ФИЗИКО-ХИМИЯ РАСТВОРОВ

УДК 547.77.022.532 + 544.164.032.732 + 547.97

# THE RESPONCE OF AN ACID-BASE INDICATOR ON THE MODIFICATION OF SODIUM N-DODECYL SULFATE MICELLES WITH A SURFACTANT CATION

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The addition of a cationic surfactant to sodium n-dodecylsulfate micellar solutions displays strong changes in the 'apparent' $\mathrm{p}K_a^a$ values of acid-base indicator, decylfluorescein, adsorbed on the interface of micelles.

Organic indicator dyes are widely used as probes for studying micelles, liposomes, and other microscopic objects, as their spectral and acid-base properties are sensitive to the nature of the microenvironment [1]. The so-called 'apparent' dissociation constant, $K_a^a$, serves as a key characteristic of an indicator dye in micellar solutions:

$$\mathrm{p}K_a^a = \mathrm{pH} + \log\{[\mathrm{HR}^z]/[\mathrm{R}^{z-1}]\} \qquad (1)$$

Here $z$ and $(z-1)$ are charges of the conjugated indicator species ($\mathrm{HR}^z \rightleftarrows \mathrm{R}^{z-1} + \mathrm{H}^+$). The ratio of the equilibrium concentrations of these species can be derived from electronic absorption, while the $\mathrm{pH}$ values of the bulk (continuous, aqueous) phase are determined as a rule by using the glass electrode. The volume of the dispersed (micellar) phase usually makes less than 1% of the total volume of solution, and the molar ratio surfactant : dye is $\geq 100$. The $\mathrm{p}K_a^a$ value of an indicator completely bound by ionic micelles, membranes, etc., may be used to evaluate the electrical potential of the charged surface, $\Psi$, since there is a well-known relationship between these quantities [1]:

$$\mathrm{p}K_a^a = \mathrm{p}K_a^i - \Psi F / 2.303RT \qquad (2)$$

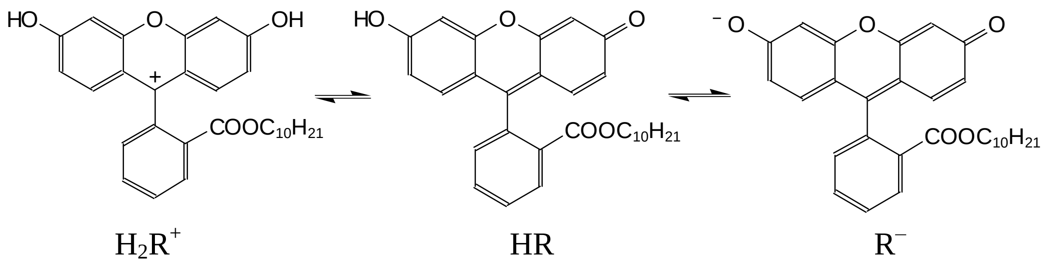
Here F is the Faraday constant, R is the gas constant, T is absolute temperature, $K_a^i$ is a constant characterizing the 'intrinsic' acidity of the reagent. The ionizing group is supposed to be situated in the Stern layer, and the $\Psi$ value refers to this part of the pseudophase.

In our previous communication [1], the influence of the nature of micellar pseudophase on the apparent dissociation constant of indicators, $K_a^a$, was studied in details. Besides, both inorganic and organic counter-ions were introduced into the micellar solutions of colloidal surfactants. The only aim of this report is to demonstrate the influence of an organic counter-ion, which itself is able to form micelles, on the $K_a^a$ values of acid-base indicators. The dye decylfluorescein was chosen as a two-step ('bifunctional') indicator with two different charge types of acid base couples $+/0$ and $0/-$:

$$\mathrm{H_2R^+} \rightleftarrows \mathrm{HR} + \mathrm{H^+}, \qquad K_{a0}^a \qquad (3)$$

$$\mathrm{HR} \rightleftarrows \mathrm{R^-} + \mathrm{H^+}, \qquad K_{a1}^a \qquad (4)$$

All the species of this bifunctional indicator are completely bound by micelles of sodium n-dodecylsulfate (SDS) owing to the long hydrocarbon tail, $-n\text{-}C_{10}H_{21}$:



As hydrophobic counter-ion, $n\text{-}C_{10}H_{21}N(C_2H_5)_3^+$ (or $Ct^+$), was added to the system under study in the form of hydrosulfate. All the experiments (Vis-spectroscopic evaluation of $pK_a^a$, accompanied by potentiometric determination of pH) were made at 25 $^0$C,

