well-known fluorescent dye rhodamine B possesses some advantages as an acid–base probe ( $\text{HR}^+ \rightleftharpoons \text{R}^\pm + \text{H}^+$ ).<sup>6</sup> Namely, the orientation of both cationic and neutral (zwitterionic) species on the micelle/water interface seems to be similar in micelles of anionic and nonionic surfactants. Besides, the charge type of acid–base couple of this indicator,  $\text{A}^+ \text{B}^\pm$  (in terms proposed by Kolthoff<sup>7</sup>), favors relative constancy of  $\text{p}K_a^i$  in micelles of different surfactants. Hence, the indicators of such type seem to be rather promising as tools for  $\Psi$  determination.

However, in solutions of cationic surfactants, contrary to the case of anionic or even nonionic ones, the binding of rhodamine B species to the micelles is far from being complete.

In this paper, we report the results of examination of another rhodamine dye, *N,N*-di-*n*-octadecylrhodamine, or DODR, (**1**) in form of  $\text{HR}^+\text{Cl}^-$ , which is tightly embedded in the micelles due to its long hydrophobic tails:



For such a strongly hydrophobic cationic dye, it is possible to determine the  $\text{p}K_a^a$  value even in cationic micelles. Moreover, the existence of two long hydrocarbon chains allows expecting the position of the probe on the surface of any ionic micelle as shown in Chart 2. The real picture can be considered as an equilibrium mixture of these two limiting positions (with unknown weight), presented in Chart 2, or, more realistic, as something average between them. In fact, the charge type of the acid–base couple in this case is also  $\text{A}^+\text{B}^\pm$ .

Rhodamine B and its derivatives and analogs are extensively used in biochemical and biomedical studies,<sup>8</sup> for instance, for site-selective labeling of a cysteine side chain of a muscle protein,<sup>8b</sup> for bioconjugation with 2'(3')-*O*-[*N*-(2-aminoethy)-carbamoyl]ATP,<sup>8c</sup> as a mitochondrial probe for measurement and monitoring of mitochondrial membrane potential in drug-sensitive and drug-resistant cells,<sup>8d</sup> and for many other purposes.<sup>8a</sup> The behavior of several hydrophobic rhodamines, especially their photophysical properties, in various environments are quantitatively studied by many authors. Namely, nanosized dispersions<sup>9</sup> such as surfactant micelles<sup>9a–c</sup> and silica hydrosols,<sup>9d</sup> water/air and water/hydrocarbon interfaces,<sup>1b,10</sup> as well as supramolecular systems<sup>11</sup> such as Langmuir–Blodgett films,<sup>11a–b</sup> functionalized cyclodextrines,<sup>11c</sup> and dendrimers<sup>11d</sup> have been examined as media for rhodamine dyes. Now we report the  $\text{p}K_a^a$  values of dye **1** in micellar solutions of different type of

surfactants and demonstrate the possibility of  $\Psi$  estimation.

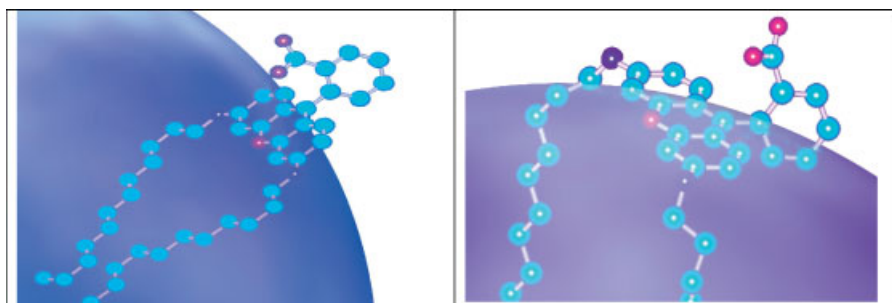
Basing on the visible spectra (Fig. 1), we attribute the ionization constant to the conversion of the cation into the zwitterion. And really, formation of colorless lactone  $\text{R}^\circ$

in such water-rich systems as direct micelles of surfactants are, is less probable.<sup>6,12</sup> Of course, relatively weak resolution of the bands of  $\text{HR}^+$  and  $\text{R}^\pm$  species requires very careful determination of the  $\text{p}K_a^a$ s, but the results appeared to be quite reproducible. Besides, the situation is somewhat similar<sup>2d–f</sup> in the case of the standard coumarin indicators used for the same purpose.

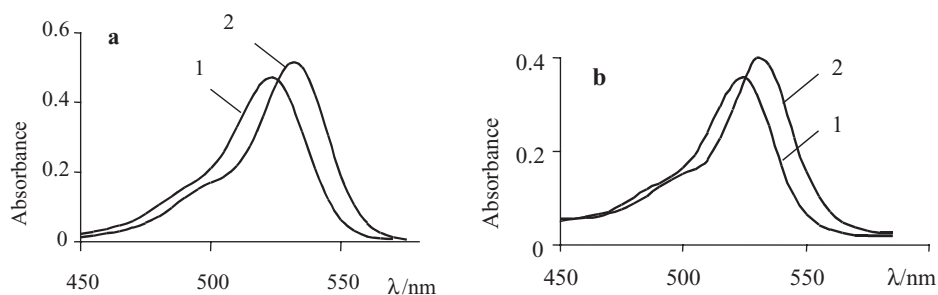
## EXPERIMENTAL

### Chemicals

The dye was synthesized by condensation of 3,6-dichlorofluorane with *n*-octadecylamine, as described in literature.<sup>13</sup> The sample was purified by column chromatography and characterized by <sup>1</sup>H NMR and elemental analysis. The purity was also confirmed using TLC (Silufol plates). The following surfactants samples were purchased from Sigma: cetyltrimethylammonium bromide, CTAB (purity 99%), sodium *n*-dodecylsulfate, SDS (99%), *N*-cetyl-*N,N*-dimethylammonium propane sulfonate (CDAPS), and nonionic surfactants Brij 35, Triton-X 100, and TWEEN 80. The samples of *n*-octadecyltrimethylammonium chloride, OTAC (Fluka, >98%) and sodium cetylsulfate, SCS (Shostka plant of chemicals, Ukraine) were kindly put to our disposal by



**Chart 2.** Possible positions of DODR on micelle/water interface (in this schematic picture, two limiting positions are depicted)



**Figure 1.** Visible absorption spectra of neutral (1), and cationic (2) DODR species; (a): in 88 mass % aqueous ethanol, 0.01 M NaOH, and 0.063 M HCl, correspondingly; (b): in CDAPS micellar solution (0.001 M), pH = 9.2 (borate buffer solution), and 0.063 M HCl, correspondingly

Professor S. N. Shtykov (Saratov State University, Russia). All the surfactants were used without further purification. Organic solvents were purified according to conventional procedures. Hydrochloric, acetic, and phosphoric acids, borax, potassium chloride, and sodium bromide were analytical-grade reagents; sodium chloride was additionally purified by re-crystallization. The standard sodium hydroxide solution, used for preparation of buffer mixtures, was obtained from saturated carbonate-free NaOH solution using CO<sub>2</sub>-free water and kept protected from the atmosphere.

