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ACID-BASE AND SOLVATOCHROMIC INDICATORS IN SURFACTANT MICELLAR SOLUTIONS OF VARIOUS TYPES: IS THE COMMON ELECTROSTATIC MODEL VALID?

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The properties of micellar solutions of over 20 colloidal surfactants (including 9 anionic) as media for protolytic reactions were studied with the help of acid-base indicators, mainly of the two-step, or 'bifunctional', Decyl Fluorescein ($H_2R^+ \rightleftarrows HR \rightleftarrows R^-$) and of the Reichardt betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide, with solvatochromic zwitterionic form $R^\pm$ ($HR^+ \rightleftarrows R^\pm + H^+$), as well as of other dyes, completely bound to micelles. The validity of the traditional electrostatic model was tested on the basis of the 'apparent' pK_a^a, which describes the dissociation of the indicator, $pK_a^a = pK_a^i - [\Psi F/(RT \ln 10)]$. The object of analysis were alterations in the pK_a^a values, caused by the transfer from water to micellar solutions ($\Delta pK_a^a = pK_a^a - pK_a^w$), from one surfactant to another, and through the variation in the composition of salt background (inorganic and organic ions). The main assumptions of the common electrostatic model – (1) constancy of the 'intrinsic' contribution to the pK_a^a value of the given indicator (pK_a^i) in any micellar system, (2) constancy of the value of the electrical potential of the Stern layer Ψ of the given micellar surface obtained by using any indicator, and (3) the possibility of complete description of salt effects with the help of ion-exchange model, – are shown in most cases to be justified only approximately, and sometimes even insufficiently. Up-to-date attempts to modify the simple electrostatic model are shown to be rather arbitrary. The pK_a^a values in nonionic micelles cannot be considered to be an optimal model of pK_a^i in ionic micelles. That is why the possibility of using the pK_a^a values in micellar solutions of a zwitterionic surfactant $C_{16}H_{33}N(CH_3)_2^+{-}(CH_2)_3{-}SO_3^-$ as pK_a^i values of the corresponding dyes in micelles of ionic surfactants is discussed. The micellar transitions caused by salts became evident in the case of hydrophobic counterions. The analysis of the pK_a^a values revealed the greatest hydration of the Stern region of anionic micelles as compared with other micellar surfaces. This is in agreement with their E_T^N values, as well as with other solvatochromic scales. The nature of ionic pairs formed by dye ions and oppositely charged surfactant head groups is discussed. The differentiating action of micellar pseudophase upon the acid-base properties of indicator couples of various charge types and nature, i.e. the disparity in their ΔpK_a^a values, manifests itself distinctly, depending on the nature of the surfactant. This effect is caused, on the one hand, by the miscellaneous character of any micellar surface, and on the other hand – by the dissimilarity among hydrophilic portions of cationic, anionic, nonionic (with oxyethylene chains), and zwitterionic surfactants, as well as of the Stern region of ionic micelles containing counter-ions of different hydrophobicity. The differentiating impact of micelles seems to be the main hindrance to exact evaluations of the interfacial electrical potential of micelles by means of acid-base indicators.

1.Introduction

1.1. Apparent dissociation constants of pK_a^a-probes in micellar systems: the electrostatic model. The chemical equilibrium in lyophilic ultramicroheterogeneous systems, in particular, in micellar solutions of colloidal surfactants, becomes more and more often the subject of investigation.[1] Organic dyes are widely used as probes for studying micelles, liposomes,

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and other microscopic objects, because their spectral and acid-base properties are sensitive to the nature of the microenvironment.[1b,e,f,2−17] The so-called 'apparent' dissociation (ionization) constant, K_a^a, serves as a key characteristic of an indicator dye in micellar solutions:[3,5-17]

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

Here z and (z−1) are charges of the conjugated indicator species ($\mathrm{HR}^z \rightleftarrows \mathrm{R}^{z-1}$ + H^+). We define the corresponding K_a^a constant as $K_{a(1-z)}^a$. The ratio of the equilibrium concentrations of these species can be derived from electronic absorption, while the 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, Ψ, as there is a well-known relationship between these quantities:[4-6,8,9,12,13,16,17]

$$\mathrm{p}K_a^a = \mathrm{p}K_a^i - \Psi F/(RT\ln 10) \tag{2}$$

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. The difference between $\mathrm{p}K_a^i$ and the thermodynamic $\mathrm{p}K_a$ in water, $\mathrm{p}K_a^w$, is determined by the activity coefficients γ_i of transfer of the forms HR^z and R^{z-1} from water to micellar pseudophase: $\mathrm{p}K_a^i = \mathrm{p}K_a^w + \log(\gamma_\mathrm{R}/\gamma_\mathrm{HR})$. At the same time for the 'true' ionization constant in the micellar pseudophase, $K_a^m = a_{\mathrm{H}^+,m}\, a_{\mathrm{R}^{z-1},m}\,(a_{\mathrm{HR}^z,m})^{-1}$, the relationship 3 is valid.

$$\mathrm{p}K_a^m = \mathrm{p}K_a^i + \log\gamma_{\mathrm{H}^+} \tag{3}$$

Both equilibrium concentrations, [i], and activities, a_i, are expressed here in the mole per liter (or M) scale. The suffixes w and m denote that the species belong to the aqueous phase and micellar pseudophase, respectively. Eq 2 can be derived, assuming that the partition of the species HR^z and R^{z-1} between the phases can be described by eq 4:

$$a_{i,m}/a_{i,w} = \gamma_i^{-1} \exp\,(-\,z_i\Psi F/RT) \tag{4}$$

The Ψ value is supposed to be the same for both species. To a first approximation, Ψ is the electrical potential of the Stern layer, and the γ_i values correspond to the transfer from the infinitely diluted solution in water to the Stern layer. Hence, the pH value in eq 1 is actually pH_w, while the true pH value of the Stern layer is $\mathrm{pH}_m = \mathrm{pH}_w + \log\gamma_{\mathrm{H}^+} + \Psi F/2.3026\ RT$. The medium effect, $\Delta\mathrm{p}K_a^a = \mathrm{p}K_a^a - \mathrm{p}K_a^w$, is essentially caused by the quantity $-\Psi F/2.3026\ RT$ (eq 2). As a result, the $\mathrm{p}K_a^a$ values at low bulk ionic strength on the whole decrease in micellar solutions of cationic surfactants (Ψ>0) and increase in solutions of anionic surfactants (Ψ<0) as compared with aqueous media. In the case of nonionic surfactants, for which $\Psi \to$ 0, the $\mathrm{p}K_a^a$ value is equal to $\mathrm{p}K_a^i$, and the influence of the non-aqueous microenvironment may be partly modelled by medium effects in water-organic mixtures. The salt effects, i.e. the influence of the salt background (according to biophysical terminology, 'supporting' electrolytes) on the $\mathrm{p}K_a^a$ value, usually fit the model of surface charge screening.[6,8,9,12,17b,d,f,j,n] The latter phenomenon leads to $\mathrm{p}K_a^a$ rise in cationic surfactants systems and to its fall − in anionic ones. Strictly speaking, a term $\log({}^m f_\mathrm{R}/{}^m f_\mathrm{HR})$ must be added to the right side of eq 2, reflecting the additional contribution of the concentration activity coefficients, ${}^{m}f$, of the species located within the Stern region. However, as the latter may be regarded as a concentrated (ca. 3-7 M) electrolyte solution, this logarithmic term is as a rule supposed to be negligible.[12] The electrostatic model, described by eqs 2,4, allows to evaluate the electrical potential of ionic micelles surfaces. The K_a^i value is often equaled to the K_a^a value of the given indicator bound by micelles of nonionic surfactants. Numerous studies[5,6,12] confirm, in outline, the adequacy of this model under conditions of complete binding of the dye by micelles.

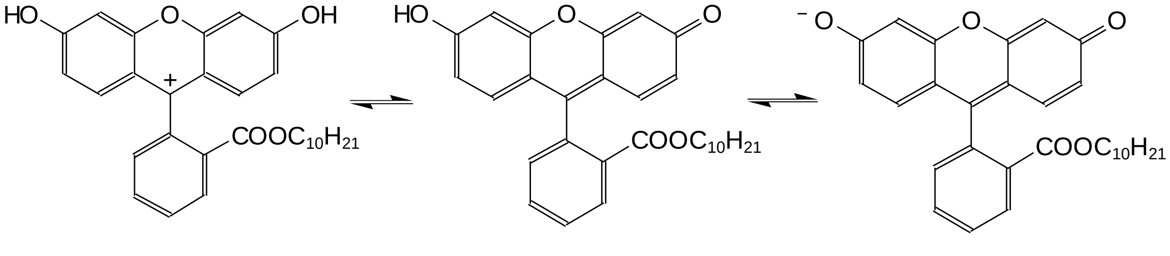
Recently the body of published new data on protolytic and other equilibria in micellar surfactant solutions have sharply increased. This is connected with the peculiarity of such systems, which can be regarded as intermediate ones between aqueous solutions and water-organic two-phase systems. However, the imperfection of the pseudophase conception may sometimes manifest itself quite essentially. Thus, even on complete binding of nitrophenols by cationic micelles, the correlations between their acidic strength and Hammett σ-constants are violated.[7] The $\mathrm{p}K_a^a$ values of series of biologically active substances, analogues of fluazinam, are shown to correlate with the $\mathrm{p}K_a$ values in homogeneous liquid systems only if employing the steric parameters of ortho-substituents.[15] Some other data seem to demonstrate the over-simplification of the common electrostatic model (eq 2), connected with the conception of the 'intrinsic' constant K_a^i .[12d,16]

1.2. The pseudophase ion exchange (PIE) model. Another well-recognized approach to the systems under discussion is based on the pseudophase ion exchange (PIE) model.[10,18] The application of this model allowed to reach a prominent progress in understanding of kinetics, acidity, and fluorescence in ionic surfactant systems. [18e,f,19] However, a set of parameters, such as ion exchange constants, degree of dissociation of the micellized surfactant, the concentration of the surfactant in the pseudophase, and in some cases − the value of ionic product of water, $[\mathrm{H}_m^+][\mathrm{OH}_m^-]$, in the Stern region, is necessary for estimation of $\mathrm{p}K_a^m$ values.[10,18c,e] Meanwhile, only few colloidal systems are so well-defined. Moreover, the Ψ values are as a rule not used for treating the data in terms of the PIE model, and hence the latter cannot be used for monitoring of the electrical properties of interfaces. Nevertheless, the adaptation of the PIE model to complicated compositions of surfactants, buffers and salts, [10,18d,20] as well as comparison of PIE and electrostatic models[17d,21,22] is very useful. So, for sodium n-dodecyl sulfate (SDS) micelles, the combination of the set of PIE parameters[10b] with the Ψ values, obtained with a hydrophobic coumarin,[12d] leads to a constant value $\log\gamma_{\mathrm{H}^+} = -0.2 \pm 0.1$ within a wide range of NaCl concentrations[23] (in cetyltrimethylammonium bromide (CTAB) micelles $\log\gamma_{\mathrm{OH}^-} = +0.76$ [21]). Gaboriaud and co-workers[9] showed the possibility of unification of the two models, replacing Ψ by its dependence on logarithm of counterions activities or concentrations; in the case of a mixed salt background the selectivity coefficients, S_i ,[9,17d,17e] can serve instead of ion exchange constants.

1.3. The goal in the present study. The common electrostatic model assumes: (1) the constancy of the Ψ value in a fixed ultramicroheterogeneous system, as estimated by using different indicators, and (2) the constancy of the $\mathrm{p}K_a^i$ value of the given indicator in any micellar pseudophase, at any salt background. The present study was undertaken in order to test the validity of these principles, examining a wide series of micellar systems by using the same indicator probes under identical conditions (surfactant concentrations, bulk ionic strength, buffer solutions).

In the case of anionic surfactants, the vast majority of the $\mathrm{p}K_a^a$ values, available in literature, are obtained in SDS micelles.[5,6,11-14,16,17,24] Hence it is hard to judge if the conclusions can be extended to all the anionic surfactants, at least to those with sulfate and sulfonate groups. Regarding SDS as a 'standard' anionic surfactant, we aimed at comparing among the $\mathrm{p}K_a^a$ values of indicators in solutions of various anionic surfactants, some nonionic surfactants, mostly used cationic surfactants, and some related systems.

1.4. The choice of acid-base and solvatochromic probes. To ensure the binding completeness, the dyes, containing hydrophobic hydrocarbon groups, are often used. However, the penetration depth of certain form of the given reagent into the micelles may depend on the peculiarities of its structure. The molecules serving as pK_a^a-probes, or at least their ionizing groups, are supposed to be situated in the Stern region. To avoid one-sided information, we considered it desirable to use indicator couples with various charge types. We have chosen the dyes of different structure, with charge types $+/0$, $0/-$, and $+/\pm$, completely bound by surfactants micelles − Decyl Fluorescein (DF):



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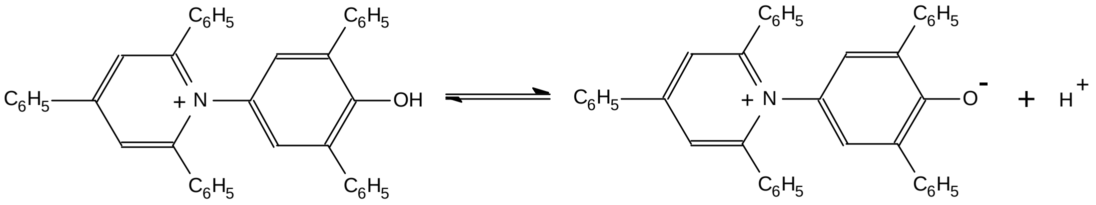
$$H_2R^+ \overset{K_{a0}^a}{\rightleftharpoons} HR \overset{K_{a1}^a}{\rightleftharpoons} R^-$$

and the standard solvatochromic dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide [Reichardt dye, (RD)]:



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colorless form colored form

$$HR^+ \rightleftharpoons R^\pm + H^+ , \quad K_{a0}^a$$

These dyes as well as their structural analogues are widely used due to their luminescent (hydroxyxanthenes) and solvatochromic (betaines)[25] properties while studying various colloidal systems,[12b,17f,26-28] in fiber optics and sensors[12j,29] etc.. Besides, it seemed of importance to compare our results with the data on pK_a^a of 7-hydroxy-4-heptadecylcoumarin,[1b,12a,c,d] 7-hydroxy-4-undecylcoumarin and 7-dimethylamino-4-heptadecylcoumarin,[6] 2-nitro-4-nonylphenol, 2-nitro-4-tert-octylphenol,[7] 5-(N-octadecanoyl) aminofluorescein.[12j] For all the listed reagents the long hydrocarbon chain ensures complete binding of their ions even by like-charged surfaces. On the other hand, the binding can be achieved without a long tail as well, due to the total hydrophobicity of the reagent. E.g., the anions of Bengal Rose B[17k] and Bromothymol Blue[17l] and may incorporate into the micelles of anionic surfactants. However, in the first case the protolytic equilibriua are quite complicated,[17k] while in the other case one has to deal exceptionally with solutions of a high ionic strength and to make additional extrapolation of the pK_a^a values to the state of complete binding.[17l]

Despite its relatively large size,[30] the standard betaine dye RD is now extensively used for studying various colloidal systems,[12b,28,33] including sol-gel systems,[28g,34] both as acid-base and solvatochromic indicator. In the case of this dye the K_{a0}^a value corresponds to the transformation of a cation not into a neutral 'usual' form R, but actually into a zwitterion $R^\pm$, as its dipolar moment is extremely high (ca. 15 D).[25]

Several other indicator dyes were used by us in selected micellar systems as well.

2.Experimental

2.1. Reagents. DF, Decyl Eosin, and Ethyl Fluorescein were synthesized as described in literature,[35] and identified with the help of ^{1}H NMR spectra, TLC, and elemental analysis. No decolorization of the dyes in organic solvents (alcohols, acetone), i.e. lactone formation, was observed.[36] This justifies the complete esterification of the carboxylic group. The solvatochromic betaine dyes were kindly put to our disposal by Professor Dr. Chr. Reichardt (Philipps University of Marburg, Germany). The samples of the dyes Bromophenol Blue, Ethyl Eosin, 6-Hydroxy-9-Phenyl Fluorone, Hexamethoxy Red and Quinaldine Red were earlier used in this laboratory.[17f,h,n,37] The surfactants samples purchased from Sigma were used as such: CTAB (99%), Tween 80, N-cetyl-N,N-dimethylammonium propane sulfonate (CDAPS), SDS (99%), SDBS (80%). The pK_a^a value of Quinaldine Red in SDBS micellar solution, prepared from the latter sample, coincides with that obtained in our laboratory earlier using a SDBS sample of high purity. Nonyl Phenol 12 (NP 12) (‘Soyuzneftekhimprom’, Kazan, Russia), cetylpyridinium bromide (Minkhimprom, USSR), and sodium n-decyl sulfonate (Diagnosticum, Lvov, Ukraine; chromatographically pure) were used without further purification. Oxyethylated alcohols were synthesized by us as described earlier.[38,39] The samples of oxyethylated anionic surfactants were synthesized and gifted to us by Dr. Yu.M. Bochkaryov (‘SintezPAV’, Shebekino, Russia). The samples of n-octadecyltrimethylammonium chloride (Fluka, >98%), sodium n-tridecyl−, n-tetradecyl− and n-hexadecyl sulfates as well as of sodium n-hexadecyl sulfonate were gifted by Professor Dr. S.N. Shtykov (Saratov State University, Russia). Sodium and potassium chlorides, sodium bromide, sodium perchlorate and tetrafluoroborate, tetra-n-butyl ammonium dihydrophosphate, potassium iodide, phosphoric, acetic, and hydrochloric acids were analytical-grade reagents, borax and tetra-n-butyl ammonium iodide were purified by re-crystallization. p-Toluensulfonic acid was purified by extraction with chloroform. The standard sodium hydroxide solution was prepared using CO_2 −free water.