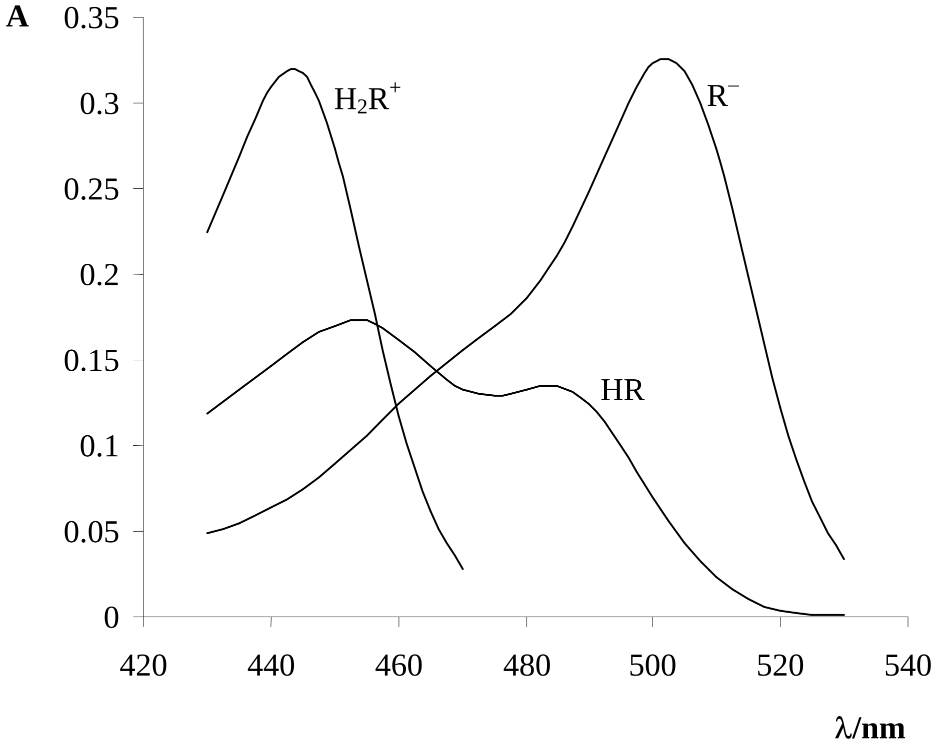


Fig.1. Absorption spectra of decylfluorescein species in 0.01 M SDS solution with addition of 0.003 M $n\text{-}C_{10}H_{21}N(C_2H_5)_3^+$ ; cuvette: 1cm.

as described earlier [1]. The sample of decylfluorescein was already used previously [1]. The Vis absorption spectra of three species of the dye in the system under study are presented in Figure 1.

The values of the dye species are as follows: 444 nm ($H_2R^+$), 455 nm and 485 nm (HR), and 502 nm ($R^-$). In 0.01 M SDS + 0.003 M $n\text{-}C_{10}H_{21}N(C_2H_5)^{3+}$ system, the following results were obtained: $pK_{a0}^a$ = 4.89 ± 0.06 (acetic buffer, ionic strength

0.01 M + 0.003 M NaOH), $pK_{a1}^{a}$ = 8.38 ± 0.02 (borate buffer, ionic strength 0.0125 M + NaOH 0.003 M). In 0.01 M SDS solution, at buffer ionic strength 0.05 M, the $pK_{a}^{a}$ equal 5.17 and 8.96, respectively [1]; the real ionic strength is somewhat higher, ca. 0.054 M, if we take into account the cmc value at 0.05 M $Na^+$ and the dissociation degree of SDS in the Stern layer [1-3]. The $pK_{a}^{a}$ values of decylfluorescein in SDS micellar solutions with different initial salt content of the bulk phase are compared in Table 1.

Table 1. The $pK_{a}^{a}$ values of decylfluorescein in SDS micellar solutions with different initial electrolytic background

| Surfactant | Initial bulk content | $pK_{a0}^{a}$ | $pK_{a1}^{a}$ |
|---|---|---|---|
| 0.01 M SDS | 0.05 M NaCl (Ref. 1) | 5.17 ± 0.01 | 8.96 ± 0.04 |
| 0.01 M SDS | 0.40 M NaCl (Ref. 1) | 4.55 ± 0.03 | 8.18 ± 0.04 |
| 0.01 M SDS | 0.003 M $Ct^+$ | 4.89 ± 0.06 | 8.38 ± 0.02 |
| $pK_{a}^{a}$ [0.05 M NaCl] − $pK_{a}^{a}$ [0.40 M NaCl] = | | 0.62 | 0.78 |
| $pK_{a}^{a}$ [0.05 M NaCl] − $pK_{a}^{a}$ [0.003 M $Ct^+$] = | | 0.28 | 0.58 |