## Procedure

Absorption spectra of the dye solutions were measured using SF-46 apparatus (Russia), against solvent blanks. pH determinations were performed at 298.15, 303.15, and 323.15 K ( $\pm 0.10$  K) with a P 37-1 potentiometer and pH-121 pH-meter equipped with ESL-63-07 glass electrode and an Ag/AgCl reference electrode in a cell with liquid junction (1 M KCl).<sup>14</sup> Standard buffers (pH 1.68, 4.01, 6.86, and 9.18) were used for cell calibration at 298.15 K; the pH values of these buffer solutions at 303.15 and 323.15 K were taken from literature.<sup>7</sup> The fluorescence spectra were determined on Hitachi F 4010 fluorometer. The fluorescence decay was studied on a nanosecond pulse fluorometer, and then mathematically treated with the Demas and Adamson phase plane method.<sup>15</sup>

The stock solutions of surfactants were prepared by dissolving weighted amounts of substances in appropriate amounts of water. The nearly transparent working solutions were prepared by the volume method, taking aliquots of stock solutions at corresponding temperatures. The dye was dissolved in stock surfactant solutions and diluted together with the surfactant; the stability of stock dye-surfactant solutions within several days was checked by their absorption spectra after dilution. In the case of TWEEN 80, the stock solution of the dye was prepared in 95.6 mass % aqueous ethanol. All spectra were referenced against solvent blanks containing all components except dyes. Suitable pH values of solutions were created by HCl

or HBr (pH  $\leq 3.5$ ) and by mixtures of sodium acetate (0.01 M) with acetic acid (pH  $\leq 5.8$ ). The theoretically calculated pH values typically coincided with the measured values ( $\pm 0.02$  units) both in the presence and in the absence of surfactants.<sup>14</sup> Higher pH values were obtained using phosphoric acid + NaOH mixtures, borate buffers, or diluted sodium hydroxide. The required ionic strength was maintained by additions of NaCl, KCl, or KBr. Some experiments were performed in HBr + KBr mixtures (total concentration 0.005 M) and in acetate buffer solutions with 0.005 M CH<sub>3</sub>COONa + acetic acid, without NaCl or KBr addition. The sequence of adding stock solutions did not affect the results.

The  $pK_a^a$  values were determined spectrophotometrically according to the standard procedure; as a rule, the dye concentrations were about  $(1-1.5) \times 10^{-6}$  M. Thus, the molar ratio surfactant : dye is  $\geq 10^3$ . The following equation was used for calculations:

$$pK_a^a = \text{pH} + \log \frac{A_R - A}{A - A_{HR^+}} \quad (4)$$

where  $A$  is the absorbance at the current pH at chosen wavelength and constant dye concentration, and  $A_R$  and  $A_{HR^+}$  are absorbances under conditions of complete transformation of the dye into the correspondent form (R, HR<sup>+</sup>).

## RESULTS AND DISCUSSION

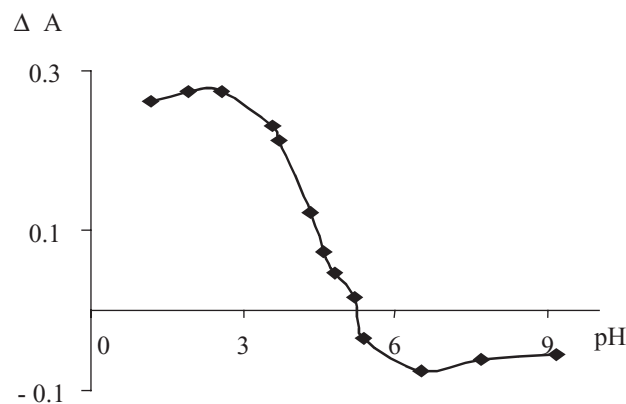
### Determination of apparent ionization constants

An example of the absorption spectra of the cationic (acid) and the neutral (basic) forms in 88 mass % aqueous ethanol and in micellar systems is presented in Fig. 1; a similar resolution of the bands is observed in all the systems studied.

The spectra of dye **1** were also examined in aqueous media, at pH 1.2 (HCl) and 12 (NaOH), with various contents of ethanol. If the concentrations of alcohol are low, for example, 2%, the dye precipitates rapidly.<sup>14</sup>

The number of working solutions used for each  $pK_a^a$  determination was 5–7. Though 11 wavelengths within the range 500–550 nm were used as analytical positions, the differences of  $A$  at 535–550 nm and 510–520 nm were utilized for final calculations because the dependence of such function versus pH is more pronounced. The ‘titration’ curve is typified in Fig. 2. The  $pK_a^a$  values were determined with confidence interval  $\pm(0.01–0.09)$ . The results were little temperature-dependent. The data obtained with two samples of dyes, synthesized separately within several years, demonstrate satisfactory reproducibility.

The protonation of nitrogen atom, resulting in dication  $H_2R^+$  formation and strong decrease in the principle absorption band intensity, is typical for rhodamine B in water, at  $pH \leq 1.5$ <sup>14</sup> and the absorbance of  $HR^+$  species cannot be measured directly.<sup>14</sup> However, this effect is suppressed in micellar solutions of anionic surfactants,<sup>3c,5,6</sup> despite the classical Hartley’s rules. The reason is the specificity of the charge type  $A^{2+} B^+$ : the shift of the equilibria  $H_2R^{2+} \rightleftharpoons HR^+ + H^+$  toward the right (i.e., the decrease in the corresponding  $pK_a$  value), numerous registered in organic solvent and water–organic mixtures, overcomes the expected stabilization of



**Figure 2.** The dependence of the  $\Delta A$  function of DODR on pH; 0.01 M SDS solution, 0.3 M NaCl, optical cell 5 cm;  $\Delta A = A^{535} + A^{540} + A^{545} - A^{510} - A^{515} - A^{520}$  (the super-scripts denote the wavelength where the absorbance,  $A$ , is measured)

the dication in SDS micelles.<sup>5</sup> And really, at least up to  $pH = 0.5$ , the absorbance stays constant (Fig. 2). The more so, further protonation of  $HR^+$  species of dye **1** is hindered in micelles of nonionic and cationic surfactants.

The determined  $pK_a^a$  values are compiled in Table 1. The dye molecules are certainly isolated from each other