2.2. pH measurements. The pH values were checked by using a glass electrode in a cell with liquid junction (1 M KCl). Standard buffer solutions (pH 1.68, 4.01, 6.86, 9.18) were used for cell calibration. The pH values of working solutions were created with HCl, with acetate (pH 3.8 to 5.4), phosphate (5.8 to 8.2), and borate (8.0 to 10.0) buffer solutions, as well as with NaOH. The constant ionic strength was maintained by additions of sodium chloride with regard to the contribution of the buffer mixtures. We have studied the influence of SDS (0.01 and 0.05 M) and of salt additions [mainly sodium chloride, C(NaCl) = 0.2 M] on the pH values of various buffer systems (borate, phosphate, acetate) as well as of HCl solutions [C(HCl) = 0.001 и 0.01 M]. In all the buffer systems at high ionic strength, the pH values of micellar solutions coincide (within the limits of experimental error) with those of corresponding surfactant−free solutions. In acetate, phosphate, and borate buffer systems without NaCl addition an analogous picture is observed. The sole exception are HCl solutions. At SDS concentrations 0.01 and 0.05 M the pH values of HCl solutions increased on the average by 0.12 and 0.50 pH units, respectively, which agrees with the common model of exchange of H^+ ions for Na^+ ions on the surface of SDS micelles.[10b] As for the influence of cationic surfactants on the pH values being especially expressed in the case of phosphate buffer solutions, we will just mention here that the experimentally obtained pK_a^a value is practically independent of the nature of the used buffer system.

2.3. Evaluation of the pK_a^a values. Absorption spectra were obtained with the SP-46 apparatus. The pK_a^a values of the dyes were determined as described earlier.[17] The emission spectra were registered with the Hitachi F-4010 apparatus; these measurements were performed in cooperation with Z.A. Sizova. Because of poor solubility of the studied hydrophobic dyes in water their stock solutions were prepared in micellar solutions of corresponding surfactants. Whenever it was impossible to reach complete dissolution, the residue was separated by filtration. The working concentrations of the dyes were within the limits of (5-9)×10^{-5} M for the betaine, (4-5)×10^{-6} M for DF, and (0.6-3)×10^{-5} M for other dyes. For preparation of stock solutions of hydrophobic dyes no organic solvents were used, as it is known[17f,l] that even small additions of organic solvents to micellar solutions of anionic surfactants display marked influence on the $\mathrm{p}K_a^a$ values of dyes. On the other hand, the formation of DF homomicelles is probably impossible here. Keeping of the solid dye with aqueous borax buffer solution (pH 9) at 50°C, accompanied by shaking and stirring makes it possible to obtain a solution with concentration 3×10^{-6} M. Under these conditions a typical absorption spectra of the R^- anion was registered, with $\lambda_{\max}$ = 495 nm. For determination of the $\mathrm{p}K_{a0}^a$ and $\mathrm{p}K_{a1}^a$ values of DF and of other hydroxyxanthenes, the analytical positions near $\lambda_{\max}$ of the species H_2R^+ and R^-, respectively, were used, while for $\mathrm{p}K_{a0}^a$ of the betaine − near $\lambda_{\max}$ of colored form. In HCl solutions at $\mathrm{pH} < 1.3$, namely, while measuring the spectra of the cationic form H_2R^+ of DF in micellar solutions of cationic and nonionic surfactants, the ionic strength exceeded 0.05 M. In the case of Bromophenol Blue, Hexamethoxy Red, and Quinaldine Red the procedure was as described earlier.[17f,h]

2.4. Checking the completeness of indicator couples binding to micelles. The studies of absorption spectra, as well as the $\mathrm{p}K_a^a$ values (Figure 1) of all the dyes used as a function of surfactant concentrations at C_S > cmc, ensure the complete binding of all the dye species under conditions, presented in the Tables and in the text. In the case of DF anion, the emission spectra were used for the same purpose too. According to Song et al.,[27] at the dye and surfactant concentrations being equal to those used by us, even a less hydrophobic dye, Butyl Fluorescein (with the group COO−n-C_4H_9 instead of COO−n-$C_{10}H_{21}$ of DF) is completely bound at pH 6.86 to micelles of CTAB, SDS, and of nonionic Triton X 100, as follows from the absorption and emission spectra. Another argument for hydrophobic dyes (DF, RD) complete binding to micelles is the stability of their solutions at concentrations much higher than their solubilities in water (i.e. the solubilization phenomenon).

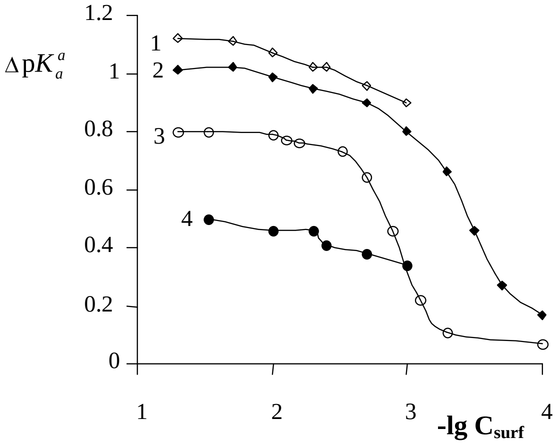


Fig.1. Dependences of $\Delta\mathrm{p}K_a^a$ ($=\mathrm{p}K_a^a-\mathrm{p}K_a^w$) on surfactants concentrations: 1-3 – Bromophenol Blue, I = 0.01 M (here $\mathrm{p}K_a^w$ = 4.08 corresponds to the given ionic strength, while the thermodynamic value equals 4.20), 4 – RD, I = 0.05 M; surfactants: 1 – $C_{12}E_{12}$, 2 – Brij 35, 3 – Triton X 305, 4 – Nonyl Phenol 12.

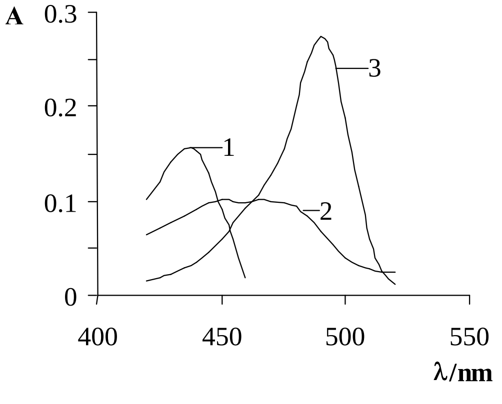


Fig.2. Absorption spectra of Ethyl Fluorescein species in aqueous solutions at I = 0.05 M (NaCl): 1– H_2R^+, 2 – HR, 3 – R^-.

3. Results

3.1. The influence of the nature and concentration of nonionic surfactant on the $\mathrm{p}K_a^a$ values of Decyl Fluorescein. 3.1.1. Medium effects, $\Delta\mathrm{p}K_{a0}^a$ and $\Delta\mathrm{p}K_{a1}^a$ in various nonionic micelles. First of all, uncharged micellar surfaces were examined. The ‘aqueous’ values, $\mathrm{p}K_a^w$, of DF are hard to determine because of low solubility of the HR species. Taking them as equal to the corresponding values of Ethyl Fluorescein, one can find the medium effects in micelles of the studied nonionic surfactants. The absorption spectra of the Ethyl Fluorescein species are depicted in Figure 2; this dye contains the group $COOC_2H_5$ instead of COO−n-$C_{10}H_{21}$ of DF. The thermodynamic values of $\mathrm{p}K_{a0}^w$ and

pK_{a1}^{w}, 2.94 ± 0.07 and 6.31 ± 0.03, respectively, were obtained by us spectroscopically, using the standard procedure. They are close to those of 6-Hydroxy-9-Phenyl Fluorone (with H instead of COO−n-$C_{10}H_{21}$; pK_{a0}^{w} = 3.10, pK_{a1}^{w} = 6.28).[37] The medium effects in micelles of the studied nonionic surfactants (Table 1) change

Table 1. The pK_a^a values of Decyl Fluorescein in micellar solutions of nonionic surfactants at I = 0.05 M (NaCl), 25 °C

Surfactant	HLB [a]	cmc,[b] M	pK_{a0}^{a}	pK_{a1}^{a}
C_S = 0.005 M				
$C_{16}E_{16}$	14.8	3.16×10^{-4}	1.92±0.01	7.14±0.02
$C_{16}E_{8}$	12.4	3.47×10^{-5}	2.30±0.05	6.90±0.01
$C_{11}E_{10}$	14.6	2.51×10^{-3}	2.22±0.01	6.88±0.01
$C_{12}E_{12}$	15.4	7.94×10^{-4}	2.13±0.02	6.91±0.01
$C_{12}E_{15}$	–	–	2.17±0.02	6.96±0.04
C(Tween 80), M	15.0	1.20×10^{-5}		
0.0007			2.00±0.04	7.21±0.02
0.003			2.25±0.01	7.12±0.03
0.01			2.12±0.05	7.20±0.04
0.05			1.83±0.08	7.24±0.07

[a] The HLB numbers demonstrate the hydrophilic-lipophilic balance (according to Griffin);
[b] cmc − critical micelle concentration (the given data refer to pure water).

within the following limits: ΔpK_{a0}^{a} = −(0.8-1.3) and ΔpK_{a1}^{a} = (0.6-0.9). This is quite usual for the acid−base couples with the given charge types (+/ 0 and 0/ −, respectively; see Figure 3) during the transfer from water to water-organic mixtures,[5,6,37,41] though in the latter case the ΔpK_a values, contrary to ΔpK_a^a, contain an additional contribution, $\log\gamma_{H^+}$, as well, which complicates the pK_a values comparison. Hence, as a first approximation, the micelles of all the nonionic surfactants with (−CH_2−CH_2−O−) chains behave themselves in a similar manner in respect to indicator dyes.

However, the variations in both pK_{a0}^{a} and pK_{a1}^{a} values of DF in solutions of various nonionic surfactants (Table 1) are though slightly yet still above the experimental error. The same refers to the variations in concentrations of the given nonionic surfactant. The greatest changes are registered for the pK_{a0}^{a} values, which can be explained supposing the solvation of the dye cation by the cavities of oxyethylene ‘tangle’ of nonionic micelles. As a result, small changes in the structure of the hydrophilic portion of nonionic micelles may influence the protolytic prop-

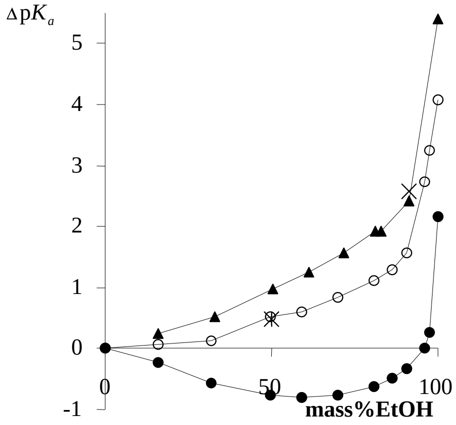
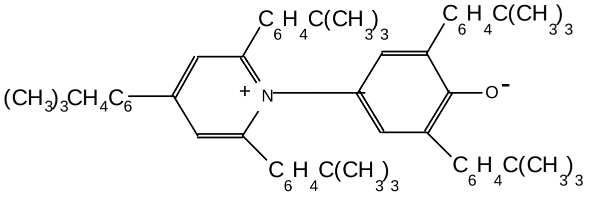


Fig.3. The variations of the medium effects, ΔpK_a = pK_a − pK_a^w, in water−ethanol mixtures. ΔpK_{a0} of 6-Hydroxy-9-Phenyl Fluorone: full circles; ΔpK_{a1} of the same dye: empty circles (calculated from the pK_a values published in ref. 37); ΔpK_{a2} values of Bromophenol Blue: triangles; ΔpK_{a0} of Rhodamine B: × (from ref. 17c); ΔpK_{a0} of 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide (RD): * (from ref. 40).

erties of indicators. No distinct regularity was revealed in the dependence of pK_a^a values of DF on the nonionic surfactant nature, namely, on HLB or cmc. Yet it is evident that for oxyethylated alcohols with fixed length of the hydrocarbon chain (C_{16}) and sharply differing oxyethylene chain length, the pK_{a0}^a values are higher, while pK_{a1}^a values – lower for a surfactant with a smaller hydrophilic portion ($C_{16}E_8$) as compared with $C_{16}E_{16}$. As the rise of an organic co–solvents fraction in a water-rich water-organic mixture (Figure 3) leads to the decrease in the pK_a values of cationic acids (such as pK_{a0}) and to the opposite effect for the pK_a of neutral acids (such as pK_{a1}), it may be assumed that the xanthene nucleus of DF, located on the border between the 'oil drop' and oxyethylene chains, is more exposed to water molecules in the case of $C_{16}E_8$, as compared with surfactants with more bulky oxyethylene 'mantle' ($C_{16}E_{16}$).

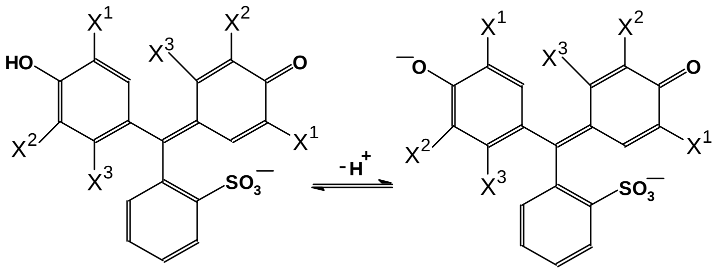
3.1.2. The dependence of the pK_a^a values of Decyl Fluorescein on the nonionic surfactant concentration. The observed dependence (Table 1) may be explained by micellar transitions (sphere →rod). This results in heightening of the hydrophobicity of the micelles, thus influencing the protolytic properties of the given indicator. In the case of the substance $C_{16}E_{12}$ within the concentration range 10^{-5} M to 0.1 M and temperatures < 40 °C and > 60° C, the solutions become turbid. Near 50 °C the turbidity disappears; for DF pK_{a1}^a = 6.8± 0.1 at 1.25×10^{-3} M of $C_{16}E_{12}$.

3.2. Other dyes in nonionic surfactant solutions. 3.2.1. Reichardt betaine. As was shown earlier,[17g] the concentration dependence is less expressed in the case of the betaine dye. The possible reason may be that the betaine dye penetrates into the hydrocarbon core of the nonionic micelle deeper than DF does, and therefore the micellar transitions display smaller influence on its acid-base properties. Note, that in 0.05 M NP 12 solution, the λ_{max} values of RD and of its analogue with five 4-tert-butyl groups in the phenyl rings, are 540 and 589 nm, respectively, while in individual organic solvents the λ_{max} values of these dyes are much closer.[25]



The charge transfer band of the mentioned dyes is very sensitive to the nature of the microenvironment (negative solvatochromism). Thus, further hydrophobization of the reagents of this type leads to their deeper penetration into the micelle of a nonionic surfactant. The pK_a^a values support this idea: in 0.01 M NP 12 solution (borate buffer solution + NaCl, ionic strength 0.05 M; 25 °C) the pK_a^a value of the standard betaine equals 9.10,[17g] while that of the penta-tert-butyl derivative is 9.63±0.09 (λ_{max} = 538 and 588 nm, respectively). At the same time, in water-organic solvents with minor possibilities of preferential solvation, e.g. in 98.7 mass.% n-butanol, the pK_a of the tert-butyl derivative is 0.1 units lower as compared with the standard dye, and the λ_{max} values coincide.[42]

3.2.2. Bromophenol Blue in nonionic surfactant micelles. For commonly used acid-base indicators the probable position in the nonionic micelles is the oxyethylene portion.[5,12g-i,17a,21] In this case the pK_a^a dependence on the surfactant nature is also observed, which can hardly be interpreted unambiguously. E.g., the pK_{a2}^a values (±0.03) of Bromophenol Blue ($HR^- \rightleftarrows R^{2-} + H^+$) under conditions of complete binding to micelles in the solutions of Triton X 305, Triton X 100, Tween 80, Brij 35, and $C_{12}E_{12}$ equal 4.88; 5.00; 5.09; 5.10; 5.20, respectively; bulk ionic strength 0.01 M (NaCl + buffer), 25 °C.

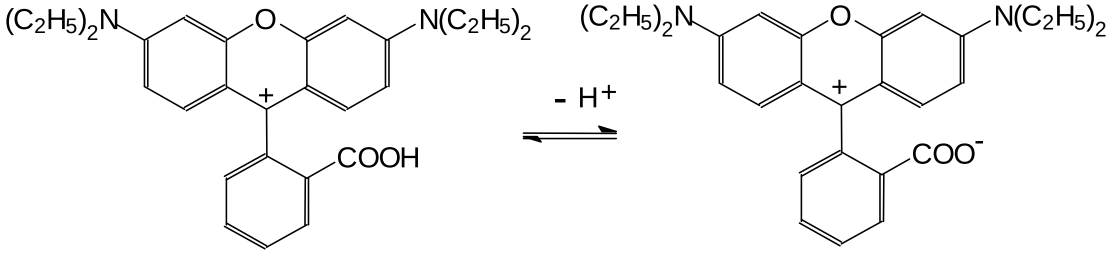


HR^- (yellow) R^{2-} (blue)

Bromophenol Blue: $X^1=X^2=Br$, $X^3=H$; Bromothymol Blue: $X^1= CH(CH_3)_2$, $X^2 =Br$, $X^3=CH_3$. It should be noted that the increase in the oxyethylene 'mantle' of micelles causes more hydrophilic environment of the indicator, as the latter, unlike DF, may be bound by the peripheral part of micelles, neighboring with the bulk (aqueous) phase.

3.2.3.Bromothymol Blue in nonionic surfactant micelles. For another sulfonephthalein, Bromothymol Blue, in micellar solutions of Nonyl Phenols 10 and 12, Tweens 20, 40, 60 and 80, Tritons X 100 and X 305, and Brij 35, the ΔpK_{a2}^a at bulk ionic strength 0.05 M (NaCl + buffer) are within the range 1.76 to 2.11.[17a,c]

3.2.4.Rhodamine B in nonionic surfactant micelles. For Rhodamine B in micellar solutions of NP 12, Tween 80, Tritons X 100 and X 305, and Brij 35, the ΔpK_{a0}^a (±0.03) values of the cation HR^+ vary



HR^+ R

from 0.88 to 1.06 at ionic strength 0.01 M ($HR^+ \rightleftharpoons R^{\pm} + H^+$; here the neural form $R^{\pm}$ is actually a zwitterion). The colorless lactone of Rhodamine B does not appear in nonionic micelles; the results in detail will be published later.