The data demonstrate that the influence of small additive of $Ct^+$ is commensurable with that of 133-fold amount of $Na^+$. Evidently, such effects cannot be explained by screening of the surface charge, as in the case of 0.40 M NaCl [1-4]. Moreover, the traditional model of describing salt effects [5] is invalid here. Really, the hydrophobic cation under study, $Ct^+$, is surely adsorbed on the SDS micellar interface; this ion behaves as a co-surfactant rather, than as counter-ion. Hence, at the given concentration the ion $Ct^+$ is practically absent from the bulk (aqueous) phase. In such case, the decrease in the $pK_{a}^{a}$ values is caused by partial neutralization of the micellar charge and, maybe, by decrease in the interfacial charge density. Note, that marked effects on the surface acid-base equilibria of indicators in SDS micellar systems displays also tetra-n-butyl ammonium cation [1-4], as well as other pseudospherical alkylammonium cations [4]. The last-named cations are known to disorder the micelle/ water interface in the case of SDS micellar systems [5]. In addition, they certainly act as dehydrating agents (‘drying’ effect). Hence, the variations in the $pK_{a}^{a}$ values can be caused by alterations of the $pK_{a}^{i}$ quantities [see eq. (2)].

The modification of the SDS micellar surface with hydrophobic cation $Ct^+$ is proved by the alteration of the absorption spectrum of the standard solvatochromic Reichardt’s dye 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenyl phenolate (Figure 2). The spectra of this dye in other micellar solutions of surfactants are given in Ref. 1.

For complete interpretation of the $pK_{a}^{a}$ values of decylfluorescein, obtained in the present study, it is necessary to clarify the possibilities of ionic association (between $H_2R^+$ and $DS^-$, $R^-$ and $Na^+$, and $R^-$ and $Ct^+$).

The results obtained in this work encourage to do further investigations of SDS micellar solutions with various organic counter-ions.

Acknowledgement. The authors are grateful to Dr. V. I. Alekseeva, Research Institute of Organic Intermediates and Dyes, Moscow, Russia, for gifting the sample of decylfluorescein, and to Professor Dr. Chr. Reichardt, Philipps University of Marburg, Germany, for gifting the sample of 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenyl phenolate.

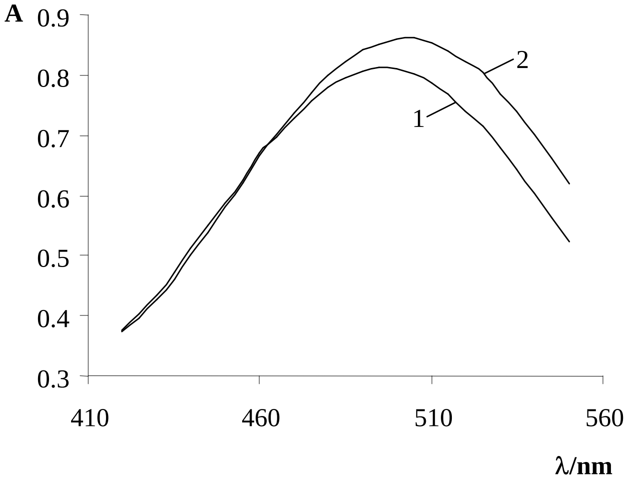


Fig. 2. Absorption spectra of 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenyl phenolate in 0.01 M SDS solutions: without additives, $\lambda_{\max}$ =497 nm (1), and with addition of 0.003 M $n$-$C_{10}H_{21}N(C_2H_5)_3^+$, $\lambda_{\max}$ = 503 nm (2); pH 12; cuvette: 5cm.

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*Поступила в редакцию* 17 *декабря* 2003 *года*

Вестник Харьковского национального университета. 2003. №596. Химия. Вып.10(33). Н.О. Мчедлов-Петросян, Н.А. Водолазкая. Отклик кислотно-основного индикатора на модификацию мицелл *н*-додецилсульфата натрия поверхностно-активным катионом.

Введение поверхностно-активного катиона *н*-децилтриэтиламмония в мицеллярный раствор *н*-додецилсульфата натрия существенно изменяет «кажущееся» значение $\mathrm{p}K_a^a$ кислотно-основного индикатора децилфлуоресцеина, адсорбированного мицеллами анионного ПАВ.