**Table 1.** The  $pK_a^a$  values of the cation  $HR^+$  of DODR (**1**) in different aqueous surfactant solutions

Surfactant	$C_s$ , M	Salt background, M <sup>a</sup>	$T$ , K	$\lambda_{max}^{abs}$ , nm (dye <b>1</b> )		$pK_a^a$	
				$HR^+$	R	dye <b>1</b>	dye <b>3</b> <sup>b</sup>
$n-C_{16}H_{33}N(CH_3)_3^+Br^-$	0.05	0.005 <sup>c</sup>	298	533	526	$2.24 \pm 0.02$	—
$n-C_{16}H_{33}N(CH_3)_3^+Br^-$	0.01	0.05	298	532	526	$2.50 \pm 0.08$	—
$n-C_{16}H_{33}N(CH_3)_3^+Br^-$	0.01	0.05 <sup>c</sup>	298	532	526	$2.53 \pm 0.04$	—
$n-C_{16}H_{33}N(CH_3)_3^+Br^-$	0.01	0.40 <sup>c</sup>	298	533	526	$3.32 \pm 0.01$	—
$n-C_{18}H_{37}N(CH_3)_3^+Cl^-$	0.003	0.05	303	532	526	$2.14 \pm 0.07$	—
$n-C_{16}H_{33}N(CH_3)_3^+Br^-$	0.01	4.00 <sup>d</sup>	298	534	526	$3.94 \pm 0.09$	—
$n-C_{16}H_{33}N^+(CH_3)_2(CH_2)_3SO_3^-$	0.001	0.05	298	531	523	$3.60 \pm 0.09$	3.58 <sup>e</sup>
TWEEN 80	0.01	0.05	298	531	525	$4.32 \pm 0.02$	4.17 <sup>f</sup>
Triton-X 100	0.01	0.05	298	532	524	$4.25 \pm 0.02$	4.15
Brij 35	0.01	0.05	298	530	524	$4.12 \pm 0.02$	4.10
$n-C_{16}H_{33}OSO_3^-Na^+$	0.01	0.05	323	534	528	$5.48 \pm 0.06$	5.49 <sup>e,g</sup>
$n-C_{12}H_{25}OSO_3^-Na^+$	0.05	0.005 <sup>h</sup>	298	533	529	$5.52 \pm 0.07$	5.70 <sup>i</sup>
$n-C_{12}H_{25}OSO_3^-Na^+$	0.01	0.05	298	532	528	$5.21 \pm 0.09$	5.32 <sup>j</sup>
$n-C_{12}H_{25}OSO_3^-Na^+$	0.10	0.05 <sup>k</sup>	298	532	528	$5.06 \pm 0.06$	5.13 <sup>l</sup>
$n-C_{12}H_{25}OSO_3^-Na^+$	0.01	0.20	298	532	528	$4.68 \pm 0.01$	4.75
$n-C_{12}H_{25}OSO_3^-Na^+$	0.01	0.30	298	532	528	$4.46 \pm 0.06$	4.67 <sup>m</sup>
$n-C_{12}H_{25}OSO_3^-Na^+$	0.01	0.40	298	532	528	$4.41 \pm 0.05$	4.50

<sup>a</sup> Initial ionic strength of the buffer system; maintained by NaCl additives to buffer mixtures or HCl solutions, unless otherwise indicated.

<sup>b</sup> From Ref. 6, unless otherwise indicated.

<sup>c</sup> HBr + KBr.

<sup>d</sup> KCl.

<sup>e</sup> From Ref. 16.

<sup>f</sup> For dye **2**:  $pK_a^a = 4.29 \pm 0.02$ .<sup>17</sup>

<sup>g</sup> ( $\pm 0.05$ ).

<sup>h</sup> Acetate buffers with constant  $CH_3COONa$  concentration and varying  $CH_3COOH$  concentrations.

<sup>i</sup> At 0.01 M SDS and 0.01 M (NaCl + acetate buffer) solution.

<sup>j</sup> At  $[Na_w^+] = 0.054$  M for dye **2**  $pK_a^a = 5.26 \pm 0.04$ .<sup>17</sup>

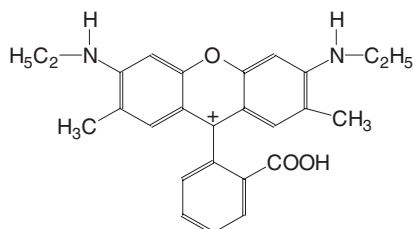
<sup>k</sup> The true bulk value of  $[Na_w^+]$  is 0.077 M, taking into account the degree of SDS dissociation in micelles.

<sup>l</sup> This value refers to  $C_s = 0.01$  M and  $[Na_w^+] = 0.077$  M.

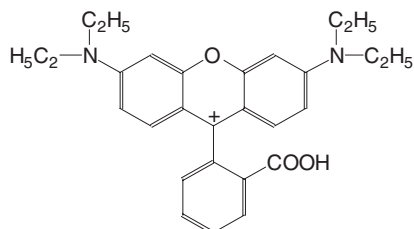
<sup>m</sup> Determined in the present study.

in micelles because under experimental conditions the number of micelles is (10–100)-fold or even more higher than that of dye molecules. The stability of solutions confirms the complete binding of the dye to micelles; in pure water, the dye is insoluble (see above).

The  $pK_a^a$  values of rhodamine 19 (**2**) and rhodamine B (**3**) in micellar solutions of nonionic, zwitterionic, and anionic surfactants agree well with those for dye **1**; in the mentioned systems, the completeness of binding of the species  $HR^+$  and  $R$  of dyes **2** and **3** by micelles was proved by special experiments.<sup>6</sup>



**2** ( $HR^+$ )



**3** ( $HR^+$ )

The data presented in Table 1 demonstrate an adequate response of the  $pK_a^a$  values of dye **1** to the charge and  $\Psi$  sign of the micellar surface as well as to the bulk counterion concentration. Salt effects in SDS micellar solutions, that is, variations in  $pK_a^a$  of probe **1** caused by addition of supporting electrolyte (NaCl), are similar to those for rhodamine B (**3**). For the last-named the linear plot  $\{pK_a^a = (4.21 \pm 0.07) - (0.83 \pm 0.09)\log[Na_w^+]\}$  is valid with regression coefficient 0.998.<sup>6</sup> The slopes of such dependences for five different indicators vary from 0.73 to 0.92.<sup>3b</sup> The data for DODR in SDS systems (Table 1) result in following equation:

$$pK_a^a = (4.05 \pm 0.04) - (0.89 \pm 0.05) \log[Na_w^+] \quad (5)$$

$(r = -0.997, n = 6)$

If the (hypothetical)  $pK_a^w$  value of water-insoluble dye **1** is equated to that of soluble analogs **2** and **3**, then the 'medium effects', that is,  $\Delta pK_a^a = pK_a^a - pK_a^w$ , can be found. The thermodynamic  $pK_a^a$  value of dye **3** is equal to 3.22.<sup>6</sup> The value of  $3.34 \pm 0.04$  was determined by us for dye **2** at ionic strength 0.05 M (HCl + NaCl); the thermodynamic value is 3.26. The mean value for dyes **2** and **3** is 3.24. Hence, in 0.01 M CTAB, 0.01 Brij 35, and 0.01 M SDS solutions, at initial ionic strength of buffers 0.05 M,  $\Delta pK_a^a = -0.71, +0.99, \text{ and } +1.97$ , correspondingly. In 0.05 M CTAB and SDS solutions, with 0.005 M initial ionic strength of buffers,  $\Delta pK_a^a = -1.00$  and  $+2.28$ , correspondingly. Thus, these values reflect the acidity alterations of the COOH group of the indicator in different micellar systems.

Our  $\Delta pK_a^a$ s in surfactant micellar solutions appeared to be lower than those of other carboxylic acids available in literature.<sup>18</sup> For 4-octadecyloxy-1-naphthoic acid in

0.05 M CTAB,  $C_{12}E_8$  (or Brij 35) and SDS solutions, the  $\Delta pK_a^a$  values equal 0.15, 2.6, and 4.05, correspondingly,<sup>18a</sup> while for lauric acid in 0.17 M *n*-dodecyl trimethylammonium chloride (bromide),  $C_{12}E_8$ , and SDS, the values are respectively 0.1 (0.9), 1.8, and 2.8.<sup>18b</sup> Hence, all the values are 0.8–2.1 units higher than corresponding ours (see above). As the ionizing group of these acids and that of the dye **1** is the same (carboxylic), this confirms the idea of smaller medium effect for the acid–base couple of  $A^+B^\pm$  charge type as compared with that of  $A^0B^-$ .