3.3. The influence of the nature of anionic surfactants on the pK_a^a values of hydrophobic dyes.

3.3.1. General comparison. As a whole, the pK_a^a values of hydrophobic dyes in micellar solutions of anionic surfactants (Table 2) sharply differ from those in micellar solutions of other colloidal surfactants, though in all the cases for DF, in accord with the charge types, $\Delta pK_{a0}^a < \Delta pK_{a1}^a$ (comp. Figure 3). All the anionic surfactants behave more or less similarly towards the studied acid-base indicators. However, the peculiarities of anionic surfactants micelles (e.g., micellar size and shape, character of head groups packing, degree of hydration of the surface) cause distinct variations in the pK_a^a values. So, for DF, the pK_{a0}^a and pK_{a1}^a values vary within the limits of 4.47 to 5.19 and 8.64 to 8.96, respectively, and the pK_{a0}^a value of the cation of RD – from 10.12 to 10.70. While for the surfactants $C_nH_{2n+1}OSO_3Na$, at n from 12 to 16, the cmc values in pure water are low enough [8.3×10^{-3} M (n = 12; 25 °C), 5.0×10^{-3} M (n = 13; 50 °C), from 2.2×10^{-3} to 2.5×10^{-3} M (n = 14, 40°C); from 0.4×10^{-3} to 0.6×10^{-3} M (n = 16; 40-60 °C)],[2,43-45] and they undergo further decrease in the presence of NaCl.[2,9b,43,45] The cmc value of sodium n-decyl sulfonate at 25 °C equals 0.040 M in pure water and 0.029 and 0.022 M at NaCl concentrations 0.053 и 0.1 M, respectively.[43]

Therefore such experimental conditions were chosen so as to ensure the micelle formation of the latter surfactant. The sole exception was the concentration of $C_{10}H_{21}OSO_3Na$ 0.02 M (Table 2). The ionic strength of the bulk phase, I, was created mainly by NaCl, while no more than 5% (in the case of acetate buffer solutions − no more than 20%) − by buffer mixtures. However, the true equilibrium concentration of Na^+ ions in the bulk phase is somewhat higher due to surfactant monomers and partial dissociation of the anionic surfactant in micelles, as shows eq 5:

$$[\mathrm{Na}_w^+] = C_{\mathrm{Na}^+} + \mathrm{cmc} + (C_{\mathrm{surf.}} - \mathrm{cmc})\times\alpha \ , \qquad (5)$$

where C_{Na^+} is the analytical concentration of Na^+ ions, created by the supporting electrolyte; cmc corresponds to the given C_{Na^+}; the dissociation degree of the micellized surfactant, α, is taken to be equal to 0.20.[17e,m] Thus, for SDS and its homologues at ionic strength of the buffer mixture 0.05 M, the 'true' equilibrium bulk value of $[\mathrm{Na}_w^+]$ equals 0.052-0.055 M. Yet this causes no additional alterations of $\mathrm{p}K_a^a$ more than by 0.01-0.03 units, as follows from the slope $\mathrm{d}(\mathrm{p}K_a^a)/\ \mathrm{dlog}[\mathrm{Na}_w^+] = -0.85$.[17f,m,n]

Possible systematic errors in α and cmc values may influence first of all the $[\mathrm{Na}_w^+]$ values in 0.03 M sodium n-decyl sulfonate solutions; it may explain the understated $\mathrm{p}K_{a0}^a$ value at small ionic strength in the solutions of this surfactant, but it cannot do the same with the corresponding discrepancy in 0.4 M NaCl solution (Table 2).

3.3.2. The influence of the size of the surfactant hydrophobic portion. Interestingly, even the length of the hydrocarbon tail of anionic surfactant influences the $\mathrm{p}K_a^a$ values, contrary to the case of cationic surfactants − alkyltrimethylammonium homologues C_{11}, C_{12}, C_{16}, C_{18}.[17j] On the other hand, this influence appears to be far from being so monotonous, as reported by the other authors, who studied the methoxy derivatives of triphenylcarbinol as $\mathrm{p}K_a$-indicators in micellar solutions of anionic surfactants with various length of the hydrocarbon tail (C_8, C_{10}, C_{12}, C_{14}).[9b] Therefore we determined the $\mathrm{p}K_a^a$ value of Hexamethoxy Red (2,2′,2″,4,4′,4″-hexamethoxy triphenylcarbinol; $\mathrm{Ar_3C^+} \rightleftarrows \mathrm{Ar_3COH} + \mathrm{H^+}$) at NaCl concentration 0.4 M in solutions of SDS (0.02 M) and of sodium n-decyl sulfonate (0.01 M). The values registered are 4.71±0.03 and 4.03±0.10, respectively, which confirms in general features the results presented in Table 2. On the other hand, the $\mathrm{p}K_a^a$ value of Hexamethoxy Red at I = 0.05 M (NaCl) equals 5.57±0.06 in 0.01 M $C_{14}H_{29}OSO_3Na$ solution, which somewhat exceeds the corresponding value in SDS solutions ($\mathrm{p}K_a^a = 5.47$). Such distinction from results obtained for Decyl Fluorescein and the betaine dye (Table 2) may be caused by the peculiarities of the location of various indicators in anionic micelles. The effects may reflect variations both of Ψ and $\mathrm{p}K_a^i$ values (eq 2). In this case the Ψ value must be regarded as the local electrical potential of the indicator's microenvironment.

Based on the above, there appears the uncertainty in the choice of a 'standard' anionic surfactant for comparison of the $\mathrm{p}K_a^a$ values of the given probes with those in other ultramicroheterogeneous systems. Namely, in liposomes, for which, as shown earlier,[17h,m] the $\mathrm{p}K_a^a$ values of the dyes are of 'intermediate' character as compared with those in micellar solutions of nonionic and anionic surfactants.

3.3.3. The influence of temperature. The solutions of sodium tri-, tetra-, and hexadecyl sulfates were studied at 50 °C, because of their high Krafft temperature ($t_{\mathrm{Kr.}}$). However, judging by the results of some supplementary experiments with surfactants, having lower $t_{\mathrm{Kr.}}$, the temperature jump from 25 to 50 °C usually leads to $\mathrm{p}K_a^a$ variations within 0.1-0.2 units. The hydrolysis of the carbalkoxy group of DF under these conditions does not take place either, as the spectrum of HR species does not change its intensity (the latter would have given evidence for formation of colorless Fluorescein lactone). It is worthy of notice, that the $\mathrm{p}K_a^a$ values of numerous indicators, both 'common' (e.g., Quinaldine Red; $\mathrm{HR}^{2+} \rightleftarrows \mathrm{R}^+ + \mathrm{H}^+$) and hydrophobic ones (containing long hydrocarbon tails), in solutions of SDBS ($t_{\mathrm{Kr..}} \approx 52$ °C) are of quite 'micellar' character even at room temperature. Probably, the indicator dyes in surfactant solutions can sometimes 'induce' a microenvironment, close to micellar ones, even at $t < t_{\mathrm{Kr..}}$

3.3.4. Mixed 'ionic + nonionic' micelles. The properties of anionic micelles with 12 oxyethylene groups apparently approach those of the mixed anionic + nonionic micelles, though the $\mathrm{p}K_{a1}^a$ value of DF in micelles of the oxyethylated sulfate is even closer to that in nonionic micelles. Table 2 also demonstrates the sensitivity of the indicator to additives of CPC to Tween 80 micelles.

3.4. Medium effects ($\Delta \mathrm{p}K_a^a = \mathrm{p}K_a^a - \mathrm{p}K_a^w$) in various surfactant systems. Table 3 demonstrates the changes in the acid-base properties of DF and RD occurring as a result of transfer from water to micellar solutions of various types, including various salt background. Besides, our experiments show, that the $\Delta \mathrm{p}K_a^a$ values appear to be strongly dependent not only on the total concentration of the electrolyte, but also on the nature of the latter. As a typical illustration, the $\Delta \mathrm{p}K_a^a$ at small concentrations of hydrophobic ions $\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4^+$ and $\mathrm{C_7H_7SO_3^-}$ in SDS and CTAB systems, respectively, are presented. The solutions of $\mathrm{C_7H_7SO_3Na}$ are obtained directly in working solutions by mixing of NaOH and p-toluenesulfonic acid stock solutions. In the presence of 0.4 M NaCl CTAB micelles convert practically completely into cetyltrimethylammonium chloride micelles (CTAC), while at I = 0.05 M, as it will be shown in section 3.7.1, these micelles are actually mixed ones (CTAX, $\mathrm{X^-} = \mathrm{Cl^-}, \mathrm{Br^-}$).

Table 3. Medium effects ($\Delta \mathrm{p}K_a^a = \mathrm{p}K_a^a - \mathrm{p}K_a^w$) in various surfactant systems, 25 °C

Micellar systems [a]	Decyl Fluorescein		Reichardt dye
	$\Delta \mathrm{p}K_{a0}^a$	$\Delta \mathrm{p}K_{a1}^a$	$\Delta \mathrm{p}K_{a0}^a$
Charge type:	+/0	0/−	+/±
SDS	2.23	2.65	2.07
SDS, 0.4 M NaCl	1.61	1.87	1.57
CPC	−2.05	−1.39	−1.54
CTAX	−2.12	−1.37	−1.21
CTAC, 0.4 M NaCl	−1.32	−0.88	−0.54
CDAPS	−1.31	−0.24	−0.63
Nonionic, with $-\mathrm{C_2H_4O}-$ groups	−0.82	0.89	0.47
SDS, 0.01 M $\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4^+$ [b,c]	1.31 ± 0.03 [d]	2.07 ± 0.01 [e]	1.26 ± 0.14 [e]
CTAB, 0.01 M $\mathrm{C_7H_7SO_3^-}$ [b,c]	−1.51 ± 0.04 [f]	−0.64 ± 0.01 [g]	−0.49 ± 0.02 [h]
$\mathrm{C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na}$	0.68	1.41	1.56
SDS + Tween 80 (1:1)	0.89	2.18	1.84
CPC + Tween 80 (1:4)	−1.44	0.56	−(0.21-0.05) [i]

[a] surfactants concentrations − as in Table 2; if not specially pointed − I = 0.05 M (NaCl); [b] without NaCl; [c] accuracy of other $\mathrm{p}K_a^a$ values is given in Table 2; [d] acetate buffer solution, I = 0.01 M; [e] borate buffer solution, I = 0.0125 M; [f] HCl solutions, 0.02−0.05 M; [g] phosphate buffer solution, I = 0.01 M; [h] 0.008 M CTAB, borate buffer solution, I = 0.025 M; [i] in CTAB − Brij 35 and CTAB − NP 12 systems, at total surfactant conc. 0.003 M, I = 0.05 M (buffer + NaBr).[17f]

3.5. Solvatochromism of the standard betaine dye in micellar media. The charge transfer band of RD is very sensitive to the nature of the microenvironment; the λ_{max} values are presented in Table 4.

Table 4. The $\lambda_{\max}$ values of the solvatochromic indicator 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide in micellar solutions of surfactants

Surfactant	C_S, M	t, °C	$\lambda_{\max}$, nm (E_T^N) [a]	
			NaCl, M	
			0.05	0.40
$C_{12}H_{25}OSO_3Na$	0.01	25	497 [b] (0.828)	497 (0.828)
$C_{12}H_{25}OSO_3Na$ + 0.01 M $N(n\text{-}C_4H_9)_4^+$ [c]	0.01	25	505 (0.800)	–
$C_{12}H_{25}OSO_3Na$	0.01	50	502 [d] (0.810)	–
$C_{13}H_{27}OSO_3Na$	0.01	50	511 (0.779)	–
$C_{14}H_{29}OSO_3Na$	0.01	50	502 [e] (0.810)	–
$C_{16}H_{33}OSO_3Na$	0.01	50	510 [f] (0.783)	–
$C_{10}H_{21}SO_3Na$	0.01	25	–	501 (0.814)
$C_{10}H_{21}SO_3Na$	0.02	25	496 (0.832)	–
$C_{10}H_{21}SO_3Na$	0.03	25	507 (0.793)	–
$C_{16}H_{33}SO_3Na$	0.01	50	505 (0.800)	
$C_{12}H_{25}C_6H_4SO_3Na$	0.01	25	495 (0.835)	–
$C_{12}H_{25}C_6H_4SO_3Na$	0.01	50	495 (0.835)	–
$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	0.01	25	495 (0.835)	–
Phospholipid liposomes [g]	0.002	25	513 (0.773)	–
$C_{12}H_{25}OSO_3Na$ + NP 12 (1:1)	0.02 [h]	25	520 (0.749)	–
$C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$	0.01	25	528 (0.724)	–
Nonionic surfactant (NP 12)	0.01	25	538 [i] (0.693)	–
$C_{16}H_{33}N^+(CH_3)_2(CH_2)_3SO_3^-$	0.001	25	550 (0.657)	–
$C_{16}H_{33}N(CH_3)_3Br$	0.01	25	540 (0.687)	543 (0.678)
$C_{16}H_{33}N(CH_3)_3Br$ + 0.01 M $C_7H_7SO_3^-$ [c]	0.01	25	540 (0.687)	–
$C_{16}H_{33}N(CH_3)_3Br$	0.01	50	542 [j] (0.681)	–
$C_{16}H_{33}NC_5H_5Br$	0.01	25	535 (0.702)	–
$C_{16}H_{33}NC_5H_5Cl$	0.01	25	538 (0.693)	–
$C_{18}H_{37}N(CH_3)_3Cl$	0.01	30	543 (0.678)	–

[a] $E_T^N = [E_T(30) - 30.7]/32.4$; $E_T(30) = 28591/\lambda_{\max}$; [b] According to ref. 28a and 12b, in 0.1 M and 0.05 M SDS solutions without NaCl: 497 nm and 493 nm, respectively; [c] without NaCl; [d] according to ref. 28a, at C_S = 0.10 M, without NaCl: 504 nm; [e] according to ref. 28a, C_S = 0.10 M, without NaCl: 504 nm; [f] according to ref. 28a, at C_S = 0.10 M, without NaCl: 508 nm; [g] phosphatidilecholine + cardiolipid (18 : 1), from ref. 17m; [h] total surfactant concentration; [i] for Brij 35 $\lambda_{\max}$ = 541 nm,[28a] for $C_{12}E_8$ the reported $\lambda_{\max}$ values vary within the range 540-542 nm,[12b,28a] for Triton X 100: within 539-546 nm,[28a,46] and for Tween 80: within 541-547 nm,[46] depending somewhat on C_S (0.01 to 0.08 M); [j] at higher CTAB concentrations, without NaCl, the maximum position is practically the same.

Because of the sloping absorption band of the betaine in the visible, the $\lambda_{\max}$ values (±1 nm) were found by using a special procedure.[47] Our $\lambda_{\max}$ values obtained with cationic surfactants are somewhat closer to the data of Zachariasse et al. and Novaki and El Seoud (535-544 nm),[28a,h,i] than to those reported by Drummond, Grieser, and Healy (532-534 nm).[12b] It turned out that the $\lambda_{\max}$ values of the betaine are in the region of 500 nm practically for all the anionic surfactants. Here, as well as in the case of pK_a^a, the lack of obvious correlations with the surfactants structure may be probably explained both by versatile influence of micelles on the behavior of indicators and by 'disturbing' action of the chromophore on the own micellar microenvironment. The $\lambda_{\max}$ values of the betaine in cationic and nonionic surfactant systems are markedly higher, the latter agreeing with the conception[1f,12i,j,17f,k,n,28a,48,49] of greater hydration of the surface of the anionic micelles as compared with that of cationic and nonionic ones (Table 4).

So, the anionic micellar surface may be really regarded as 'water-like'.[12i,17f,k,n] The absorption spectra of RD in micellar solutions of a nonionic and oxyethylated anionic surfactants, at the same dye concentration, are depicted in Figure 4. Interestingly, the sequence of the effective polarity of micellar microenvironments, obtained by Mukerjee and co-workers[48] by using the electronic absorption band of a nitroxide spin probe 2,2,6,6-tetramethylpiperidinyl-1-oxy, is in agreement with the data of Table 4: SDS > palmitoyl lysolecitin > cetyl trimethylammonium chloride > $C_{12}H_{25}N(CH_3)_2^+-(CH_2)_3-SO_3^-$.

3.6. The positions of absorption bands of Decyl Fluorescein in micellar media. The data for DF lead to the analogous conclusion: in micellar solutions of anionic, cationic, and nonionic surfactants, the λ_{max} values of the cation H_2R^+ are equal to 444, 447, and 448 nm, respectively, and those of the anion R^- – to 504, 513, and 510 nm, respectively. To compare: the λ_{max} values of the species H_2R^+ and R^- of 6-Hydroxy-9-Phenyl Fluorone in water equal 437 nm and 491 nm, respectively;[17a] in the case of Ethyl Fluorescein the corresponding values are 437-438 nm and 490-491 nm (Figure 2). Thus, the spectra of DF also confirm, that the surface of anionic micelles is much stronger hydrated, than that of cationic and nonionic ones. In CTAB micelles the red shift (ca. 20 nm) was also registered by Song et al.[27] for Butyl Fluorescein anion against the band in water. The λ_{max} values in $C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$ micellar solutions are close to those in nonionic micelles. An example of the absorption spectra of the species H_2R^+, HR, and R^- of DF in micellar media is given in Figure 5.

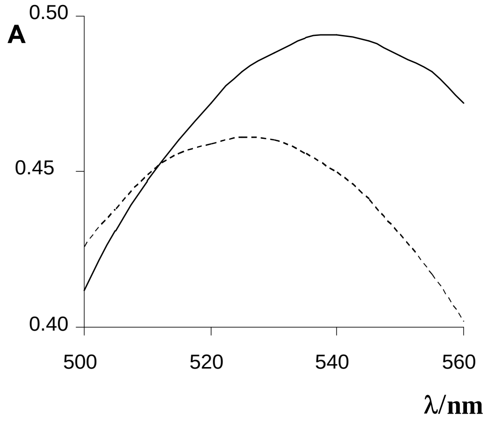


Fig.4. Absorption spectra of the form $R^{\pm}$ of the dye 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide (RD) in micellar solutions of Nonyl Phenol 12 (——) and of an oxyethylated anionic surfactant ($C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$) (- - - -), C_S = 0.005 M, pH = 12.

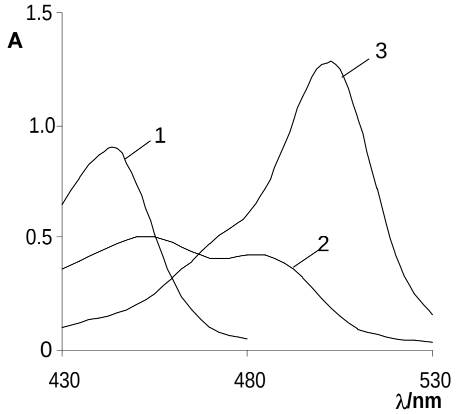


Fig.5. Absorption spectra of Decyl Fluorescein species in sodium dodecyl sulfate micellar solutions (0.01M) at I = 0.4 M (NaCl): 1 – H_2R^+, 2 – HR, 3 – R^-.

3.7. Comparison of the obtained pK_a^a with literature data. 3.7.1. Data for hydroxyxanthenes. To compare our results obtained for DF with the literature data for structurally similar compounds, it is necessary to remember that the hydrophobic tail was introduced into their molecules without esterification of the carboxylic group. As a consequence, such compounds dissociate in three steps, and the neutral form can transform into the colorless lactone. In this connection it is not worthwhile to analyze here in detail the papers treating the last two steps of Fluorescein ionization (neutral $\rightleftarrows$ dianion) as one.[26]

The pK_a^a value, attributed to the hydroxy group of 5-(N-octadecanoyl) aminofluorescein in nonionic micelles (8.04),[12j] agrees sufficiently with the value 7.20 of DF (Table 2), if one keeps in mind the well-known effect of the negative charge influence on the $\mathrm{p}K_a$ value of the remaining group[36] (see also section 4.2). Approximately the same difference is observed between the $\mathrm{p}K_a^a$ value of 5-(N-octadecanoyl) aminofluorescein (5.78), determined in 0.05 M solution of n-dodecyltrimethylammonium chloride,[12j] and the $\mathrm{p}K_{a1}^a$ of DF, 5.04, obtained by re-calculation of the value of 4.94 (Table 2) to the bulk equilibrium concentration $[\mathrm{Cl}_w^-]$ = 0.022 M. The latter, in its turn, is calculated starting from cmc ($C_{12}H_{25}N(CH_3)_3Cl$) = 0.015 M.[43] Generally, for indirect evaluation of the $\mathrm{p}K_a^a$ values, experimentally obtained at other bulk phase contents, eq 6 can be used. The corresponding parameters have been obtained by us earlier for Bromophenol Blue in CTAB + chloride system:[17d]

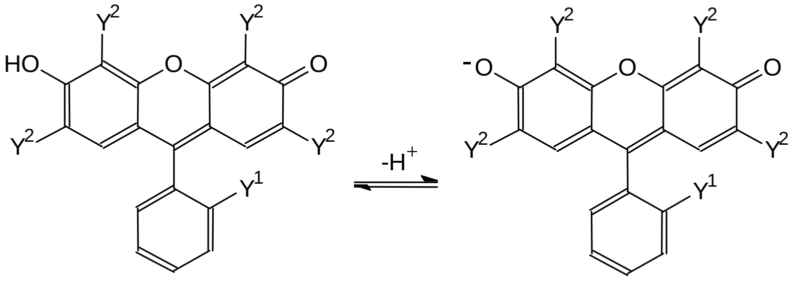
$$\mathrm{p}K_a^a = \text{const} + \log \sum_i S_i [\mathrm{X}_{i,w}^-]^{b_i} \qquad (6)$$

$S_{\mathrm{Br}^-} \equiv 1$, $S_{\mathrm{Cl}^-} = 0.32$, $b_{\mathrm{Br}^-} = 0.83$, $b_{\mathrm{Cl}^-} = 0.73$.[17d] The reciprocal S_{Cl^-} value is close to the ion-exchange constant $K_{\mathrm{Cl}^-,\mathrm{Br}^-}$, thus equal to 3.1.[17d] Such a value agrees well with those obtained for water-micelle, water-air, and water charged bilayer interfaces, by using spectrophotometric, potentiometric, kinetic (ca. 3),[19] flotation (3.05),[50a] and osmometric (3.10)[50b] techniques. Similar relations are obtained for the alkyl pyridinium systems as well.[17j] If we deal with a mixture of counter ions (e.g., Cl^- + Br^-) in a cationic surfactant system, then the calculations of the equilibrium content of the bulk (aqueous) phase are to be carried on by using the constants of ion exchange on the micellar surface. Thus, in the system CTAB (0.01 M) + NaCl (0.05 M) the equilibrium content of the aqueous phase, calculated with $K_{\mathrm{Cl}^-,\mathrm{Br}^-} = 3.1$, corresponds to the bulk concentrations $[\mathrm{Cl}_w^-]$ = 0.043 M, $[\mathrm{Br}_w^-]$ = 0.007 M. The ratio $[\mathrm{Cl}_m^-]$: $[\mathrm{Br}_m^-]$ in CTAX micelles is ca. 2.5.

The agreement of the results is much poorer in the case of SDS solutions. So, the $\mathrm{p}K_a^a$ of 5-(N-octadecanoyl) aminofluorescein ($\mathrm{HR}^- \rightleftarrows \mathrm{R}^{2-} + \mathrm{H}^+$) equals 8.84 at C(SDS) = 0.05 M;[12j] the re-calculation to $[\mathrm{Na}_w^+]$ = 0.053 M results in $\mathrm{p}K_a^a$ = 8.42. This value is not higher, as it could have been expected, but even 0.5 units lower than the $\mathrm{p}K_{a1}^a$ of DF (8.96, see Table 2). One of the possible reasons of such a discrepancy lies in the essential difference in the orientation of the dyes, possessing long hydrophobic tails in different parts of molecules, within SDS micelles.

3.7.2. Data for the Reichardt betaine. Drummond, Grieser, and Healy[12b] reported also the $\mathrm{p}K_a^a$ values of RD in micellar solutions of various surfactants. In $C_{12}H_{25}O(CH_2CH_2O)_8H$ solutions the $\mathrm{p}K_a^a$ (9.06-9.31) are in sufficient agreement with our value for the nonionic surfactant (Table 2). The $\mathrm{p}K_a^a$ value in SDBS solutions is 0.4 units lower than in SDS solutions, other conditions being equal,[12b] which is confirmed by our results as well (Table 2). As for the $\mathrm{p}K_a^a$ values in ionic surfactant systems,[12b] they are in a much poorer agreement with ours. The conversion of the $\mathrm{p}K_a^a$ values to the identical equilibrium composition of the bulk by using the cmc values and relationships of the above type (eqs 5,6), demonstrate, that in SDS solutions our values are ca. 0.40 units higher, while in cationic surfactant solution − ca. 0.50 units lower than in the cited paper.[12b] Probably, the use of unbuffered solutions[12b] in the pH region 7 to 11 may be the cause of the discrepancy. It should also be noted that the influence of both the hydrocarbon tail length of the cationic surfactant and the SDS concentration on the $\mathrm{p}K_a^a$ value of the betaine dye, registered by Drummond, Grieser, and Healy,[12b] can be easily explained by the variations of the bulk ionic strength. According to our results, the pK_{a0}^{a} values of the RD cation in SDS 0.01 and 0.05 M solutions agree well if the true $[Na_{w}^{+}]$ values are considered.

3.8. Dissociation of indicators bound by cationic micelles at bulk ionic strength 4.0 M. In addition to the above studies we decided to examine the behavior of the chosen indicators and some relative dyes at as high as possible bulk ionic strength. The results of pK_{a}^{a} determination and the ΔpK_{a}^{a} ($\Delta pK_{a}^{a} = pK_{a}^{a} - pK_{a}^{w}$) values in CTAB solutions in the presence of 4.0 M KCl are presented in Table 5. The second step of dissociation of hydroxyxanthene dyes studied is shown below:



6-Hydroxy-9-Phenyl Fluorone: $Y^1 = Y^2 = H$; Ethyl Fluorescein: $Y^1 = CO_2C_2H_5$; $Y^2 = H$; Decyl Fluorescein: $Y^1 = CO_2C_{10}H_{21}$; $Y^2 = H$; Ethyl Eosin: $Y^1 = CO_2C_2H_5$; $Y^2 = Br$; Decyl Eosin: $Y^1 = CO_2C_{10}H_{21}$; $Y^2 = Br$; Sulfone Fluorescein: $Y^1 = SO_3^-$; $Y^2 = H$; Fluorescein: $Y^1 = CO_2^-$; $Y^2 = H$.

The chloride system was chosen because at high Br^- concentrations the growth of CTAB micelles may be abnormal,[4,21] thus making the solutions unstable. On the other hand, at 4.0 M Cl^- the CTAB micelles completely transform into CTAC micelles. The choice of potassium cation as co-ion is made taking into account that it is less hydrated than the sodium cation; the results can be compared with our data obtained earlier under identical conditions.[51] The λ_{max} values of DF ions H_2R^+ and R^- equal 448 nm and 516.5 nm, respectively. This confirms complete binding of the species. Moreover, the further dehydration of micellar surface is demonstrated by the value λ_{max} = 562 nm of the RD (E_T^N = 0.623). Note, that in 0.05 M n-dodecyltrimethylammonium chloride (DTAC) solution at 4.0 M NaCl the value λ_{max} = 537 nm was reported.[12b] The latter value is close to those in DTAC, CTAC, and CTAB solutions with low bulk ionic strength[12b] (see also Table 4), which confirms, that the DTAC micelles are sphere-shaped even in 4.0 M NaCl solutions.[52] Contrary to it, the λ_{max} values of RD in CTAC and CTAB micelles in concentrated salt brines agree with the well-known fact of 'sphere → rod' transitions. And really, in 0.003 M CTAB solutions in the presence of 2.0 M and 4.0 M NaBr the λ_{max} values of RD equal 553 nm and 545 nm, correspondingly. The medium effects, ΔpK_{a}^{a} , for hydroxyxanthenes are compared in Table 5 with those obtained by us as well as by other authors[12b,c,e,g,j] for acid-base couples of various charge types, including three dyes with highly polar neutral species.[12e] The pK_{a}^{a} values in both cetyltrimethyl- and n-decyltrimethylammonium systems at 4.0 M Br^- are ca. 0.4-0.5 units lower than that at 4.0 M Cl^-.[12b,c,e,g,,17b,d]

4. Discussion

4.1. The analysis of pK_{a}^{a} linear combinations. 4.1.1. Differences of pK_{a1}^{a} and pK_{a0}^{a} values of Decyl Fluorescein as a criteria of micellar properties. A common approach to the clarification of the solvation properties of the micellar pseudophase as a media for protolytic equilibria is to compare the pK_{a}^{a} values of the indicators with their pK_a values in water-organic mixtures.[5,6,12b,g-j,15,16,17k] Strictly speaking, the latter values are rather to be compared with the pK_{a}^{m} values (eq 3), which are unavailable for direct determination. As today the data on the exact Ψ values of some ionic surfactants micelles are still somewhat ambiguous, and as the γ_{H^+} values in micellar pseudophases and in water-organic mixed solvents are extrathermodynamical quantities, let us first of all examine the difference between the $\mathrm{p}K^a_{a1}$ and $\mathrm{p}K^a_{a0}$ values of DF. In micellar solutions of the majority of anionic surfactants the mentioned difference varies between 3.54 and 3.84 (Table 6).

Table 5. The $\mathrm{p}K^a_a$ values of indicator dyes in micellar solutions of cetyl trimethylammonium chloride (0.003 M), 4.00 M KCl, 25 °C

Indicator	charge type	$\mathrm{p}K^a_a$	$\Delta\mathrm{p}K^a_a$
Decyl Fluorescein, $\mathrm{p}K^a_{a0}$	+/0	2.13 ± 0.01	−0.81
Reichardt dye, $\mathrm{p}K^a_{a0}$	+/±	8.60 ± 0.02 [a,b]	−0.03 [c]
Ethyl Eosin, $\mathrm{p}K^a_{a1}$	0/−	1.11 [d]	−0.79
Decyl Eosin, $\mathrm{p}K^a_{a1}$	0/−	1.18 ± 0.05	−0.72
4-heptadecyl-7-hydroxy coumarin, $\mathrm{p}K^a_{a1}$	0/−	8.31 [e,f]	+0.34 [e]
6-Hydroxy-9-Phenyl Fluorone, $\mathrm{p}K^a_{a1}$	0/−	6.67 ± 0.03	+0.39
Ethyl Fluorescein, $\mathrm{p}K^a_{a1}$	0/−	6.59 ± 0.03	+0.28
Decyl Fluorescein, $\mathrm{p}K^a_{a1}$	0/−	6.61 ± 0.07	+0.30
Sulfofluorescein, $\mathrm{p}K^a_{a2}$	−/=	7.00 ± 0.01 [d]	+0.24
Fluorescein, $\mathrm{p}K^a_{a2}$	−/=	7.17 ± 0.06 [d,g]	+0.37
Bromophenol Blue, $\mathrm{p}K^a_{a2}$	−/=	3.86 [d]	−0.34
Bromothymol Blue, $\mathrm{p}K^a_{a2}$	−/=	8.26 [d,h]	+0.96
Thymol Blue, $\mathrm{p}K^a_{a2}$	−/=	10.47 [d]	+1.27

[a] In the system 0.05 M DTAC + 4 M NaCl, $\mathrm{p}K^a_{a0}$ = 8.82 ± 0.03, from ref.12b; [b] in analogous bromide system $\mathrm{p}K^a_{a0}$ = 9.30 ± 0.06, from ref.12b; [c] for three cationic dyes with highly polar neutral species, 1-hexadecyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, 1-hexadecyl-5-hydroxyquinoline, and 1-hexadecyl-6-hydroxyquinoline, the $\Delta\mathrm{p}K^a_{a0}$ values in DTAC + 4 M NaCl system are −0.09, +0.14, and +0.53;[12e] in analogous bromide systems the values are on the average 0.35 units higher;[12e] [d] from ref. 51; [e] from ref. 12c; [f] in analogous bromide system $\mathrm{p}K^a_{a1}$ = 8.72, ref.12c; [g] for 5-(N-octadecanoyl) aminofluorescein in 0.05 M DTAB + 4 M NaBr $\mathrm{p}K^a_{a2}$ = 7.47, from ref.12j; [h] in 0.05 M DTAB + 4 M NaBr, $\mathrm{p}K^a_{a2}$ of Bromothymol Blue is 8.58, from ref.12g.

The deviation of these values from the 'aqueous' one (for Ethyl Fluorescein and 6-Hydroxy-9-Phenyl Fluorone: $\mathrm{p}K^w_{a1} - \mathrm{p}K^w_{a0}$ = 3.37 and 3.18, respectively) is ca. 0.5. If we assume the positions of all the species of the given dye in micelle being the same, it will allow to exclude the quantities Ψ and γ_{H^+} from consideration. Then the variations of the quantity ($\mathrm{p}K^w_{a1}$ − $\mathrm{p}K^w_{a0}$) are obviously caused by the combination of transfer activity coefficients, γ:

$$(\mathrm{p}K^a_{a1} - \mathrm{p}K^a_{a0}) - (\mathrm{p}K^w_{a1} - \mathrm{p}K^w_{a0}) = \Delta\mathrm{p}K^a_{a1} - \Delta\mathrm{p}K^a_{a0} = \log\{\gamma_{\mathrm{R}^-}\,\gamma_{\mathrm{H_2R}^+}/\gamma^2_{\mathrm{HR}}\} \qquad (7)$$

The values ($\Delta pK_{a1}^{a} - \Delta pK_{a0}^{a}$) are shown in Table 6. Note, that for the four anionic surfactants of the general formulae $C_nH_{2n+1}OSO_3Na$, at I = 0.05 M (NaCl), the difference ($pK_{a1}^{a} - pK_{a0}^{a}$) is strictly constant (3.76±0.03). This allows to attribute the variations in the pK_{a}^{a} values (see Table 2) entirely to the differences in the Ψ values in the region of location of the indicator species in these micelles. This is the more probable as the emission spectra of DF (R^{-}) in micellar solutions of SDS and n-decyl sulfonate are very similar (Table 7). This similarity confirms the same solvation character in the both systems, and as a consequence, the proximity of the γ values. It cannot be excluded that the diminished $|\Psi|$ value of $C_{10}H_{21}SO_3Na$ micelles is connected with the higher hydrophilicity of the latter surfactant as compared with SDS, shown in extraction studies.[53]

Table 6. Differences and sums of pK_{a1}^{a} and pK_{a0}^{a} of Decyl Fluorescein in various surfactant systems, 25 °C

Micellar system [a]	$pK_{a1}^{a} - pK_{a0}^{a}$	$\Delta pK_{a1}^{a} - \Delta pK_{a0}^{a}$	$\Delta pK_{a1}^{a} + \Delta pK_{a0}^{a}$	
			I = 0.05 M	I = 0.40 M
$C_{16}H_{33}SO_3Na$ (50 °C)	3.50	0.13	4.57	
$C_{12}H_{25}OSO_3Na$	3.79	0.42	4.88	
$C_{12}H_{25}OSO_3Na$, 0.4 M NaCl	3.63	0.26		3.48
$C_{13}H_{27}OSO_3Na$	3.76	0.39	4.35	
$C_{14}H_{29}OSO_3Na$	3.77	0.40	4.26	
$C_{16}H_{33}OSO_3Na$ (50 °C)	3.75	0.38	4.56	
$C_{10}H_{21}SO_3Na$ (0.03 M)	4.30	0.93	3.99	
$C_{10}H_{21}SO_3Na$ (0.01 M), 0.4 M NaCl	3.84	0.47		2.69
$C_{12}H_{25}C_6H_4SO_3Na$	3.59	0.22	4.79	
$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	3.81	0.44	4.10	
$C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$	4.10	0.73	2.09	
$C_{12}H_{25}OSO_3Na$+Tween 80 (1:1)	4.66	1.29	3.07	
Tween 80	5.08	1.71	0.07	
$C_{16}H_{33}N(CH_3)_2^{+}(CH_2)_3SO_3^{-}$	4.44	1.07	−1.55	
$C_{16}H_{33}N(CH_3)_3X$	4.12	0.75	−3.49	
$C_{16}H_{33}N(CH_3)_3Cl$, 0.4 M NaCl	3.81	0.44		−2.20
$C_{16}H_{33}NC_5H_5Cl$	4.13	0.76	−3.54	
$C_{16}H_{33}NC_5H_5Cl$+Tween 80 (1:4)	5.37	2.00	−0.88	
SDS, 0.01 M $N(n\text{-}C_4H_9)_4^{+}$ [b]	4.09	0.72	3.38	
CTAB, 0.01 M $C_7H_7SO_3Na$ [b]	4.24	0.87	−2.15	

[a] surfactants concentrations − as in Table 2; if not specially pointed: I = 0.05 M (NaCl);
[b] without NaCl, see Table 3.

Table 7. Excitation and emission maxima of Decyl Fluorescein anion, R^{-}, in anionic surfactant solutions at room temperature [a]

surfactant	C_S, M	λ_{max}^{ex}, nm[b]	λ_{max}^{em}, nm[c]	relative intensity [c]
$C_{10}H_{21}SO_3Na$	0.03	505	531.6	100
$C_{12}H_{25}OSO_3Na$	0.01	505	532.2	81

[a] the dye concentration is constant; pH 9.2, I = 0.05 M (NaCl), 0.3 mass.% ethanol; [b] excitation; [c] emission.