The cited literature data have been obtained at low and somewhat indefinite bulk ionic strengths. For precise comparison of the data obtained in ionic surfactant systems at different bulk ionic strength, the exact values of bulk counterion concentrations must be calculated. For instance, in anionic surfactant solutions, for the equilibrium  $[Na_w^+]$  value Eqn (6) is valid:<sup>1f,2f,3,5,6</sup>

$$[Na_w^+] = C_{Na^+} + cmc + \alpha(C_s - cmc) \quad (6)$$

where  $C_{Na^+}$  is the total initial sodium ions concentration in the buffer + NaCl system,  $\alpha$  is the degree of counterion dissociation in micelles,<sup>2f,3,5,6,19</sup> and  $cmc$  is the critical micelle concentration at the given salt background. The  $cmc$  values were taken from literature, and in some cases iterative procedure was used to refine these quantities for the given salt background.<sup>14</sup> Analogously, the  $[Br_w^-]$  concentration in CTAB solutions can be calculated.

For re-calculation of the  $pK_a^a$  values, determined at one  $[Br_w^-]$  or  $[Na_w^+]$  value, to another bulk concentrations of counterions, the slopes  $\partial pK_a^a / \partial \log[Br_w^-] = +0.83^{3c}$  and  $\partial pK_a^a / \partial \log[Na_w^+] = -0.83$  can be used. The latter is the mean value from those for decyl eosin, lipid coumarin, methyl yellow, hexamethoxy red, quinaldine red,<sup>3b</sup> and rhodamine B.<sup>6</sup>

### Determination of electrical surface potential with DODR

Let us consider the results of  $\Psi$  determination of versatile micellar interfaces by applying dye **1** and using the relation  $\Psi = 59.16 (pK_a^i - pK_a^a)$  for 298.15 K [derived from Eqn (1)]. Today, at least seven approaches for  $pK_a^i$

estimation are known. Namely,  $pK_a^i$  was equated to: (1)  $pK_a^a$  of the given indicator in nonionic micelles with oxyethylene hydrophilic portion;<sup>1c,d,2d-g,3a,b</sup> (2)  $pK_a^a$  of the given acid in nonionic micelles with maltoside hydrophilic portion;<sup>20</sup> (3)  $pK_a - \log \gamma_{H^+}$ , where the ionization constant is determined in a chosen water–organic mixture, and  $\gamma_{H^+}$  is the activity coefficient of proton transfer from water to this mixed solvent;<sup>2d,4a-c</sup> (4)  $pK_a^w$ , that is,  $pK_a$  in water;<sup>2c</sup> (5)  $pK_a^w$ , by applying simultaneously two indicators;<sup>2d,21</sup> (6)  $pK_a^a$  in the given ionic micelles, but with extremely high (4–6 M) salt background, strongly screening the interfacial charge;<sup>4a</sup> (7)  $pK_a^a$  of the given indicator in micelles of zwitterionic surfactant, for example, CDAPS.<sup>3c,5</sup> A method, based on utilization of a hydrophobic ‘bi-functional’ indicator ( $H_2R^+ \rightleftharpoons HR \rightleftharpoons R^-$ ), was also proposed.<sup>3c</sup>

All these approaches are more or less approximate, and in several cases their discrepancies became evident.<sup>3c,5</sup> For instance, the application of CDAPS as a standard media for  $pK_a^i$  estimation leads to agreement between the  $\Psi$  values of cationic surfactant micelles, evaluated by using a set of six sulfonephthaleins:  $\Psi = +99 \pm 7$  mV for the *N*-cetylpyridinium chloride at bulk  $Cl^-$  concentration of 0.053 M  $Cl^-$ ,<sup>3c</sup> while using the  $pK_a^a$ s of these dyes in nonionic micelles as  $pK_a^i$ , the  $\Psi$  values vary from +113 to +179 mV. In CDAPS solutions at ionic strength of 0.01 M the value  $\Delta pK_a^a$  of bromothymol blue is found to be equal to 0.90, which is close to the value 0.85, obtained by Mukerjee, Cardinal, and Desai<sup>22</sup> in micellar solutions of another betaine surfactant,  $C_{12}H_{25}N(CH_3)_2^+CH_2CO_2^-$ . However, such application of CDAPS is unfavorable just for indicators with long hydrocarbon tails.<sup>3c</sup>

Screening of the interfacial charge even with 4 M of indifferent electrolyte can be still incomplete.<sup>2e,3c,4c</sup> Moreover, the solutions with extremely high salt concentration, that is, 6 M NaBr, became very viscous;<sup>4a</sup> on the other hand, some surfactants (SDS, *N*-cetylpyridinium chloride) can be salted out from aqueous media.

Equating the  $pK_a^i$  value of an indicator to  $pK_a^w$  means that the  $\gamma_R/\gamma_{HR}$  ratio is unity. Such assumption is in general case invalid.

The  $pK_a^i$  estimation by using water–organic mixtures for mimicking micellar interfacial regions also has some disadvantages. For instance, we have demonstrated,<sup>3c,5</sup> that the satisfactory fitting of the model, reported by several research groups, is reached by using the old-fashioned  $\gamma_{H^+}$  values, while the use of the  $\gamma_{H^+}$  values, calculated by means of the most recognized tetraphenylborate assumption,<sup>23</sup> leads to essentially different  $pK_a^i$  values. The  $\Psi$  values can differ up to ca. 100 mV, depending on the chosen  $\log \gamma_{H^+}$  values.<sup>3c</sup> Probably, powerful differentiating impact of micellar pseudophase on protolytic equilibria of dissolved substances hinders modeling its properties with any water–organic mixture.

Equating of  $pK_a^i$  value (in our designations) of myristic acid to the  $pK_a^a$  value (‘observed’ value) in sugar-derived

surfactants was proposed recently.<sup>20</sup> It must be noted, that some results with acid–base indicators in such surfactant systems have been already published earlier,<sup>22,24</sup> and the possibility of specific interactions between the carboxylic group and hydrophilic alkylglucoside portion of the surfactant was supposed.<sup>24</sup>

The mostly used approach is based on using  $pK_a^a$  values in micelles of nonionic oxyethylated surfactants as  $pK_a^i$ . However, it must be pointed out, that the  $pK_a^a$  values of the given indicator dye in different nonionic micelles never coincide exactly.<sup>3c</sup> The  $pK_a^a$  values of  $HR^+$  cations of dyes **1** and **3** in micelles of three different nonionic surfactants (Table 1) are from this viewpoint rather typical.

Moreover, if cationic indicator dyes are used, then the  $|\Psi|$  values of SDS micelles thus obtained are unlikely low (extremely negative).<sup>3a,4c</sup> This effect was explained by ion pairing between  $DS^-$  and dye cation.<sup>2f,4a,c</sup> Another explanation is based on (expected) strong difference between  $pK_a^i$  in SDS micelles and  $pK_a^a$  in nonionic ones for the charge type of acid–base couple  $A^+B^0$ .<sup>3</sup> And really, the micelle/water interface of anionic micelles is known to be hydrated to much higher degree than those of nonionic and cationic ones. This fact is proved by the values of the normalized Reichardt’s polarity parameter,  $E_T^N$ ,<sup>3a,c,4a</sup> which equals 0.828, 0.687, and 0.693 in SDS, CTAB, and nonionic surfactant micelles, respectively.<sup>3c</sup> Therefore, the decrease in  $pK_a$ , typical for cationic acids on going from water to water–organic mixtures,<sup>7</sup> must be less expressed just in SDS dispersions.