In micellar solutions of a nonionic surfactant the value ($\mathrm{p}K_{a1}^{a}$ − $\mathrm{p}K_{a0}^{a}$) is markedly higher (5.08). This may be understandable assuming that the dehydration of the micellar surface leads to the further decrease in the $\mathrm{p}K_{a0}^{i}$ value and to the increase in the $\mathrm{p}K_{a1}^{i}$ value (compare with the medium effects for the same dye in water-ethanol mixtures, Figure 3). The values ($\mathrm{p}K_{a1}^{a}$ − $\mathrm{p}K_{a0}^{a}$) in $C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$ solution (4.10) and in the SDS + Tween 80 1:1 mixture (4.66) are of intermediate nature, and the same is the case with cationic surfactant solutions (4.12), cationic surfactant at bulk ionic strength 4.0 M (4.48), and CDAPS micellar medium (4.44). The low value of the discussed difference ($\mathrm{p}K_{a1}^{a}$ − $\mathrm{p}K_{a0}^{a}$) for anionic surfactants agrees with the higher values of the polarity parameter $E_{\mathrm{T}}^{\mathrm{N}}$ (Table 4), in accord with the conception of stronger hydration of the Stern region of anionic micelles, based on various spectral data.[12e,i,j,17f,k,48,49] Only the results obtained for $C_{10}H_{21}SO_3Na$ at I = 0.05 M (NaCl) (4.30) and for CTAC at I = 0.4 M (NaCl) (3.81) drop out of the mentioned regularity.

It is of extreme interest, that the difference between the $\mathrm{p}K_{a}^{a}$ values of two hydrophobic coumarins of charge types 0/ − and +/ 0, reported by Fernandez and Fromherz (=7.6),[6] does not change in going from Triton X 100 to SDS micelles. However, these dyes, though similar, have hydrocarbon tails of different length (C_{11} and C_{17}) and different substituents in the 7th position of the coumarin moiety (hydroxy and dimethylamino), so eq 7 cannot be directly applied to them.

4.1.2. Water-organic mixtures. The difference ($\mathrm{p}K_{a1}$ − $\mathrm{p}K_{a0}$) of DF in a mixture of water with n-butanol (82 mass % of alcohol), a solvent with ε^{25} = 20.8 and $E_{\mathrm{T}}^{\mathrm{N}}$ = 0.657, is equal to 6.03,[36] while in 80 mass % acetone (ε^{25} = 29.6 and $E_{\mathrm{T}}^{\mathrm{N}}$ = 0.648) − to 6.28. Here the ($\mathrm{p}K_{a1}$ − $\mathrm{p}K_{a0}$) values essentially exceed those in all the surfactant systems. The value of the discussed differences ($\mathrm{p}K_{a1}$ − $\mathrm{p}K_{a0}$) = 3.46 to 3.86 and ($\Delta\mathrm{p}K_{a1}$ − $\Delta\mathrm{p}K_{a0}$) = 0.28 to 0.68 for 6-Hydroxy-9-Phenyl Fluorone is reached at a content of 16-32 mass % alcohol in water-ethanol mixtures (Figure 6, curve 1),[37] where ε^{25} = 69-60, $E_{\mathrm{T}}^{\mathrm{N}}$ = 0.91-0.82. Yet it would be premature to associate micellar media with a water-ethanol mixture of distinct composition, as the ($\mathrm{p}K_{a1}$ − $\mathrm{p}K_{a0}$) values vary from 4.46 to 5.07, or ($\Delta\mathrm{p}K_{a1}$ − $\Delta\mathrm{p}K_{a0}$) = 1.28 to 1.89, within the limits of 50-90 mass % of ethanol, as can be seen in Figure 3.

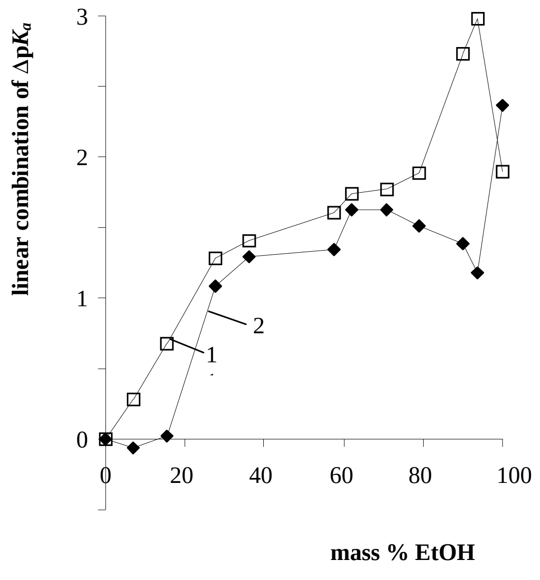


Fig.6. Linear combinations of medium effects of 6-Hydroxy-9-Phenyl Fluorone in water - ethanol mixtures: 1 – ($\Delta\mathrm{p}K_{a1}$− $\Delta\mathrm{p}K_{a0}$) = $\{\log\{\gamma_{\mathrm{R}^-}\,\gamma_{\mathrm{H_2R}^+}/\gamma_{\mathrm{HR}}^2\}$; 2 – $(\Delta\mathrm{p}K_{a0}+\Delta\mathrm{p}K_{a1}) - 2\log\gamma_{\mathrm{H}^+} = \log\gamma_{\mathrm{R}^-} - \log\gamma_{\mathrm{H_2R}^+}$.

The medium effects ($\Delta\mathrm{p}K_{a}$) of the dyes, depicted in Figure 3, agree with the semi-quantitative conception of charge types of the acid-base couples (Kolthoff, Bates).[41] The $\Delta\mathrm{p}K_{a}$ values are positive for the charge type **O/**− ($\mathrm{p}K_{a1}$ of Ethyl Fluorescein and 6-Hydroxy-9-Phenyl Fluorone); the increase in $\mathrm{p}K_{a2}$ of Bromophenol Blue (charge type − / =) is somewhat sharper. This is in agreement with the $\Delta\mathrm{p}K_{a2}^{a}$ values of Bromophenol Blue (0.68 to 1.00) and Bromothymol Blue (1.8 to 2.1, see above) in nonionic surfactants. The U-shaped dependence is typical for cationic acids with charge type +/ 0 ($\mathrm{p}K_{a0}$ of Ethyl Fluorescein and 6-Hydroxy-9-Phenyl Fluorone). Meanwhile the $\Delta\mathrm{p}K_{a0}$ values of RD and of Rhodamine B are substantially positive (Figure 3), reflecting the zwitterionic character of the $\mathrm{R}^{\pm}$ species. Hence, though the $\Delta\mathrm{p}K_a$ values in H_2O-EtOH mixtures contain an additional contribution, $\log\gamma_{\mathrm{H}^+}$, they reflect the sign and size of the $\Delta\mathrm{p}K_a^a$ values in nonionic surfactants (see also section 3.1). The medium effects for the mentioned dyes in mixtures of water with acetone, 1,4-dioxane, and with dimethyl sulfoxide are qualitatively similar.[17c,54]

4.1.3. The difference between the $\mathrm{p}K_{a0}^a$ value of the conjugated cation of 2,6-diphenyl-4-(2,4,6-triphenylpyridinio-1) phenoxide and $\mathrm{p}K_{a0}^a$ of Decyl Fluorescein in micellar solutions. This equals 5.5±0.1 in the case of $C_nH_{2n+1}OSO_3Na$, at I = 0.05 M (NaCl). In cationic and nonionic surfactant solutions this difference is 0.9-1.5 units higher, which reflects the peculiarities of charge types (Figure 3).

4.1.4. Attempts to estimate the Ψ values from the analysis of the sum ($\mathrm{p}K_{a0}^a$ + $\mathrm{p}K_{a1}^a$) of Decyl Fluorescein. Now let us consider the sum of the $\mathrm{p}K_{a0}^a$ and $\mathrm{p}K_{a1}^a$ values of DF. It can be easily derived that:

$$0.8686\ \Psi F/RT = \log(\gamma_{\mathrm{R}^-}/\gamma_{\mathrm{H_2R}^+}) - \Delta(\mathrm{p}K_{a0}^a + \mathrm{p}K_{a1}^a) \qquad (8)$$

Here $\Delta(\mathrm{p}K_{a0}^a + \mathrm{p}K_{a1}^a) = \Delta\mathrm{p}K_{a0}^a + \Delta\mathrm{p}K_{a1}^a$ (Table 6). Assuming that $\gamma_{\mathrm{R}^-} = \gamma_{\mathrm{H_2R}^+}$ (see below), one can calculate the Ψ value of ionic micelles. So, for SDS micelles at I = 0.05 M (NaCl) $\Psi = -144$ mV, while at I = 0.4 M (NaCl) $\Psi = -103$ mV. However, we were unable to find such a smooth dependence of Ψ on hydrocarbon tail length of $C_nH_{2n+1}OSO_3Na$, as in the study where hydrophobic coumarins were used;[8] probably, the reason is that the $\mathrm{p}K_{a0}^a$ and $\mathrm{p}K_{a1}^a$ values were determined for two coumarins with hydrophobic tails of unequal length. For SDS micelles in the presence of 0.05 M $NaClO_4$ a value $\Psi = -92$ mV was estimated in the cited study.[8] For CPC at I = 0.05 M (NaCl) Ψ = 105 mV, and in a mixture of CPC with Tween-80 (1:4) the electrical potential drops to 26 mV. Note, that for five nonionic surfactants, including 4 different concentrations of Tween 80 (Table 1), such approach leads to the value of (2±5) mV. In the study offering this procedure of Ψ evaluation by using two coumarins,[6] for the SDS micelles at 0.024 M solution of the surfactant, at $[\mathrm{Na}_w^+]$ = 0.01 M, the Ψ value was found to be equal to −136 mV. Such a procedure, especially by using of only one indicator, able of two-step ionization, like DF, seems to be somewhat more reliable, than the equating of $\mathrm{p}K_a^i$ to $\mathrm{p}K_a^w$.[5,55]

Possible drawbacks of such approach to the Ψ values may be connected with: (1) equating of the $\mathrm{p}K_a^w$ values of DF to those of Ethyl Fluorescein, and (2) equating of γ_{R^-} to $\gamma_{\mathrm{H_2R}^+}$. However, even in 82 mass % n-butanol, a mixed solvent with molar fraction of water 0.474, favorable for preferential solvation, the $\mathrm{p}K_{a0}$ value of DF is only 0.15 units lower, and the $\mathrm{p}K_{a1}$ value − only 0.12 units higher than those of Ethyl Fluorescein.[36] In CTAC micelles, at 4.0 M Cl^-, the $\mathrm{p}K_{a1}^a$ values of the two dyes coincide (Table 5). The second assumption may turn out to be more approximate, as the R^- and $\mathrm{H_2R}^+$ ions are not so well-shielded and protected from specific solvation (hydration), as $\mathrm{B(C_6H_5)_4^-}$ and $\mathrm{As(C_6H_5)_4^+}$ or $\mathrm{P(C_6H_5)_4^+}$ ions. Using the $\mathrm{p}K_a$ values of 6-Hydroxy-9-Phenyl Fluorone, given in Figure 3, and the recommended values of $\log\gamma_{\mathrm{H}^+}$ (based on the tetraphenyl borate assumption),[56] it is possible to estimate the difference of medium effects for ions, $\log\gamma_{\mathrm{ion}}$:

$$\log\gamma_{\mathrm{R}^-} - \log\gamma_{\mathrm{H_2R}^+} = \Delta\mathrm{p}K_{a0} + \Delta\mathrm{p}K_{a1} - 2\log\gamma_{\mathrm{H}^+} \qquad (9)$$

As it is seen in Figure 6, $\log\gamma_{R^-} > \log\gamma_{H_2R^+}$ within the major range of ethanol concentrations. This is easy to explain by stronger hydration of anions in water, as compared with that of cation. This effect must make its contribution in all kinds of micelles, making the calculated Ψ value (eq 8, with $\gamma_{R^-} = \gamma_{H_2R^+}$) more negative. However, it must be taken into account, that in the case of anionic micelles the above effect is of less significance, because their surface is much stronger hydrated, than that of cationic micelles (see sections 3.5, 4.1). So, the E_T^N values of SDS and CPC micellar microenvironments correspond to 15 mass % and 60 mass % EtOH, respectively.

Surprisingly, the effect does not manifest itself in nonionic micelles, where the calculated Ψ value is close to zero (see above), and hence $\log\gamma_{R^-}$ is really $\approx$ $\log\gamma_{H_2R^+}$. Meanwhile, in such micelles the cation may be even more stabilized (see also section 3.1.1). In order to avoid the explanation of the effect by positive charging of nonionic micellar surfaces due to a weak ‘crown-effect’ of oxyethylene chains (resulting in Na^+ binding), one must offer some reasons for excessive stabilization of the anion R^- or/ and relative destabilization of the cation H_2R^+. For instance, it can be a stronger ability of H-bonding of water molecules bound by the oxyethylene ‘mantle’, as compared with that of bulk water, or more exposed position of the DF cation on the micellar surface. The same procedure, applied by Fernandez and Fromherz[6] to the two different, but structurally similar indicators, 7-hydroxy-4-undecylcoumarin and 7-dimethylamino-4-heptadecylcoumarin (charge types 0/ − and +/ 0, respectively), leads to the value $\Psi = 0$ for micelles of Triton X 100.

On the other hand, some additional stabilization due to specific ionic interactions can be expected for R^- in cationic micelles, while for H_2R^+ − in anionic ones (see also section 4.2). This must lead to additional decrease in the quantity $\log(\gamma_{R^-}/\gamma_{H_2R^+})$ in cationic micelles, and to increase − in anionic ones. This, in turn, can result in making the calculated Ψ value (eq 8, with $\gamma_{R^-} = \gamma_{H_2R^+}$) more positive and negative, correspondingly. Thus, the approach described in section 4.1.4, probably gives more distorted Ψ values for SDS micelles, than for CPC ones.

Along with these procedures of Ψ evaluation, the approach of Khaula et al.[13] is worthy of notice. The positive side of the latter is admitting the possibility of pK_a^i variations for the given indicator throughout various micellar systems. However, acknowledging only the Born component of the Gibbs energy of solvation, ΔG_{solv}, is an evident oversimplification, as it is well-known, that the ΔG_{solv} value is far from being exhausted by the electrostatic contribution. The simplest argument in favor of our viewpoint is the difference in ΔpK_a^a, as well as different pK_a^a variations from one micellar system to another, repeatedly registered for different indicators of the same charge type.

4.2. The nature of possible ionic pairs of dye ions with oppositely charged surfactant head groups. Basing upon spectral data, the association between dye ions and oppositely charged surfactant head groups is supposed by numerous researchers.[12,16,57] Though sometimes, e.g. in the case of the species HR^+ of RD in anionic micelles, such an association seems to be unlikely for sterical reasons. However, in general case the coexistence of oppositely charged ions within the Stern layer is favorable for specific inter-ionic interactions. In such terms the protolytic reactions of the dye species in ionic micelles can be regarded as competition with ion association, e.g., $(H_2R^+\text{surf}^-)_m \rightleftarrows HR_m + H_w^+ + \text{surf}^-_m$, or $HR_m + \text{surf}^+_m \rightleftarrows (R^-\text{surf}^+)_m + H_w^+$. Then the apparent pK_a^a contains an additional contribution, e.g.:

$$pK_{a1}^a = pK_{a1}^a('true') - \log(1 + K_{ass}[\text{surf}_m^+]) \qquad (10)$$

Here K_{ass} is constant of ion association in the pseudophase. The 'true' apparent $\mathrm{p}K_a^a$ value describes the equilibria without ion association. However, taking into account the peculiarities of the discussed systems, it is possible just to include the term with K_{ass} into $\log\gamma_{\mathrm{R}^-}$. On the other hand, the comparison of $\mathrm{p}K_a^a$ values of DF, Ethyl Fluorescein, and 6-Hydroxy-9-Phenyl Fluorone with those of their analogues with anionic groups in 2'-position of the 9-aryl moiety (see section 3.8) allows to illuminate to some extent the nature of (possible) ionic pairs. And really, the additional negatively charged group, being not conjugated with the ionizing OH group, causes increase in the corresponding $\mathrm{p}K_a^a$, in view of Bjerrum – Kirkwood – Westheimer relations:[12e,g,36,51,58]

$$\delta \mathrm{p}K_a^a = 24.3\ \varepsilon_{eff}^{-1}\ x^{-1} \tag{11}$$

Here ε_{eff} is the effective dielectric constant of the space between the mentioned groups, x is the distance between the groups, nm. The difference between the $\mathrm{p}K_{a1}^w$ values of Ethyl Fluorescein and 6-Hydroxy-9-Phenyl Fluorone on the one hand, and the $\mathrm{p}K_{a2}^w$ values of Fluorescein and Sulfone Fluorescein on the other, equals 0.48, and in micellar media (Table 5) it is the same (0.46). In CPC micellar solutions at I = 0.05 the mentioned difference, $\delta \mathrm{p}K_a^a$, becomes even somewhat higher (0.8-0.9).[17b,51] Thus, the possible association of the sulfonate or carboxylate groups of the dyes (Y^1 = SO_3^-, CO_2^-) with cationic surfactants head groups cannot be regarded as a neutralization of their charge, contrary to the reported viewpoint.[12g] In other words, such ionic pairs can be regarded in general case as rather solvent-separated than intimate ones. Moreover, the Stern layer can be regarded even as a molten salt or as a kind of ionic liquid.

Besides, if the dye ion is located within the Stern region, having the same charge, the ion association with the counterion cannot be excluded. For instance, the R^- ion can interact with the Na^+ cation in anionic micelles, while the $\mathrm{H_2R^+}$ ion – with Cl^- anions in cationic micelles. Formation of ionic triplets, e.g. $(\mathrm{surf}^-\ H_2R^+\ \mathrm{surf}^-)_m$, $(Na^+\ R^-\ Na^+)_m$, or $(\mathrm{surf}^+\ R^-\ \mathrm{surf}^+)_m$, $(Cl^- H_2R^+\ Cl^-)_m$, etc. also cannot be excluded.

Note, that in CTAB micellar solutions (0.01 M), at pH 13, i.e. under conditions of roughly equal $[\mathrm{OH}_m^-]$ and $[\mathrm{Br}_m^-]$ values,[59] the dianions R^{2-} of Bromophenol Blue are strongly protected from fading ($\mathrm{R}^{2-} + \mathrm{OH}^- \rightarrow \mathrm{ROH}^{3-}$).[60a] Contrary to it, the fading rate of the structurally similar triphenylmethane cation of Crystal Violet strongly increases in such micelles;[60a] similar effects are reported for methoxysubstituted triphenylcarbonium cations.[6b] Thus, one can regard these results as evidence of both 'dye anion + CTA^+' and 'dye cation + counterion (i.e. OH^-)' interactions.