As it was shown above, the ‘medium effect’ for DODR in nonionic micelles is  $\Delta pK_a^a = pK_a^i - pK_a^w \approx 1.0$ , close to that for hydrophobic coumarins with charge type  $A^0B^-$ .<sup>2d,e</sup> Such a positive and relatively low change in  $\gamma_R/\gamma_{HR}$  quantity on transferring of the acid–base couple from water to micellar pseudophase is natural for charge type  $A^+B^\pm$ . In nonionic micelles, indicators with charge type  $A^+B^0$  demonstrate sharp decrease in  $pK_a^a$ , up to  $\Delta pK_a^a = \Delta pK_a^i = -2.1$  for the indicator methyl yellow.<sup>3a</sup> Therefore, it is reasonable to expect that the medium effects for dye **1** are small and therefore more similar in nonionic and ionic micelles than those for indicators with  $A^+B^0$  charge type.

Using the average  $pK_a^a$  value in nonionic micelles, equal to 4.23, as the  $pK_a^i$  value in ionic micelles, the  $\Psi$  values can be evaluated (Table 2).

The values +17 and –11 mV demonstrate the strong screening of surface charge of cationic and anionic micelles by 4.0 M  $Cl^-$  and 0.4 M  $Na^+$ , correspondingly, while the value  $\Psi = +37$  mV calculated using the  $pK_a^a$  of 3.60 in CDAPS micelles may reflect the local electrical potential near the phenylcarboxylic moiety of the dye **1** in zwitterionic micelles. Interestingly, Drummond and Grieser<sup>2e</sup> also suppose that the hydrophobic indicator 4-hexadecyl-7-hydroxycoumarin does not ‘sense’ the overall surface potential of micelles of a betaine surfactant  $C_{12}H_{25}NH_2^+C_2H_4CO_2^-$ , but rather the local

**Table 2.** Evaluation of the  $\Psi$  values of micelles using the  $pK_a^i$  values of DODR

Surfactant <sup>a</sup>	Bulk counterion concentration, M <sup>b</sup>	$\Psi$ , mV obtained with DODR $\pm(7-11)$ mV	$\Psi$ , mV calculated using Eqn (7)
<i>n</i> -C <sub>18</sub> H <sub>37</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	0.053	+124	—
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	0.019 <sup>c</sup>	+118	+110
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	0.053	+102	—
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	0.053 <sup>c</sup>	+100	+88
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	0.403 <sup>c</sup>	+54	—
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup>	4.00 <sup>d</sup>	+17	—
<i>n</i> -C <sub>16</sub> H <sub>33</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	0.05	+37	—
<i>n</i> -C <sub>16</sub> H <sub>33</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.052	-74	—
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.020 <sup>e</sup>	-76	-84
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.054	-58	-66
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.077	-49	-61
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.203	-27	—
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.303	-14	—
<i>n</i> -C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup>	0.403	-11	—

<sup>a</sup>The  $C_S$  and  $T$  values are as indicated in Table 1.

<sup>b</sup>Created by the buffer system and NaCl; the contribution of surfactant counterions is also taken into account.

<sup>c</sup>HBr + KBr.

<sup>d</sup>KCl.

<sup>e</sup>Sodium acetate, without NaCl addition.

potential in the vicinity of the ammonium group. The dipolar character of the hydrophilic portion of betaine surfactants allowed to explain the behavior of indicator dyes both in terms of dissociation-field effect<sup>22</sup> and of gradient of the local surface acidity, due to the existence of local electrostatic potential profiles.<sup>2c</sup>

### Comparison with the results of theoretical calculations

The  $\Psi$  values for ionic micelles with radius  $r$  can be estimated theoretically from the approximate solution of nonlinearized Poisson–Boltzmann equation, obtained for spherical particles by Oshima, Healy, and White,<sup>25</sup> using the  $\alpha$  value and the area of the surfactant head group,  $S_i$ , for calculation of the surface charge density:

$$\frac{\alpha}{S_i} - \frac{2\epsilon\epsilon_0 kRT}{F} \sinh(Y/2) \times \left( 1 + \frac{2}{kr \cosh^2(Y/4)} + \frac{8 \ln[\cosh(Y/4)]}{(kr)^2 \sinh^2(Y/2)} \right)^{\frac{1}{2}} = 0 \quad (7)$$

where  $Y = \Psi F/RT$ ,  $k^{-1}$  is the Debye length,  $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$ ,  $\epsilon = 78.5$  at  $T = 298.15 \text{ K}$ . The iterative procedure easily allows obtaining the  $Y$  value.

The calculations demonstrate, however, that the uncertainty of  $\Psi$  values obtained by using Eqn (7) is caused first of all by uncertainty of  $\alpha$  values. It is well known, that the latter, obtained by using various experimental values, differ markedly from each

other.<sup>2f,3b,c</sup> So, for SDS micelles conductometric estimations lead to  $\alpha = 0.3-0.4$ ,<sup>21</sup> or even higher, while pNa measurements and analysis of salt effects upon cmc values result in  $0.20-0.26$ .<sup>26</sup> The majority of colloidal systems are not well enough defined and the complete set of parameters ( $r$ ,  $\alpha$ , and  $S_i$ ) is as a rule unknown for them. Moreover, micelles are known to become non-spherical along with increase in supporting electrolyte concentration. This also hinders the use of Eqn (7).

However, even in case if the possibility of exact calculations is doubtful, Eqn (7) allows to obtain reliable estimates of  $\Psi$  values. For instance, the  $\Psi$  values for SDS spherical micelles was calculated using the values  $r = 2.0 \text{ nm}$ ,  $S_i = 0.60 \text{ nm}^2$ , and  $\alpha = 0.25$  as most probable.<sup>6</sup>

For spherical cetyltrimethylammonium bromide micelles, the parameters  $r = 2.6 \text{ nm}$ ,<sup>27</sup>  $S_i = 0.474 \text{ nm}^2$ ,<sup>28</sup> and  $\alpha = 0.27$ <sup>19</sup> can be used. Taking into account the somewhat conventional character of the  $pK_a^i$  value used by us, the agreement of the  $\Psi$  values obtained using DODR as indicator with those calculated theoretically looks satisfactorily (Table 2). Increase in surfactant concentration, for example, up to  $0.1 \text{ M}$ , makes the calculations somewhat uncertain because in the presence of NaCl, micellar shape is known to deviate from ideal spherical. Also, at high bulk ionic strength, the micelles become nonspherical, and the formula Eqn (7) cannot be used.