4.3. Theoretical calculations of the electrical potential. The Ψ values for ionic micelles with radius r can be estimated from the approximate solution of nonlinearized Poisson-Boltzmann equation, obtained for spherical particles by Oshima, Healy, and White,[61] using the area of the surfactant head group, S_i, for calculation of the surface charge density:

$$\frac{\alpha}{S_i} - \frac{2\varepsilon\varepsilon_o kRT}{F}\sinh(Y/2)\left(1+\frac{2}{kr\cosh^2(Y/4)}+\frac{8\ln\left[\cosh(Y/4)\right]}{(kr)^2\sinh^2(Y/2)}\right)^{\frac{1}{2}} = 0\ , \tag{12}$$

where $Y = \Psi F/RT$, k^{-1} is the Debye length, $\varepsilon_o = 8.854\times10^{-12}$ F m^{-1}, ε = 78.5; T = 298.15 K.

The SDS micelles are probably most studied among other colloidal objects, and the r value of ca. 1.8 nm (or somewhat higher, ca. 2.0 nm), is estimated rather exactly by many authors.[8,12d,62] The aim of our calculations (Table 8) was to reveal the influence of the choice of S_i and α values on the calculated Ψ values, at fixed I values.

Table 8. The values of the surface electrical potential, Ψ, calculated by eq 12 (25 ^{o}C)

No	Surfactant	I, M	r (mic), nm	S_i, nm^2	α	Ψ, mV
1	SDS	0.008	1.8	0.609	1	−193 [a]
2	SDS	0.01	1.8	0.50	1	−199
3	SDS	0.01	1.8	0.609	0.55	−148
4	SDS	0.01	1.8	0.609	0.20	−78
5	SDS	0.01	1.8	0.66	0.20	−73
6	SDS	0.01	1.8	0.66	0.25	−88
7	SDS	0.01	1.8	0.66	0.30	−100
8	SDS	0.01	2.0	0.90	0.20	−59
9	SDS	0.05	1.8	0.609	1	−147 [b]
10	SDS	0.05	1.8	0.609	0.55	−111
11	SDS	0.05	1.8	0.609	0.30	−75
12	SDS	0.05	1.8	0.384	0.55	−140
13	SDS	0.05	1.8	0.384	0.20	−78
14	SDS	0.05	2.0	0.60	0.20	−57
15	SDS	0.05	1.8	0.459	0.20	−68
16	SDS	0.05	1.8	0.506	0.20	−63
17	SDS	0.05	1.8	0.609	0.20	−54
18	SDS	0.05	1.8	0.663	0.20	−50
19	SDS	0.05	1.8	0.66	0.30	−71
20	SDS	0.05	1.8	0.66	0.35	−79
21	SDS	0.102	1.86 [c]	0.609	0.30	−63 [d,e]
22	SDS	0.102	1.86 [c]	0.609	0.53	−93 [d,e,f]
23	SDS	0.102	1.86 [c]	0.384	0.20	−65
24	SDS	0.382	21.2 [c]	0.609	0.30	−42
25	SDS	0.40	1.8	0.66	0.20	−26
26	SDS	0.40	1.8	0.66	0.30	−38
27	SDS	0.40	1.8	0.384	0.55	−87
28	CPC	0.05	2.6	0.675	0.27	70
29	CPC	0.05	2.6	0.675	0.35	84
30	CPC	0.05	2.6	0.50	0.27	86
31	CPC	0.05	2.6	0.50	0.35	100

[a] according to ref. 12d: −195 mV; [b] according to ref.12d: ca. −150 mV; [c] from ref. 12d; [d] at I = 0.1 M the following ζ values are reported: − 77 mV[12d] and ζ = −68 mV[4]; the shear surface potential −75 mV (0.1 M NaCl) is reported; [64b] [e] by using indicator measurements, the following Ψ values are obtained: −100 mV,[6] −77,[8] and −95 mV[12d]; [f] the value Ψ = −93 mV presented in the Table, was calculated by using the r, S_i, and α values from ref.12d.

The contribution of Na^+ ions, dissociated from SDS micelles, to the I values were taken into account (see eq 5). The micelles were regarded as spherical, and the dielectric saturation was neglected, because our calculations showed that variation in ε is not the most decisive factor. Numerous S_i values for SDS are available in literature, e.g.: 0.63 nm^2,[63a] 0.663 nm^2,[63b] 0.518 nm^2 (SDS on H_2O/ air interface)[63c], 0.689 nm^2 (H_2O/n-$C_{16}H_{34}$ interface),[63c] and so on. Some earlier reports[63d-f] communicate S_i values 0.437 nm^2, 0.384 nm^2, or even 0.20 nm^2, obtained from the surface tension isotherms. From the surface charge density 0.263 C m^{-2} for α = 1, reported by Hartland, Grieser, and White,[12d] the value S_i = 0.609 nm^2 can be calculated. The values S_i = 0.459 nm^2 and 0.506 nm^2, resulting from the unification of various sets of published data, are used as well. The correctness of our calculation technique is confirmed by coincidence of the Ψ values for the hypothetical 'bare' micelle (without counterions in the Stern layer, α = 1) with that evaluated by Hartland, Grieser, and White[12d] (Table 8, No 1,9). Calculations of Ψ at the inner boundary of the diffuse layer at I = 0.05 M and r = 1.7 nm, made by Bell and Dunning, [64a] lead to the value $-$(136-138) mV.

The calculations demonstrate, that the uncertainty of Ψ values obtained by using eq 12 is caused first of all by uncertainty of α values. It is well known, that the latter, obtained by using various experimental values, differ markedly.[12d,19b,c,62a,c] So, for SDS micelles conductometric estimations lead to α = 0.3-0.4,[12d,62a] or even higher,[8] while pNa measurements and analysis of salt effects upon cmc values result in 0.20-0.26.[12d,62a,c]

It is reasonable to compare the calculated Ψ values with the values of the electrokinetic potential (zeta-potential), ζ, taking into account, that $|\Psi| > |\zeta|$. Some data for I = 0.1 M, given in Table 8, demonstrate, that the required Ψ values can be obtained by using relatively high α and/ or low S_i values. However, low S_i values are characteristic of such conditions (e.g. for cylindrical packing [63a]), where the α values are also relatively low. At I = 0.05 M the value ζ ca. -84 mV can be expected,[12d] and hence from this viewpoint the Ψ value ca. -100 mV or more negative can be regarded as probable. Thus, if $\Psi = -$(100-110) mV, then the value $\log(\gamma_{\mathrm{R}^-}/\gamma_{\mathrm{H_2R}^+})$ is within the range 1.5-1.1 units (see eq 8).

The majority of colloidal systems are not well enough defined, and the complete set of parameters (radius, surface charge density, etc.) is as a rule unknown for them. Some calculations were made for CPC micelles, I = 0.05 M; the r value was equated to that of CTAB (= 2.6 nm [65]). Table 8 demonstrates the increase in the Ψ values of 30 mV from a system with α = 0.27,[17b] S_i = 0.675 nm^2, [63b] to that with α = 0.35 and S_i = 0.50 nm^2. The last Ψ value (100 mV) is close to that estimated by us in section 4.1.4; note, that just for the cationic micelles the mentioned solvation and ion association effects, which influence the $\gamma_{\mathrm{R}^-}/\gamma_{\mathrm{H_2R}^+}$ value, probably compensate each other.

4.4. Attempts to model pK_a^i in ionic micelles. 4.4.1. Utilization of the calculated Ψ value. According to eq 2, $pK_a^i = pK_a^a + \Psi F/2.3026RT$. Thus, for SDS micelles with the mean value $\Psi = -66$ mV (25 °C) the pK_{a0}^i values of RD and DF are 9.58 and 4.05, and the pK_{a1}^i value of DF is 7.84. The value $\Psi = -110$ mV results in the values 8.83, 3.30, and 7.09, respectively, and $\Psi = -144$ mV $-$ in the values 8.25, 2.72, and 6.52, respectively. For CPC micelles, I = 0.05 M, the calculated value Ψ = 100 mV leads to the pK_a^i values 8.78, 2.48, and 6.61. The pK_a^a values in nonionic micelles (= pK_a^i) are 9.10, 2.12, and 7.20, respectively (Table 2). Thus, the sets of the pK_a^i values of the dyes, estimated in such a manner, are at any Ψ values essentially different in various micellar systems. Interestingly, in all the cases the pK_{a0}^i value of DF in nonionic micelles is certainly lower, than in ionic ones.

4.4.2. Modelling of micellar surfaces by water-organic mixtures. Many authors assume that the mean solvent characteristics of micellar interfacial regions can be mimicked by water-organic mixtures.[5,6,12b,e-j,16,21] The ε value of micellar interface is supposed to be equal to that of such a water-organic mixture, where the $\lambda_{\max}$ value of a solvatochromic probe (dodecyl pyridinium iodide, Reichardt betaine, etc.) is the same as in micelles. Then the pK_a value of the given acid-base indicator in such a mixture is equated to the micellar pK_a^m value (eq 3), and the intrinsic pK_a^i value is calculated as $pK_a^i = pK_a^m - \log\gamma_{\mathrm{H}^+}$, by using the medium effect of proton in the chosen mixed solvent. As a rule, mixtures of 1,4-dioxane and ethanol with water are used for this purpose. Indeed, mixtures of water with 1,4-dioxane are similar to the hydrated oxyethylene region of nonionic micelles. Of course, the choice of a suitable organic solvent for mimicking surfaces of ionic micelles is always somewhat ambiguous. So, the surfaces of cationic micelles display differentiating action similar to that of water-acetone mixtures (see section 4.7). Furthermore, isodielectric water-organic mixtures are known to posses different $E_{\mathrm{T}}^{\mathrm{N}}$ values, and the $\mathrm{p}K_a$ values of a given acid in such mixed solvents can differ markedly. For instance, ε^{25} = 24 corresponds to 64 mass.% 1,4-dioxane and 90 mass % acetone. The $E_{\mathrm{T}}^{\mathrm{N}}$ values are 0.64 and 0.57, respectively (which corresponds to a 25 nm difference in $\lambda_{\max}$ of RD), the $\mathrm{p}K_a$ values of benzoic acid are 7.40 and 9.75, and the $\mathrm{p}K_{a2}$ values of Bromophenol Blue are 7.02 and 8.05.[17c,66] (All the data refer to 25 $^{\mathrm{o}}$C). On the other hand, preferential solvation of different solvatochromic probes can manifest itself distinctly. So, as it was shown by Carr and co-workers by using two betaine dyes, namely 2,6-dichloro-4-(2,4,6-triphenylpyridinio-1) phenoxide and RD, the plots of $E_{\mathrm{T}}(33)$ vs. $E_{\mathrm{T}}(30)$ are definitely non-linear in mixed solvents.[67]

According to Fernandez and Fromherz,[6] the ε value of micellar surfaces is close to 32. According to Drummond and Grieser,[12b] for $C_{12}E_8$ and CTAC micelles ε is 30 and 34, correspondingly. Both groups of researchers prefer the mixture of water with 1,4-dioxane for modelling micellar surfaces, and use the $\log\gamma_{\mathrm{H}^+}$ values obtained by assuming the medium effects of H$^+$ and Cl$^-$ ions to be equal, which leads to $\log\gamma_{\mathrm{H}^+}$ ca. 0.4 to 0.8.[6,12b,68] However, during recent decades the tetraphenylborate assumption (Grunwald, Popovych, and others) have become mostly recognized among dozens of proposed extrathermodynamical approaches for $\log\gamma_{\mathrm{H}^+}$ estimation.[56] In H$_2$O - 1,4-dioxane mixtures with ε = 30 to 40 the recommended values of the medium effects of hydrogen ion are close to $\log\gamma_{\mathrm{H}^+}$ = −0.7.[56b] Thus, the $\mathrm{p}K_a^i$ values become 1.1-1.5 units more positive.

A similar picture is observed with water-ethanol mixtures. For instance, the value ε = 36,[69] estimated for CTAB micellar surface by using n-dodecylpyridinium iodide as a solvatochromic probe, corresponds to that of 73.8 mass % ethanol at 25 $^{\mathrm{o}}$C. The $\log\gamma_{\mathrm{H}^+}$ value in this mixture equals +0.89 according to Grunwald's early assumption,[70] +0.11 if we assume γ_{R^-} = $\gamma_{\mathrm{H_2R}^+}$ for 6-Hydroxy-9-Phenyl Fluorone,[37] and −0.79 in case the tetraphenylborate assumption is used.[56b] Hence, the rather reliable value $\mathrm{p}K_{a2}^i$ = 10.97 of Thymol Blue in CTAB micelles, calculated by Funasaki,[21] leads to $\mathrm{p}K_{a2}^m$ = 11.86 or 10.18, for $\log\gamma_{\mathrm{H}^+}$ = +0.89 and −0.79, correspondingly (eq 3).

Finally, the $\mathrm{p}K_a^i$ values obtained in this manner can be used for Ψ estimation: Ψ = $(2.3026\ RT/F)\times(\mathrm{p}K_a^i - \mathrm{p}K_a^a)$. In this case the calculated Ψ values can differ up to ca. 100 mV, depending on the chosen $\log\gamma_{\mathrm{H}^+}$ value.

4.4.3. Using the $\mathrm{p}K_a^a$ values in nonionic micelles as $\mathrm{p}K_a^i$ in other colloidal systems. All the mentioned in sections 3.1, 3.2 shows the drawbacks of the ways of Ψ estimation based on the common electrostatic model. Indeed, if more accurate Ψ values are required, then at least three questions arise: (1) which indicator (out of completely bound by micelles) is more suitable, (2) which nonionic surfactant is to be used and (3) what surfactant concentration (C_{S} > cmc) is to be chosen to determine the $\mathrm{p}K_a^a$ value identified with $\mathrm{p}K_a^i$?

For these purposes, besides the hydrophobic coumarins,[1c,6,8,12a,c,d,k] Neutral Red[12h] and Methyl Yellow[12i] have been used, characterized in nonionic surfactant systems by essentially different $\Delta\mathrm{p}K_a^a$ values, and also various nonionic surfactants: Triton X 100,[6] Tween 80,[13,16] Brij 35,[5,12g-i] $C_{12}E_8$.[1c,12b,c,e] Recently an attempt was made to explain the extremely negative Ψ values, obtained with the help of cationic indicators in SDS micelles by a standard procedure, through the hypothesis of ionic association between the indicator cation and the sulfogroup.[12d,h,i,16] The Ψ values obtained by using hydrophobic hydroxycoumarin (charge type **0/−**) are more reliable;[12d] similar results were obtained by using the dye Decyl Eosin.[17n] The coincidence of Ψ values of SDS micelles obtained with a cationic and a neutral indicator,[6] is rather an exception. However, on one hand, it is hard to predict quantitatively the increase in $\mathrm{p}K_a^a$ of the cationic indicator, caused by ion pairing with the sulfate group, while in the case of a neutral indicator the $\mathrm{p}K_a^a$ value can be effected by (possible) interactions between R^- and Na^+ ions (see section 4.2). On the other hand, as was supposed earlier,[17f,n] at transfer from more hydrated SDS micelles to less hydrated nonionic ones the $\mathrm{p}K_a^i$ values of indicators with charge type +/ 0 may change sharper than those of charge type 0/ −. The analysis of the differences ($\mathrm{p}K_{a1}^a$ − $\mathrm{p}K_{a0}^a$) in anionic and nonionic micelles (Table 6), given in section 4.1.1, support this idea.

The stated considerations bring back the long-standing question:[12c,17a,c] if nonionic micelles, whose hydrophilic oxyethylene interface is so dissimilar from the Stern region of the ionic micelles, serve for modeling of all the effects of the latter, excluding the surface charge? In other words, how great is the difference among the $\mathrm{p}K_a^i$ values of an indicator in ionic micelles and in nonionic ones with oxyethylene hydrophilic portion?

The dependence of the $\mathrm{p}K_a^a$ values of indicators on the nature of nonionic surfactants is reflected in the Ψ values of the charged surfaces, defined by the relationship $\Psi = (2.3026\ RT/F) \times (\mathrm{p}K_a^i - \mathrm{p}K_a^a)$, assuming that $\mathrm{p}K_a^i$ of the given indicator equals the $\mathrm{p}K_a^a$ value in nonionic surfactant systems (eq 2). The scatter reaches 20 mV on an average. Still greater are scattered the Ψ values obtained by using various indicators. So, for SDS micellar systems at I = 0.05 M (NaCl), the Ψ values, calculated with the help of $\mathrm{p}K_{a0}^a$ and $\mathrm{p}K_{a1}^a$ values of DF and of $\mathrm{p}K_{a0}^a$ value of RD, are equal to −180, −104, and −95 mV, respectively, while at I = 0.4 M (NaCl): −144, −58, and −65 mV, respectively. For CTAX micelles the possible Ψ values are 77, 134 and 99 mV at I = 0.05 M (NaCl) and 30, 105 and 60 mV at I = 0.4 M (NaCl), respectively. An attempt to use the $\mathrm{p}K_a^a$ values of sodium 1-oxy-2-(11-octadecyl amidocarboxy)-naphthalene-4-sulfonate and of dodecylanilinium[13] leads, if calculated according to the usual procedure, to the tremendous discrepancy between the Ψ values, in particular, 200-250 mV. Note, that even the use of two p-alkyl substituted o-nitrophenols with differing hydrocarbon portions, p-tert-octyl and p-n-nonyl,[7] leads to discrepancy between the Ψ values for both SDBS and CTAB micelles reaching 30 mV, while the size of the aromatic moiety of these probes is too small to perturb significantly the Stern region.

The most probable reason is the dissimilarity of the surface of nonionic surfactant micelles (oxyethylene chains) from that of the Stern region of ionic surfactants micelles. The latter is actually a highly concentrated electrolytic solution, neighboring with hydrocarbon chains. On the other hand, attempts to estimate the $\mathrm{p}K_a^i$ values through mimicking micellar surfaces by water-organic mixtures are connected with using of extrathermodynamic γ_{H^+} values. Any difference between the $\mathrm{p}K_a^i$ values, obtained in such a manner and in nonionic micelles can be explained in terms of association and/ or of specific salt effects. However, such explanations, being actually attempts to modify the simple electrostatic model, seem to be rather arbitrary.

Therefore it seemed natural to find out micelles with a neutral surface of another type as a ‘standard’ pseudophase for modelling the $\mathrm{p}K_a^i$ values. For this purpose the micelles of zwitterionic surfactants may be offered.

4.5. The peculiarities of acid-base equilibria in zwitterionic sulfobetaine micelles. We have studied the behavior of a vast series of indicators of various charge types in micellar solutions of a zwitterionic surfactant CDAPS, $C_{16}H_{33}N(CH_3)_2^+{-}(CH_2)_3{-}SO_3^-$.[71] And indeed, the agreement between the Ψ values of ionic, especially − cationic, surfactant micelles, evaluated by using various indicators, is much better, if the $\mathrm{p}K_a^a$ values in solutions of the given zwitterionic surfactant are regarded as $\mathrm{p}K_a^i$. For example, using for this purpose a set of 6 sulfonephthaleins, we obtained Ψ = 99 ± 7 mV for the CPC micelles (0.05 M Cl^-). Yet it is the pK_{a0}^{a} and pK_{a1}^{a} values of Decyl Fluorescein and pK_{a0}^{a} values of RD that are not just lower, than in nonionic surfactant systems, but even lower than the pK_{a}^{w} values in water. These reagents are probably too deeply sunk in the hydrocarbon core of CDAPS micelles, so that the chromophore is situated mainly in the region of alkylammonium portion, where the local electrical potential is positive. The $\lambda_{\max}$ values of the betaine dye (Table 4) and of the H_2R and R^- species of DF (446 nm and 515 nm, respectively) are close to those in cationic micelles. Besides, the pK_{a0}^{a} and pK_{a1}^{a} values of DF and the pK_{a0}^{a} value of RD, obtained in CDAPS solutions (Table 2), appeared to be 0.5-0.6 units less than the values obtained by us in CTAC solutions, in the presence of 4.0 M KCl (i.e. under conditions of almost complete screening of the surface charge of cationic micelles). Interestingly, Drummond and Grieser[12c] 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 potential in the vicinity of the ammonium group.

The similar effect was reported earlier[17h] for phospholipid liposomes: the pK_{a}^{a} values of hydrophobic indicators, unlike the pK_{a}^{a} of ‘normal’ indicators, are in this case somewhat closer to the pK_{a}^{a} values in anionic micelles than to those in non-ionic ones. Note, that phosphatidylcholine is also a zwitterionic surfactant; however, here the ‘inner’ charge is negative, and the ‘outer’ − positive, contrary to CDAPS.

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[69c] and of gradient of the local surface acidity, due to the existence of local electrostatic potential profiles.[12c]

Our investigation of the dye species partition between the bulk (aqueous) phase and the CDAPS pseudophase allowed to estimate the pK_{a}^{a} values of 15 indicators under conditions of complete binding, as a rule, at bulk ionic strength 0.05 M. Strong differentiating impact of the CDAPS is similar to that of micelles of cationic surfactants. The medium effects (ΔpK_{a}^{a} = pK_{a}^{a} − pK_{a}^{w}) vary between +1.3 (ΔpK_{a2}^{a} of Thymol Blue) and −1.9 (ΔpK_{a1}^{a} of Methyl Orange). In CDAPS solutions at I = 0.01 M the value ΔpK_{a2}^{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[69c] in micellar solutions of another betaine surfactant, $C_{12}H_{25}N(CH_3)_2^+CH_2CO_2^-$.

The possibility of using the pK_{a}^{a} values in CDAPS solutions as the ‘intrinsic’ (pK_{a}^{i}) values of the corresponding dyes in micelles of ionic surfactants is to be further studied.

4.6. The changes in the pK_{a}^{a} values of Decyl Fluorescein and Reichardt dye at the transfer from cationic surfactants to anionic ones and from *I* = 0.05 M to *I* = 0.4 M (NaCl). In accord with the common electrostatic model for a set of completely bound dyes, the difference between the pK_{a}^{a} values in anionic and cationic surfactant solutions, as well as the difference between the pK_{a}^{a} values at two different ionic strengths are expected to be constant. Yet our data (Table 9, 10) do not confirm it. This makes the adequacy of the simple electrostatic model doubtful. The observed facts may be caused by variations in both Ψ and pK_{a}^{i} values (eq 2).

Moreover, even for similar indicators, judging by literature, such phenomena are not rare. Thus, for three dyes, 1-hexadecyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, 1-hexadecyl-5-hydroxyquinoline and 1-hexadecyl-6-hydroxyquinoline, the difference between the pK_{a}^{a} values in micellar solutions of anionic and cationic surfactants varies within 0.9 pK_{a} units under quite identical conditions.[12e] For 2-nitro-4-nonyl phenol, an indicator with minimal size of the chromophore system, the pK_{a}^{a} value in SDBS micellar solutions is 4.19 units higher, than that in CTAB solutions, while for 2-nitro-4−tert-octyl phenol the mentioned difference equals only 3.03.[7] The $\mathrm{p}K_a^a$ differences between SDS and CTAB systems, published for 1-oxy-2-(11-octadecyl amidocarboxy)-naphthalene-4-sulfonate, dodecylanilinium, p-nitroanilide of bis-(chloromethyl)phosphinic acid, 4-octadecyloxy-1-naphthoic acid, 7-hydroxy-4-heptadecyl coumarin, hydroxycoumarin and aminocoumarin,[6,12a,13,55] being re-calculated to bulk ionic strength of 0.05 M (NaCl), vary within the limits of 1.7 $\mathrm{p}K_a$ units, and are on an average 3.5 $\mathrm{p}K_a$ units.

While at the transfer from SDS to CTAX micellar solutions the specificity of the indicator manifests itself first of all at small ionic strength, the use of $C_{10}H_{21}SO_3Na$ instead of SDS leads to a contrary result (Table 9).

The decrease in the quantity [$\mathrm{p}K_a^a$ (in anionic micelles) − $\mathrm{p}K_a^a$ (in cationic micelles)] along with the increase in the bulk ionic strength can be easily explained in terms of electrostatic model as a result of reducing of $|\Psi|$ or, in addition, of decrease in α values (Table 9, 10). However, this theory is unable to explain, why this decrease occurs in a different manner for different indicators. The increase in the bulk ionic strength is known to sometimes increase the thickness of the Stern layer, as well as to dehydrate the micellar surface.[72] Probably, these changes, as well as micellar shape and size transitions, inevitable at such a rise in the bulk ionic strength,[2,4,18f,45,73] make additional contribution to the $\mathrm{p}K_a^a$ values, the given effect being different for different indicators. This results in unlikeness of $\mathrm{p}K_a^a$ changes at the transfer from I = 0.05 M to I = 0.4 M. In the case of CTAX the situation is complicated due to the shift of the ionic equilibrium ($Br_m^- + Cl_w^- \rightleftarrows Cl_m^- + Br_w^-$). In going from SDS micelles, 0.05 M NaCl to CTAC micelles, 4.0 M KCl, the decrease in the $\mathrm{p}K_{a1}^a$ value of Decyl Fluorescein (Tables 2,5) is 2.35, while in the case of Decyl Eosin[17n] (Table 5) it equals 3.35.

4.7. Modification of the Stern region. 4.7.1. Ionic micelles. The rise in the supporting electrolyte concentration results in the surface charge screening, in the decrease in $|\Psi|$, and in corresponding changes of $\mathrm{p}K_a^a$. In the terms of the PIE theory this influence may be explained by exchange of H^+ and OH^- by M^+ and X^-, respectively, in the Stern region. This causes a change in the indicator ratio, which provides the constancy of K_a^m. However, at introducing even small amounts of hydrophobic counter-ions, $N(n\text{-}C_4H_9)_4^+$ and $C_7H_7SO_3^-$, into micellar solutions of SDS and CTAB, respectively, we registered practically the same effects, as in 0.4 M NaCl (Tables 2,3). The similar observations were made by us systematically for other indicators as well[17e,j] and can be interpreted in, at least, four ways: (1) by the abnormally high ability of the mentioned organic ions for displacement of the ions H^+ and OH^-, respectively, characterized by high values of ion exchange constants,[10] or selectivity coefficients, S_i;[9,17d,e,j] (2) by the decrease in the surface charge density caused by enlargement of counterions, which may incorporate into the Stern region; this, in accord with the classical relationships of the double electrical layer theory, automatically decreases the $|\Psi|$; (3) by excessive adsorption of hydrophobic counter ions, leading to the neutralization of the surface charge;[17i] (4) by hydrophobization and dehydration of the micellar surface, resulting in the alterations in the $\mathrm{p}K_a^i$ values.

The latter is especially expressed in the case of $N(n\text{-}C_4H_9)_4^+$ addition to SDS solutions (Table 6). For this surfactant, possessing a rather ‘water-like’, i.e. strongly hydrated, surface,[12e,i,j,17f,k,48,49] the additives of organic molecules (ions) sharply dehydrate the surface, which leads to much stronger decrease in the $\mathrm{p}K_{a0}^a$ value of DF, than in $\mathrm{p}K_{a1}^a$.

Not only our data, but also those published by others, evidence considerable changes in the structure of ionic surfactants micelles at the introduction of highly hydrophobic counterions.[74] So, in the system $C_{14}H_{29}N(CH_3)_3^+$ + salicylate, the $\mathrm{p}K_a^a$ value of the indicator of 4-

heptadecyl-7-hydroxycoumarin in the presence of 0.1 M $HSal^-$ is ca. 1 unit higher than in the corresponding bromide system.[1c] The Ψ value, obtained according to the 'standard' scheme by using the pK_a^i evaluated in nonionic surfactant solutions, equals 38 mV.[1c] Meanwhile, the electrophoretic measurements lead to the value of the electrokinetic potential $\zeta = -3$ mV,[1c] which can evidence the change of the charge sign due to specific adsorption of $HSal^-$ ions. On the other hand, viscosimetric data point to the formation of 'worm-like' anisometric micelles of cationic surfactants under these conditions, which makes the pronounced changes in γ_R and γ_{HR}, and hence in pK_a^i rather probable.

Table 9. Variations of pK_a^a at the transfer from cationic to anionic surfactant

Indicator	CTAX → SDS			CTAX → $C_{10}H_{21}SO_3Na$	
	I = 0.05 M	I = 0.4 M	I = 4.0 M	I = 0.05 M	I = 0.4 M
Decyl Fluorescein, pK_{a0}^a	4.35 (4.38)[a]	2.93	3.04	3.65	2.43
Decyl Fluorescein, pK_{a1}^a	4.02 (4.04)[a]	2.75	2.35	3.83	2.46
Reichardt dye, pK_{a0}^a	3.28 (3.61)[a]	2.11	2.10	3.12	1.48

[a] The values in parentheses refer to transfer from CPC to SDS.

Table 10. Variations of pK_a^a at the transfer from I = 0.05 M to I = 0.4 M (NaCl)

Indicator	I = 0.05 M → I = 0.4 M			I = 0.40 M → I = 4.0 M
	SDS	$C_{10}H_{21}SO_3Na$	CTAX	CTAC
Decyl Fluorescein, pK_{a0}^a	−0.62	−0.42	0.80	0.45
Decyl Fluorescein, pK_{a1}^a	−0.78	−0.88	0.49	1.18
Reichardt dye, pK_{a0}^a	−0.50	−0.70	0.67	0.51

Thus, the application of the classical ion exchange model to explain salt effects and to monitor electrical potentials of charged surfaces, considering the pK_a^i values being constant, is unreliable in such cases. The studies of the acid-base equilibria of Bromophenol Blue in the CTAB-tosylate system, as well as of Methyl Yellow and Hexamethoxy Red in SDS-tetra-n-butyl ammonium system show the following. The selectivity coefficients S_i (eq 6) of hydrophobic counterions, calculated from the pK_a^a values of indicators by using the Gaboriaud model (see section 1.2), are much higher than those estimated from the cmc. For instance, the pK_a^a values of Bromophenol Blue in CTAB micellar solution at $[Br^-_w] = 0.01$ M and 0.1 M equal 2.35 and 3.16, while at $[C_7H_7SO^-_{3w}] = 0.01$ M and 0.1 M: 3.35 and 4.33, respectively.[17i] The S_i values for $H_{13}C_6\text{-}SO_3^-$, $H_7C_7\text{-}SO_3^-$, and $HSal^-$ in CTA^+ system are 14± 2, 23± 5, and ca. 60, respectively ($S_{Br^-} \equiv 1$),[17j] while the cmc values of cetyltrimethylammonium salicylate and of several substituted benzoates are only 5 times lower than that of CTAB.[74a,75] The value of the ion exchange constant, describing the equilibrium ($Br^-_m + H_7C_7\text{-}SO^-_{3w} \rightleftarrows Br^-_w + H_7C_7\text{-}SO^-_{3m}$) in CTAB micelles, determined spectrophotometrically, equals 19.[76] While the S_i value of $N(n\text{-}C_4H_9)_4^+$ cation in dodecyl sulfate system, obtained with the help of indicator method, equals 125± 5 ($S_{Na^+} \equiv 1$),[17e] the cmc value of n-tetrabutylammonium dodecyl sulfate is only 7 times lower than that of SDS.[17e,77] This can be explained by assuming that the pK_a^i values of indicators are altered along with ion exchange, accompanied by changes in the hydration of the Stern region.

4.7.2. The peculiarities of RD behavior. Recently we have reported a number of the pK_a^a values of RD (5×10^{-5} M) in micellar systems of cationic surfactants, obtained in various buffer systems and with different salt background.[74f] In CTAB (0.001-0.005 M) + NaBr (0.01 M) solutions the pK_a^a value is on the average 7.47 (ΔpK_a^a = 1.17); λ_{max} = 540 nm. In 0.005 M CTAB solutions the replacing of NaBr by sodium tosylate (0.01 M) results in pK_a^a increase up to 8.16 (ΔpK_a^a = −0.48; see also Table 3), with the same λ_{max} value. However, if under such conditions the CTAB concentration is 5 times lower, the absorption maximum is shifted to 465 nm, and the pK_a^a value (8.61) is also close to the 'aqueous' one (pK_a^w = 8.64[12b,28c]). Such unusual findings, registered by us for a series of organic anions, were explained in terms of displacing of the large-sized dye towards outlying areas of the micellar palisade, due to micellar 'sphere → rod' transitions.[74f] This illustrates unexpected difficulties which can arise in the study of common micellar systems with a widely used solvatochromic betaine dye.

4.7.3. The peculiarities of salt effects in CDAPS micellar systems. In the case of CDAPS the influence of NaCl (0.01 to 0.5 M) is near to negligible. The addition of small amounts of hydrophobic anions (0.01 M of ClO_4^-, I^-, BF_4^-, or $C_7H_7SO_3^-$) displays expressed, in several cases even abnormal, effects on the dyes pK_a^a (up to 0.7 units, Table 11). Contrary to it, the introduction of the ion $N(n\text{-}C_4H_9)_4^+$ in combination with hydrophilic anions gives no effect. These observations are in excellent agreement with the phenomenon of strong adsorption of hydrophobic anions on the surface of zwitterionic micelles, known from conductometric, potentiometric, chromatographic and kinetic studies, as well as NMR and fluorescent spectroscopy.[79] And really, the increase in the pK_{a2}^a value of Bromothymol Blue reflects the decrease in the Ψ value due to the mentioned adsorption. Note, that the pK_{a2}^a value of the dye in CTAB and CPC micelles, at 0.05 M Br^- and 0.05 M Cl^-, equals 6.95 and 6.36, correspondingly,[17b,d,f] in CTAC micelles, at I = 4.0 M KCl: 8.26 (Table 5), in nonionic micelles, I = 0.05 M NaCl: 9.1-9.4,[17a,c,l] while in SDS micelles, at I = 0.2 M NaCl, 9.90 ± 0.06.[17l]

Table 11. The influence of salts on the pK_{a2}^a value of Bromothymol Blue in CDAPS solutions (0.0004 M), borate buffer solutions, ionic strength 0.0125 M, 25 °C

Additive	pK_{a2}^a	$\Delta\Delta pK_{a2}^a$ [a]	λ_{max} (R^{2-}), nm
none	7.30 [b]	–	617
none (except buffer)	8.16±0.01	0	625
0.2 M NaCl	8.15±0.05	−0.01	624
0.5 M NaCl	8.05±0.01	−0.11	625
0.01 M $NaClO_4$	8.88±0.05	0.72	621
0.01 M $C_7H_7SO_3Na$	8.74±0.01	0.58	619
0.01 M $NaBF_4$	8.66±0.01	0.50	624
0.01 M KI	8.58±0.01	0.42	625
0.01 M $N(n\text{-}C_4H_9)_4I$	8.57±0.06	0.41	620
0.01 $N(n\text{-}C_4H_9)_4H_2PO_4$	8.02±0.01	−0.14	624

[a] $\Delta\Delta pK_{a2}^a = pK_{a2}^a - 8.16$; [b] Thermodynamic pK_{a2}^w value, from ref.78.

Preferential binding of hydrophobic anions can be understood taking into account that their associate with alkylammonium group of CDAPS, being actually a 'hydrophobic salt', is protected from water by the negatively charged and therefore strongly hydrated micellar surface.

Contrary to it, in the case of hydrophobic cation binding, a positively charged layer between long (C_{16}) and short (C_3) hydrophobic chains would appear, accompanied by the 'hydrophobic salt' formation on the micellar interface.

4.8. Differentiating impact of micelles. As shown in Table 3, the medium effects, $\Delta pK_a^a = pK_a^a - pK_a^w$, vary significantly for the indicators under study. Besides, in the case of surfactants of various nature this differentiating action manifests itself in a dissimilar way. For instance, the difference between pK_{a1}^a of DF and Decyl Eosin[17n] in SDS micelles (0.05 M NaCl) is 4.43, while in CTAC micelles (4.0 M KCl): 5.43. The differentiating impact of anionic surfactant micelles was pointed out by Gaboriaud.[9] For indicator couples of various charge types in SDS micellar solutions, 0.05 M Na^+, the ΔpK_a^a vary from −1.6 to +3.1.[80]

The differentiating impact of cationic micelles was registered repeatedly. According to Minch and co-workers,[57a] the ΔpK_a^a of a series of CH-acids in CTAB micellar media vary from −0.5 to −4.6 units. The marked disparity in the ΔpK_a^a values of a vast set of nitrophenols[7,57a] is observed in this media as well. In CPC micelles, 0.05 M Cl^-, the ΔpK_a^a values of eight sulfonephthaleins vary from −2.16 (Bromophenol Blue) to −0.37 (Thymol Blue).[17b] Though in CTAC micelles, 4.0 M Cl^-, all the ΔpK_a^a of the last-named dyes are ca. 1.8 higher, their values can be ranged practically into the same sequence as medium effects in micellar solutions at low bulk ionic strength, as well as in water-acetone and water-dimethyl sulfoxide mixtures.[51,54,81] In these media, contrary to alcohols and water-alcohol mixtures, R^{2-} anions of bromo-derivatives (with negative charge strongly delocalized in the 'quinone-phenolate' moiety), are relatively more stabilized due to ion-dipole interactions (London forces), as compared with R^{2-} species with alkyl substituents. A typical example, presented in Figure 7, demonstrates that the 'differentiating power' of this micellar system is close to that of 52 mass % acetone, a mixed solvent with E_T^N = 0.743 (obtained by us) and ε^{25} = 47. The data, given in Table 5, show that both charge type and substituents strongly influence the ΔpK_a^a values.