DODR seems to be a rather promising probe for determination of interfacial electrical potentials in various colloidal systems, at least for comparison with results obtained with other indicators (see below). Even utilization of the  $pK_a^i$  value obtained in nonionic micelles as  $pK_a^i$  in micelles of ionic surfactant leads in this case to



reasonable  $\Psi$  values for SDS and cetyltrimethylammonium micelles. Two hydrocarbon tails are expected to penetrate into the micellar core, and this favors the exposition of the ionizing carboxylic group the micellar palisade for any probable position of the indicator (Chart 2). If stable ion associates between positively charged xanthene moiety and anionic surfactants head groups really exist, they are probably similar for both  $\text{HR}^+$  and  $\text{R}^\pm$ . However, electrostatic association of the  $\text{COO}^-$  groups with counterions  $\text{Na}^+$  in the Stern region of anionic micelles and with the positively charged tetraalkylammonium headgroups in the case of cationic surfactant micelles cannot be excluded. In the event that such associates exist they can be regarded as rather water-separated than intimate ones. Moreover, the Stern layer can be regarded even as a molten salt or as a kind of ionic liquid.<sup>3c</sup>

### Comparison of the $\Psi$ values with those obtained using other indicators

It seems reasonable also to compare the  $\Psi$  values, determined using DODR, with the results obtained with other indicators (Tables 3 and 4).

The counterion concentrations were estimated using Eqn (6). However, the true salt background in the studies with lipoid coumarins<sup>2d-f,18a</sup> is probably somewhat higher, if the components of dilute buffer systems<sup>2d</sup> or small  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{NaOH}$  additives<sup>2e,f,18a</sup> used for pH adjusting<sup>2d-f,18a</sup> are taken into account.

As a rule, the  $\Psi$  values determined with DODR are less negative in SDS and somewhat less positive in CTAB systems. The differences in the case of cationic surfactant system are not so expressed and correspond on the average to  $\approx 0.2 \text{ p}K_a$  units. In SDS micellar solutions, the deviations are much more marked.

If ion association of  $\text{COO}^-$  group of  $\text{R}^\pm$  species with  $\text{CTA}^+$  cations takes place in the Stern region, this effect should have result in additional increase in the apparent  $\Psi$  value of CTAB micelles.

The charge type of DODR acid–base couple is like that in the case of Reichardt's betaine ( $\text{A}^+\text{B}^\pm$ ), and the ionizing group is as in the case of 4-octadecyloxy-1-naphthoic acid ( $\text{COOH}$ ). The value  $\Psi = -76 \text{ mV}$ , obtained for SDS system using DODR, is relatively close to the values estimated with these indicators (Table 4). The values obtained with lipoid hydroxycoumarins and decyl eosin, indicators with charge type  $\text{A}^0\text{B}^-$ , are *ca.* 50 mV lower, while utilization of hexamethoxy red and methyl yellow, indicators with charge type  $\text{A}^+\text{B}^0$ , results in evidently erroneous  $\Psi$  values (*ca.*  $-220 \text{ mV}$ ), which are even more negative than the expected value of a 'bare' *n*-dodecylsulfate micelle without counterions.<sup>2f,3a</sup>

As anionic micelles are much better hydrated than nonionic ones, the increase in  $\text{p}K_a$ , typical for acid–base couples of  $\text{A}^0\text{B}^-$  and  $\text{A}^+\text{B}^\pm$  types on going from water to water–organic mixtures,<sup>7</sup> must be less expressed just in SDS dispersions. Thus, the deviations of the  $\text{p}K_a^i$  values in SDS micelles from those in nonionic ones results in overestimation of  $|\Psi|$  values if indicators of  $\text{A}^+\text{B}^0$  charge type are used, and in underestimation of  $|\Psi|$  if probes with  $\text{A}^0\text{B}^-$  and  $\text{A}^+\text{B}^\pm$  acid–base couples are utilized.

Hence, the  $\Psi$  values of SDS micelles can be somewhat more negative than those determined using the last-named indicators. In the case of DODR, such values will be still close to results of theoretical estimates [Eqn (7), Table 2], and the contradiction with the electrokinetic potential values<sup>2f,3c</sup> will be less marked.

In any case, it is hard to explain the discrepancies between the  $\Psi$  values obtained with DODR and coumarins (Table 4) using the concept of ion association of DODR with  $\text{DS}^-$  anions. Contrary to it, the (possible) association of  $\text{COO}^-$  group of DODR with  $\text{Na}^+$  in

**Table 3.** Comparison of the  $\Psi$  values of CTAB micelles, as estimated using different indicators

Indicator, reference	$C_s, \text{ M}$	$[\text{Br}_w^-], \text{ M}$	$\Psi, \text{ mV}^a$	$\Psi, \text{ mV}$ , recalculated to $[\text{Br}_w^-] = 0.019 \text{ M}$
DODR, this work	0.050	0.019	+118	+118
4-Heptadecyl-7-hydroxycoumarin <sup>b</sup>	0.050	0.014	+117 <sup>c</sup> (+145) <sup>d</sup>	+110 <sup>c</sup> (+138) <sup>d</sup>
4-Undecyl-7-hydroxycoumarin <sup>e</sup>	0.024	0.007	+148	+127
4-Heptadecyl-7-hydroxycoumarin <sup>f</sup>	0.050	0.014	+139	+132
Reichardt's betaine <sup>g</sup>	0.050	0.014	+141	+134
4-Octadecyloxy-1-naphthoic acid <sup>c</sup>	0.050	0.014	+143	+136
4-Heptadecyl-7-hydroxycoumarin <sup>i</sup>	0.050	0.014	+151	+144

<sup>a</sup>  $\Psi = 2.3025 RT (\text{p}K_a^i - \text{p}K_a^a)$ .

<sup>b</sup> Ref. 18a; 295 K; Teric N 9 and  $\text{C}_{12}\text{E}_8$  used for  $\text{p}K_a^i$  determination ( $=9.05$ ).

<sup>c</sup> Calculated by us using the data of Table 1 (Ref. 18a).

<sup>d</sup> Values reported by the authors of Ref. 18a.

<sup>e</sup> Ref. 2d; Triton-X 100 used for  $\text{p}K_a^i$  determination ( $=8.85$ ).

<sup>f</sup> Ref. 4a.

<sup>g</sup> Ref. 4a; the  $\text{p}K_a^i$  value of 9.60 was used by the authors; if the value of 9.31, obtained in Ref. 4a in 0.204 M  $\text{C}_{12}\text{E}_8$  solution is used, then the value  $\Psi = +124 \text{ mV}$  instead of +141 mV appears.

<sup>h</sup> Ref. 18a; 295 K; Brij 35 and  $\text{C}_{12}\text{E}_8$  used for  $\text{p}K_a^i$  determination (mean value: 6.65).

<sup>i</sup> Ref. 2e;  $\text{C}_{12}\text{E}_8$  used for  $\text{p}K_a^i$  determination ( $=9.04$ ).

**Table 4.** Comparison of the  $\Psi$  values of SDS micelles, as estimated using different indicators

Indicator, reference	$C_s$ , M	$[Na_w^+]$ , M	$\Psi$ , mV <sup>a</sup>	$\Psi$ , mV, recalculated to $[Na_w^+] = 0.020$ M
DODR, this work	0.050	0.020	-76	-76
Reichardt's betaine <sup>b</sup>	0.050	0.0185	-83	-81
4-Octadecyloxy-1-naphthoic acid <sup>c</sup>	0.050	0.0185	-85 <sup>d</sup> (-93) <sup>e</sup>	-83 <sup>d</sup> (-91) <sup>e</sup>
4-Heptadecyl-7-hydroxycoumarin <sup>f</sup>	0.050	0.0185	-102 <sup>d</sup> (-105) <sup>e</sup>	-100 <sup>d</sup> (-103) <sup>e</sup>
4-Undecyl-7-hydroxycoumarin <sup>g</sup>	0.024	0.012	-134	-123
4-Heptadecyl-7-dimethylaminocoumarin <sup>h</sup>	0.024	0.012	-134	-123
<i>n</i> -Decyl eosin <sup>i</sup>	0.020	0.012–0.014	-143	-134
<i>n</i> -Decyl eosin <sup>i,j</sup>	0.010	0.020	-134	-134
4-Heptadecyl-7-hydroxycoumarin <sup>k</sup>	0.020	0.065	-110	-135
4-Heptadecyl-7-hydroxycoumarin <sup>l</sup>	0.020	0.0185	-144	-142
Hexamethoxy red <sup>m</sup>	0.020	0.019	-217	
Methyl yellow <sup>m</sup>	0.020	0.019	-230	

<sup>a</sup>  $\Psi = 2.3025RT (pK_a^i - pK_a^a)$ .