A study of dodecyltrimethylammonium bromide and SDS micelles, made by Vitha and Carr[1f] using the Kamlet−Taft solvatochromic comparison method, revealed lower hydrogen-bond donor acidity and higher hydrogen-bond acceptor basicity of cationic micelles as compared with those of anionic ones. In terms of these solvent parameters, the cationic micelles are closer to dipolar aprotic solvents (dimethyl sulfoxide), than SDS micelles are. On the other hand, the latter are closer to water, than are the cationic micelles. This is in agreement with our data, showing the similarity of the differentiating impact of cationic micelles and water-acetone mixtures (Figure 7).

Strong differentiating action of ionic micelles may be probably caused by the miscellaneous character of micellar surfaces, first of all − by the peculiarities of water structure in the Stern region as well as from the proximity of the hydrocarbon chain of the surfactant. Surfactant micelles are known to be highly disordered, strongly hydrated clusters.[72,82] The recognized structural models of ionic micelles presume the entry of at least one CH_2 group of the hydrocarbon chain into the Stern region.[18f] Thus, the micellar interface is a unique mixture of water, hydrocarbon, and 3 to 7 M of electrolyte. Such a mixture is unattainable in homogeneous systems, and this is the cause for difficulties in modelling of the Stern region effect on protolytic equilibria through comparing of ΔpK_a^a in micelles with ΔpK_a or even ($\Delta pK_a - \log\gamma_{H^+}$) in aqueous organic solvents.

The dissimilarity of hydrophilic portions of ionic and nonionic (with oxyethylene chains) surfactants is evident. According to Funasaki,[5] the ΔpK_a^a values in nonionic micelles are strongly governed by the various depths of penetration of indicator species into the oxyethylene mantle of the micelle. And really, the ΔpK_{a0}^a value of the standard betaine is 0.5 units lower than that of its penta-tert-butyl derivative (see section 3.2.1), and the ΔpK_{a2}^{a} value of Bromothymol Blue is ca. 1.0 to 0.6 units higher than that of relatively more hydrophilic sulfonephthaleins Bromophenol Blue and Thymol Blue.[17a,c,f]

The differentiating impact of micelles seems to be the main hindrance to exact evaluations of the interfacial electrical potential of micelles. Study of mixed ionic + nonionic micelles [17f,h,o,63b,83] gives the possibility of smooth alterations of the microenvironment, governing the equilibrium state of the dyes.

In non-aqueous media, the differentiation of the acid strength comes to the distinction among the γ_R / γ_{HR} values. In the case of water-organic mixtures such distinctions may be caused, among other reasons, by selective or preferential solvation (Figure 3) media with low dielectric constant the ionic association may also be of significance. The differentiating action of micellar media probably points, at least, to the lack of the invariability of the pK_a^i value for the given indicator in micelles of various types, and different variations in the pK_a^i in various micellar systems.

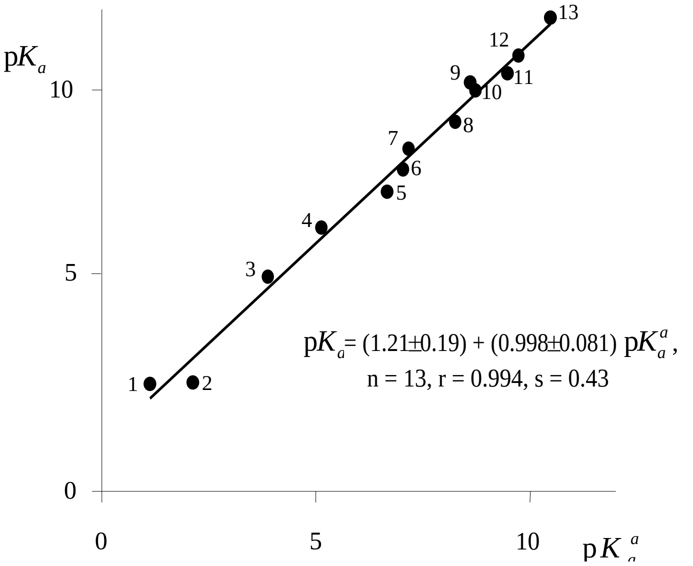


Fig.7. The dependence of pK_a in 52 mass % $(CH_3)_2CO$ *vs.* pK_a^a in CTAC micelles, 4.0 M Cl^-: 1 – pK_{a1}^a of Ethyl Eosin, 2 – pK_{a0}^a of 6-Hydroxy-9-Phenyl Fluorone, 3,4 – pK_{a2}^a of Bromophenol Blue and Bromocresol Green, 5 – pK_{a1}^a of 6-Hydroxy-9-Phenyl Fluorone, 6-8 – pK_{a2}^a of Bromocresol Purple, Fluorescein, and Bromothymol Blue, 9 – pK_{a0}^a of Reichardt betaine, 10-13 – pK_{a2}^a of Phenol Red, o-Cresol Red, m-Cresol Purple, and Thymol Blue. The pK_a values in 52 mass % $(CH_3)_2CO$ are taken from ref. 17c, 51,81.

If, however, we suppose, that the regions of location of various indicators or even of various species of the same indicator are so unlike, as not only to tell on the γ values, but also to cause perceptible differences in the electrical potential near a corresponding indicator species, then the application of the pseudophase model in its classical version is all the more incorrect. It should be kept in mind that there is a lot of data which prove essential distinction in the nature of microenvironments of various ions and molecules in the same micelles, obtained by means of NMR spectroscopy.[12a,74a,b,84] For instance, the problem of the position of pyridinium N-phenolate betaines within the 'normal' micelles of colloidal surfactants has been touched on by many authors,[12b,28a,b,h,i] who have mostly proceeded from the NMR data. Though the proximity of the phenolate moiety of these dyes to the quaternary nitrogen atom of the cationic surfactant is generally recognized, the viewpoints on the orientation of the rest portion of the dipole molecule are somewhat contradictory. The possible (adsorption $\rightleftarrows$ absorption) equilibria of species bound to micelles,[85] or even the multiplicity of positioning of organic reagents is confirmed as well by the electronic spectroscopy. [1a,2,17h,86] Probably, the application of molecular modelling would essentially contribute to the explanation of acid-base equilibria in micellar media.

5. Concluding Remarks

1. The common electrostatic model of acid-base indicators dissociation in micelles, based on the relation $pK_a^a = pK_a^i - [\Psi F/(RT \ln 10)]$, is certainly adequate in outline. However, 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: the constancy of the

'intrinsic' contribution to the $\mathrm{p}K_a^a$ value of the given indicator ($\mathrm{p}K_a^i$) in any micellar system, the constancy of the electrical potential of the Stern layer Ψ of the given micellar surface as obtained by using any indicator, and the possibility of complete description of salt effects with the help of ion-exchange model.

2. The 'bifunctional' character of the acid-base indicator Decyl Fluorescein allows to exclude from consideration the γ values of the neutral form in the given micellar system, and to obtain more versatile information about microheterogeneous systems.

3. Whereas dissimilarity among $\mathrm{p}K_a^a$ values in solutions of various anionic surfactants can rather be explained by the difference in the Ψ values, in other cases the difficulties in dividing the mentioned effects into Ψ and $\mathrm{p}K_a^i$ contributions are essential. The changes in the micellar structure caused by adding salts grew evident in the case of electrolytes containing hydrophobic counterions. At the same time, the analysis of the $\mathrm{p}K_a^a$ values, their linear combinations and their changes as compared with the $\mathrm{p}K_a$ in water, $\mathrm{p}K_a^w$, confirmed the differentiating action of micelles upon indicators of various nature, as well as markedly greater hydration of anionic micellar surfaces among other surfactant systems. The latter finding agrees well with spectral data reported by others.

4. Ion pairs between dye ions and oppositely charged surfactant head groups can be regarded in general case (may be, excepting the case of possible H-bonding) as rather solvent-separated than intimate ones. Besides, if the dye ion is located within the Stern region, having the same charge, the ion association with the counter-ion cannot be excluded.

5. The improvements of the model, e.g. the methods of $\mathrm{p}K_a^i$ estimation, up to now proposed in literature, are open to criticism. The algorithms of selection of suitable indicators for ε and $\mathrm{p}K_a^i$ determination, based on modelling of micelles with water-organic mixtures, seem to be somewhat artificial. For instance, the satisfactory fitting of the model, reported by several research groups, is reached by using the old-fashioned γ_{H^+} values, while the use of the γ_{H^+} values, calculated by means of the recognized tetraphenylborate assumption, leads to essentially different $\mathrm{p}K_a^i$ values.

6. The $\mathrm{p}K_a^i$ values of given indicators in given micelles could be estimated if the Ψ values were known. However, theoretical calculations of Ψ values of ionic micelles are somewhat indefinite even for such well-defined system as SDS micelles.

7. The $\mathrm{p}K_a^a$ values in oxyethylated nonionic micelles cannot be considered to be an optimal model of $\mathrm{p}K_a^i$, as the variation of the structure of such surfactants leads to essential (to 0.4 units) changes in the $\mathrm{p}K_a^a$ values. The use of a zwitterionic surfactant aimed at the same purpose may lead to systematic error just in the case of hydrophobic indicators, while in the case of common sulfonephthalein series such approach is more promising.

8. Strong differentiating impact of micelles is caused first of all by the miscellaneous character of any micellar surface. This impact of micelles seems to be the main hindrance to exact evaluations of the Ψ values by using acid-base indicators.

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Kharkov University Bulletin. 2002. №573. Chemical Series. Issue 9(32). Н.О.Мчедлов-Петросян, Н.А.Водолазкая, А.В.Тимий, Е.М.Глузман, В.И.Алексеева, Л.П.Саввина. Кислотно-основные индикаторы в мицеллярных растворах коллоидных ПАВ различных типов: действенна ли общепринятая электростатическая модель?

Изучены свойства мицеллярных растворов более 20 коллоидных ПАВ (включая 9 анионных) в качестве сред для протекания протолитических реакций с помощью кислотно-основных индикаторов, главным образом, двухступенчатого или «бифункционального», децилфлуоресцеина ($H_2R^+ \rightleftarrows HR \rightleftarrows R^-$) и бетаинового красителя Райхардта, 2,6-дифенил-4-(2,4,6-трифенилпиридиний-1) феноксида, с сольватохромной формой $R^{\pm}$ ($HR^+ \rightleftarrows R^{\pm} + H^+$), и других красителей, полностью связанных мицеллами. Проверка адекватности традиционной электростатической модели проведена на основании «кажущихся» значений pK_a^a, описывающих диссоциацию индикаторов, $pK_a^a = pK_a^i - [\Psi F/(RT\ln 10)]$. Проанализированы изменения значений pK_a^a при переносе сопряженных форм индикатора из воды в мицеллярные растворы ПАВ ($\Delta pK_a^a = pK_a^a - pK_a^w$); при переходе от одного типа ПАВ к другому; при варьировании солевого фона объемной (водной) фазы (неорганические и органические ионы). Показано, что главные допущения традиционной электростатической модели – (1) постоянство значения pK_a^i для данно-

го индикатора в любой мицеллярной системе; (2) одинаковость значений электростатического потенциала слоя Штерна, ψ для данной мицеллярной поверхности, определенного с помощью различных индикаторов; (3) возможность полного описания солевых эффектов с помощью ионообменной модели – в большинстве случаев выполняются лишь ориентировочно, а иногда и неудовлетворительно. Не могут считаться оптимальной моделью неэлектростатической составляющей $\mathrm{p}K_a^a$ в ионных мицеллах ($\mathrm{p}K_a^i$) значения $\mathrm{p}K_a^a$ в мицеллах неионных ПАВ. Обсуждена возможность использования значений $\mathrm{p}K_a^a$ в мицеллярных растворах цвиттерионного ПАВ $C_{16}H_{33}N(CH_3)_2^+{-}(CH_2)_3{-}SO_3^-$ в качестве значений $\mathrm{p}K_a^i$ соответствующих красителей в мицеллах ионных ПАВ. Мицеллярные перестройки становятся явными при добавках гидрофобных противоионов. При анализе значений $\mathrm{p}K_a^a$ сделан вывод о большей гидратированности слоя Штерна анионных мицелл по сравнению с другими мицеллярными поверхностями. Это утверждение хорошо согласуется со значениями $E_{\mathrm{T}}^{\mathrm{N}}$ и с другими сольватохромными шкалами. Обсуждена природа ионных пар, образованных ионами красителя и противоположно заряженными головными группами ПАВ. Обнаружено дифференцирующее действие мицеллярной псевдофазы на кислотно-основные свойства индикаторов различных типов заряда и природы.

Table 2. The $\mathrm{p}K_a^a$ values of hydrophobic dyes in micellar solutions of surfactants

Surfactants	C_S, M	t, °C	Decyl Fluorescein { $\mathrm{p}K_{a0}^{w} \to 2.94$, $\mathrm{p}K_{a1}^{w} \to 6.31$}				Reichardt dye { $\mathrm{p}K_{a0}^{w}$ =8.63[a]}	
			$\mathrm{p}K_{a0}^{a}$ ($H_2R^+ \rightleftarrows HR + H^+$)		$\mathrm{p}K_{a1}^{a}$ ($HR \rightleftarrows R^- + H^+$)		$\mathrm{p}K_{a0}^{a}$ ($HR^+ \rightleftarrows R^{\pm} + H^+$)	
			I, M [c]				*I*, M [c]	
			0.05	0.40	0.05	0.40	0.05	0.40
$C_{16}H_{33}SO_3Na$	0.01	50	5.16 ± 0.02	—	8.66 ± 0.04	—	—	—
$C_{12}H_{25}OSO_3Na$	0.01	25	5.17 ± 0.01	4.55 ± 0.03	8.96 ± 0.04	8.18 ± 0.04	10.70 ± 0.01	10.20 ± 0.03
$C_{12}H_{25}OSO_3Na$	0.01	50	—	—	—	—	10.61 ± 0.04	—
$C_{13}H_{27}OSO_3Na$	0.01	50	4.92 ± 0.05	—	8.68 ± 0.03	—	10.29 ± 0.03	—
$C_{14}H_{29}OSO_3Na$	0.01	50	4.87 ± 0.03	—	8.64 ± 0.09	—	10.50 ± 0.01	—
$C_{16}H_{33}OSO_3Na$	0.01	50	5.03 ± 0.05	—	8.78 ± 0.08	—	10.47 ± 0.07	—
$C_{10}H_{21}SO_3Na$	0.01	25	—	4.05 ± 0.08	—	7.89 ± 0.05	—	9.57 ± 0.03
$C_{10}H_{21}SO_3Na$	0.02	25	—	—	—	—	9.67 ± 0.05	—
$C_{10}H_{21}SO_3Na$	0.03	25	4.47 ± 0.02	—	8.77 ± 0.05	—	10.27 ± 0.01	—
$C_{12}H_{25}C_6H_4SO_3Na$	0.01	50	5.10 ± 0.04	—	8.64 ± 0.03	—	10.12 ± 0.03	—
$C_{12}H_{25}C_6H_4SO_3Na$	0.01	25	5.19 ± 0.04	—	8.78 ± 0.04	—	10.34 ± 0.04	—
$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	0.01	25	4.77 ± 0.03	—	8.58 ± 0.06	—	10.91 ± 0.03	—
$C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$	0.01	25	3.62 ± 0.02	—	7.72 ± 0.04	—	10.19 ± 0.04	—
$C_{12}H_{25}OSO_3Na$+Tween 80 (1:1)[b]	0.02 [d]	25	3.83 ± 0.04	—	8.49 ± 0.02	—	10.47 ± 0.03 [e]	
Nonionic surfactant	0.01	25	2.12 (Tween 80)	—	7.20 (Tween 80)	—	9.10 (NP 12) [f]	—
Phospholipid liposomes [g]	0.002	25	—	—	8.42 ± 0.05 [h]	—	10.12 ± 0.09 [h]	—
$C_{16}H_{33}N(CH_3)_2^{+}(CH_2)_3SO_3^{-}$	0.001	25	1.63 ± 0.05 [i]	—	6.07 ± 0.02 [i]	—	8.0 ± 0.08 [j]	—
$C_{16}H_{33}N(CH_3)_3Br$	0.01	25	0.82 ± 0.02	1.62 ± 0.08	4.94 ± 0.02	5.43 ± 0.01	7.42 ± 0.02	8.09 ± 0.03
$C_{16}H_{33}N(CH_3)_3Br$	0.01	50	—	—	—	—	7.22 ± 0.05	—
$C_{16}H_{33}NC_5H_5Br$	0.01	25	—	—	4.91 ± 0.02	—	7.18 ± 0.03	—
$C_{16}H_{33}NC_5H_5Cl$	0.003	25	0.79 ± 0.10	—	4.92 ± 0.07	—	7.09 ± 0.01[k]	—
$C_{16}H_{33}NC_5H_5Cl$+Tween 80 (1:4)[b,l]	0.003	25	1.50 ± 0.05	—	6.87 ± 0.04	—	—	—
$C_{18}H_{37}N(CH_3)_3Cl$	0.01	30	—	—	—	—	7.30 ± 0.01	—

[a] from ref.12b; [b] mole : mole; [c] *I* is ionic strength of the bulk phase, created by NaCl, with taking into account the contribution of the buffer mixture, but with no consideration of the dissociation of micelles, excepting the experiments with $C_{10}H_{21}SO_3Na$ at concentration of this surfactant 0.03 M; [d] total concentration of the anionic and nonionic surfactants; [e] In the 1:1 mixture with $C_{12}H_{25}OSO_3Na$ Nonyl Phenol 12 (NP 12) was used instead of Tween 80; [f] from ref.17g; [g] from ref.17m; [h] Mixed liposomes of phosphatidilecholine and cardiolipid (with molar ratio 18 : 1); [i] this value is constant within the surfactant concentration range $(0.08\text{-}1)\times10^{-3}$ M; [j] This value is constant within the C_S range $(0.5\text{-}1)\times10^{-3}$ M; [k] C_S = 0.01 M; [l] from ref. 17o.