<sup>b</sup> Ref.<sup>4a</sup>; the authors of the cited paper does not consider this  $\Psi$  value as the surface electrostatic potential, taking into account the peculiarities of the indicator location.<sup>4a</sup>

<sup>c</sup> Ref.<sup>18a</sup>; 295 K; Brij 35 and C<sub>12</sub>E<sub>8</sub> used for  $pK_a^i$  determination (mean value: 6.65).

<sup>d</sup> Calculated by us using the data of Table 1 (Ref.<sup>18a</sup>).

<sup>e</sup> Values reported by the authors of Ref.<sup>18a</sup>.

<sup>f</sup> Ref.<sup>18a</sup>; 295 K; Teric N9 and C<sub>12</sub>E<sub>8</sub> used for  $pK_a^i$  determination (=9.05).

<sup>g</sup> Ref.<sup>2d</sup>; Triton-X 100 used for  $pK_a^i$  determination (=8.85).

<sup>h</sup> Ref.<sup>2d</sup>; Triton-X 100 used for  $pK_a^i$  determination (=1.25); this is a rare case of coincidence of the  $\Psi$  value determined using an indicator with A<sup>+</sup>B<sup>0</sup> charge type with those obtained using acid–base couples of A<sup>0</sup>B<sup>-</sup> type.

<sup>i</sup> Ref.<sup>3b</sup>; NaCl + acetate buffer, or without NaCl; TWEEN 80 used for  $pK_a^i$  determination (=2.61).

<sup>j</sup> At bulk Na<sup>+</sup> conc. 0.05 M, measurements with *n*-decyl fluorescein<sup>3c</sup> lead to  $\Psi$  values being 10 mV less negative, than those obtained with *n*-decyl eosin.

<sup>k</sup> Ref.<sup>2f</sup>; C<sub>12</sub>E<sub>8</sub> used for  $pK_a^i$  determination (=9.10).

<sup>l</sup> Ref.<sup>2e</sup>; the  $pK_a^i$  value taken from Ref.<sup>2f</sup>.

<sup>m</sup> Ref.<sup>3a</sup>; Nonyl phenol 12 used for  $pK_a^i$  determinations; in this paper, it was underlined that such  $\Psi$  values are certainly too negative to be realistic.<sup>3a</sup>

SDS micelles can decrease the  $pK_a^a$  value, and thus the estimated  $\Psi$  value becomes less negative. Similar effect can be expected in the case of 4-octadecyloxy-1-naphthoic acid (Table 4). In the zwitterionic species of Reichardt's betaine, the effective negative charge on the phenolate oxygen is also known to be high (high dipole moment in the ground state). In the case of coumarin and ethyleosin anions, the negative charge is strongly delocalized on the conjugated system. These effects can also contribute to the differences in  $\Psi$  values, obtained with DODR, 4-octadecyloxy-1-naphthoic acid, and Reichardt's betaine, on the one hand, and those obtained with lipid hydroxycoumarins, on the other.

In any case, the DODR dye can be used also for monitoring of  $\Psi$  alterations, occurring along with variations in bulk ionic background [Eqn (5)]. The response of absorption on bulk pH changes can be utilized in various sensor devices; however, fluorescence is much more promising for such a purpose. (Figure 3)

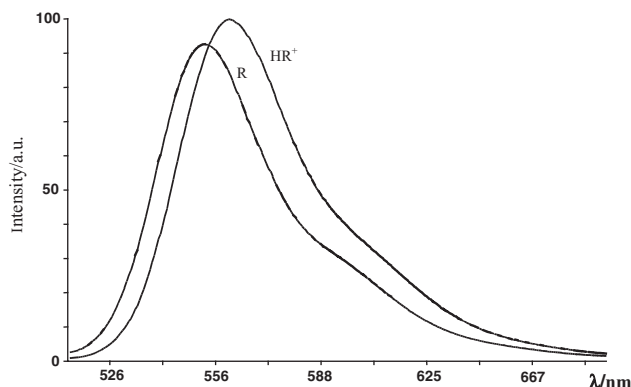
### Utilization of emission spectra for $pK_a^a$ determinations

It seems reasonable also to utilize the fluorescent properties of DODR for acidity monitoring. Figure 4

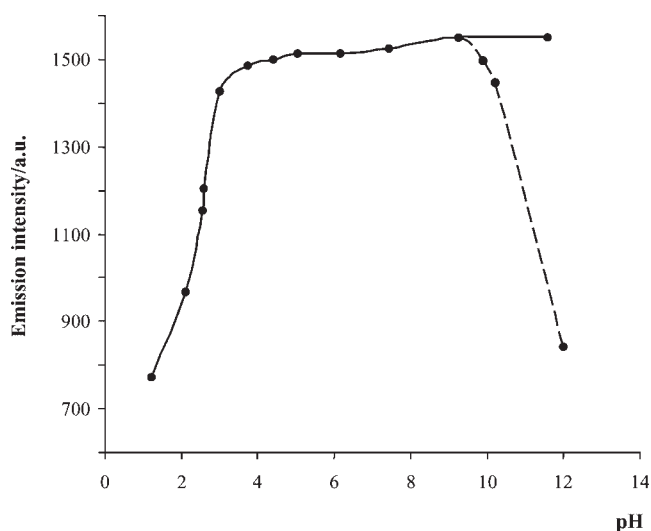
demonstrates the resolution of emission spectra of species HR<sup>+</sup> and R.

The  $\lambda_{\max}^{\text{em}}$  values of HR<sup>+</sup> and R equals 561 and 554 nm, correspondingly, both in CTAB micellar solution with 0.05 M NaCl and in SDS micellar solution with 0.4 M NaCl.

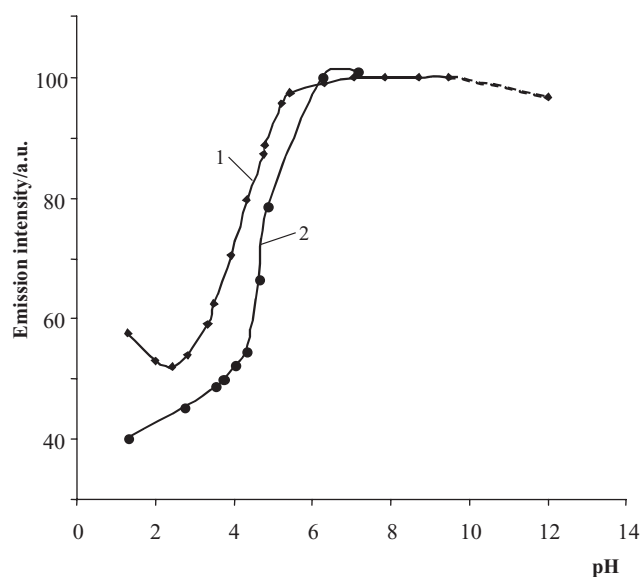
Figures 4 and 5 reflect the response of relative intensity of emission,  $I_{\text{rel}}$ , on the variations of bulk pH in two rather different micellar systems. Quantum yield,  $\phi$ , demonstrates similar, though less expressed alterations along with changes in pH. The measurements were made at



**Figure 3.** Emission spectra of neutral and cationic *N,N'*-di-*n*-octadecylrhodamine species in micellar solution of CTAB (0.01 M); 0.01 M NaOH and 0.063 M HCl, correspondingly;  $T = 298.15$



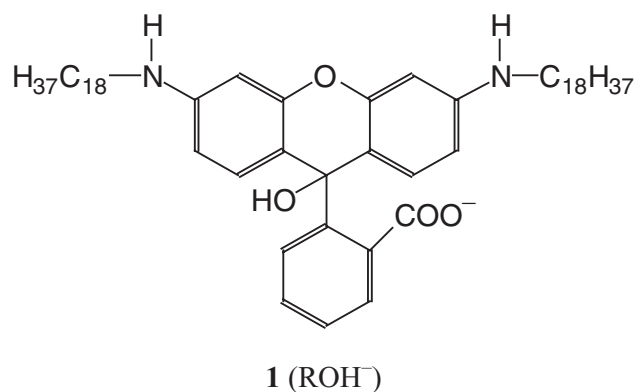
**Figure 4.** The dependence of *N,N'*-di-*n*-octadecylrhodamine fluorescence intensity at 546 nm on pH in micellar solutions of CTAB (0.01 M); ionic strength 0.05 M (HCl + NaCl);  $T = 298.15$  K; solid line: immediately after preparation; dotted line: after 14 days



**Figure 5.** The dependence of fluorescence intensity at 547 nm on pH in micellar solutions of SDS (0.01 M); HCl or acetate buffer solutions, ionic strength 0.4 M (NaCl);  $T = 298$  K: 1, *N,N'*-di-*n*-octadecylrhodamine (**1**), 547 nm and 2, rhodamine B (**3**), 571 nm

547–546 nm, where the difference between emission spectra of  $HR^+$  and R are most distinct. The total  $I_{rel}$ -pH curves are reproduced twice in independent series of experiments.

In cationic surfactant micelles, at high pH values, the fluorescence intensity decreases in time, and after keeping for several hours this effect becomes dramatic (Fig. 4, dotted line). This is caused by well-known reaction of formation of colorless carbinol,  $ROH^-$ , resulting in  $sp^3$ -hybridization of the central carbon atom of rhodamine zwitterion.<sup>29</sup>



The nucleophilic attack is known to occur very rapidly for cationic dyes bound by cationic surfactant micelles, because of high local concentration of  $HO^-$  ions in the Stern layer. This effect is well documented for crystal violet and some other triphenylcarbonium cations.<sup>30,31</sup> In the case of DODR in CTAB micelles, slow  $ROH^-$  formation in alkaline region cannot hinder the  $pK_a^a$  determinations, which are performed at low and medium pH.

The  $pK_a^a$  calculated using  $I_{rel}$  values and thus being actually the pHs of the inflection points of corresponding dependences, or  $pH_{1/2}$ , are  $2.50 \pm 0.06$  (CTAB, 0.05 M NaCl) and  $4.23 \pm 0.05$  (SDS, 0.4 M NaCl). The values in the ground state are  $2.50 \pm 0.06$  and  $4.41 \pm 0.05$  (Table 1).

The fluorescence lifetime values,  $\tau$ , of cationic and zwitterionic forms coincide, and are practically equal in cationic and anionic surfactant systems. For instance, under conditions indicated in Fig. 4, they are  $3.9 \pm 0.1$  ns in CTAB micelles and  $4.0 \pm 0.1$  ns in SDS micelles, correspondingly. Therefore the  $HR^+$  and R species emit preferably before the equilibrium in the excited state is reached. The excited state values,  $pK_a^{a*}$ , can be estimated by using the Förster–Weller cycle. For the aforesaid micellar systems  $pK_a^{a*} = 3.10$  and  $4.71$ , correspondingly. Hence, the  $pH_{1/2}$  value obtained from emission data (Figs 4 and 5) coincide exactly with  $pK_a^a$  in the ground state for cationic surfactant system and is even somewhat lower in the case of SDS micelles.

However, the mentioned discrepancy is too small to warrant detailed discussion. An attempt may be made to explain the slight (0.2 units) but reproducible negative deviation of  $pH_{1/2}$  from  $pK_a^a$  in the ground state may in following way. If the rate constant of the bimolecular recombination reaction ( $R + H^+ \rightarrow HR^+$ ) is essentially smaller than the common diffusion-controlled reactions of benzoate ions with the proton ( $k \sim 10^{10} s^{-1} M^{-1}$ )<sup>32</sup> for simple electrostatic reasons, then the zwitterion stronger contributes the total emission at the chosen analytical wavelength. However, in the case of rhodamine B (**3**) in analogous system (Fig. 5), the  $pH_{1/2}$  ( $4.60 \pm 0.12$ ) coincides with the  $pK_a^a$  in ground state ( $4.54 \pm 0.03$ ). Thus, such an explanation can be made only for the

DODR, which is more tightly fixed in micelles due to long hydrocarbon chains.

With DODR in SDS micelles, another specific effect takes place. A slight minimum of intensity is observed near pH 2.5, which is also repeatedly reproduced. Additional experiments demonstrated that small alterations of emission band occur at high hydrogen ions concentrations. The possible reason is the exchange between  $\text{Na}^+$  and  $\text{H}^+$  counterions in the Stern layer, which causes some changes in micellar structure and hydration character and, in turn, in the emission band of the cation  $\text{HR}^+$ . Again, in the case of rhodamine B (**3**) this (slight) effect does not manifest itself (Fig. 5), probably, owing to not so tight fixation of this less hydrophobic dye in the micelles as compared with DODR.

On the whole, the results obtained demonstrate that dye **1**, DODR, can be applied for fluorometric estimations of electrical interfacial potentials in biological systems and for monitoring the pH values. Especially, such a response of fluorescence on bulk acidity can be exploited in optical pH sensors basing on self-assembled aggregates.

## CONCLUSIONS

The possibility of application of *N,N'*-di-*n*-octadecylrhodamine (DODR) as an acid–base indicator for micelle/water interface is demonstrated for four types of surfactants and various concentrations of supporting electrolyte.

Both cation and zwitterion possess a positively charged aminoxanthene moiety, which allows eliminating the (possible) ion association of the cation with surfactant headgroup in the case of SDS micelles. In the case of well-defined surfactant micelles, such as SDS and CTAB, the estimates of the electrical potential of Stern layer made by using DODR agree with the results of theoretical calculations. The response to changes in salt background is adequate from viewpoint of the electrostatic model.

The distinct dependence of fluorescence intensity of the dye bound to micelles versus pH of the bulk water ensures the possibility of using DODR as a promising fluorescent interfacial acid–base indicator.

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