ФИЗИКО–ХИМИЯ ИСТИННЫХ И ОРГАНИЗОВАННЫХ РАСТВОРОВ

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DETERMINATION OF INTERFACIAL ELECTROSTATIC POTENTIALS OF SURFACTANT MICELLES USING ACID-BASE INDICATORS: RESULTS AND LIMITATIONS

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In this paper, the different methods of estimation of the electrostatic potential, Ψ, of surfactant micelles via acid-base indicators are compared. All the methods are based on the determination of the indices of the so-called "apparent" ionization constants, pK_a^{app}. The approach developed in this Laboratory and based on using the indicator *N,N'*-di-*n*-octadecylrhodamine is utilized for determination of the Ψ value in the Stern layer of cetyltrimethylammonium-based micelles in the presence of tosylate ion.

Key words: Surfactant micelle, electrostatic potential, indicator dye, apparent ionization constant, cetyltrimethylammonium, tosylate.

Introduction

The interpretation of the equilibrium data in ionic surfactants micellar solutions, microemulsions, and other lyophilic micro- and ultramicroheterogeneous systems requires the knowledge of the electrical potential, Ψ, of the nanoparticle/water interface [1-4]. There are three main means to estimate the Ψ values: electrokinetic investigations, theoretical calculation, and utilization of pH indicators.

Direct electrochemical measurements allow getting only the value of the electrokinetic potential of micelles, ζ (zeta-potential), to be deliberately lower than Ψ by absolute magnitude.

Theoretical calculation of Ψ value is not way out. For example, Ohshima, Healy, and White proposed a formula originating from the approximate solution of the nonlinear Poisson – Boltzmann equation for spherical colloidal particles [5]. The numerical results, however, are available for well-defined colloidal systems only, because a set of parameters is used in the calculations. Even more so, the variations of both the degree of counter ion binding at the micellar interface and molecular areas, as determined via different experimental approaches, result in substantial scatter of thus calculated Ψ values. In addition, some uncertainty is brought by the choice of the value of the relative permittivity of the micellar interface. Polymorphism of micelles caused by the varying of surfactant or/and the background electrolyte concentrations [1,4] also complicates the Ψ estimations. It should be also taken into account that quantum-chemical calculations for common surface-active ions in vacuum reveal some distribution of the head group charge to the rest of the diphilic ion, first of all to the neighboring methylene group [6].

Therefore, the indicator method is the most acceptable and universal for evaluation of Ψ. Within the framework of this approach, the "apparent" ionization constant of the indicator, K_a^{app}, is a key value. In fact, it is a two-phase equilibrium constant, because the pH value is determined in the bulk (aqueous) phase, while the indicator ratio in the micellar pseudophase is available for spectrophotometric [7-9], spectrofluorimetric [10], or ESR measurements [11-17]. Some other techniques have also been reported [18]. The concentrations of working solutions ensure that the micelle: indicator ratio is NLE 1. Here we consider only the case of practically complete binding of indicators to the pseudophase. Near the surface of the cationic surfactant micelles and in their Stern layer, the inspissation of the HO^- ions takes place, while in the case of anionic surfactants the concentration of the H^+ exceeds that in the bulk aqueous phase.

According to the conventional electrostatic model [1, 4], the following equations are valid for the for K_a^{app} indices:

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$$\mathrm{p}K_\mathrm{a}^\mathrm{app} = \mathrm{p}K_\mathrm{a}^\mathrm{w} + \log\frac{{}^\mathrm{w}\gamma_\mathrm{B}^\mathrm{m}}{{}^\mathrm{w}\gamma_\mathrm{HB}^\mathrm{m}} - \frac{\Psi F}{RT\ln 10} = \mathrm{p}K_\mathrm{a}^\mathrm{i} - \frac{\Psi F}{RT\ln 10}, \quad (1)$$

$$\mathrm{p}K_\mathrm{a}^\mathrm{app} = \mathrm{p}K_\mathrm{a}^\mathrm{m} - \log{}^\mathrm{w}\gamma_{\mathrm{H}^+}^\mathrm{m} - \frac{\Psi F}{RT\ln 10}. \quad (2)$$

Here HB and B are the equilibrium species of the indicator (the charges are omitted for simplicity), ${}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{m}$ stands for the activity coefficient of transfer from water to micellar pseudophase, F is the Faraday constant, R is the gas constant, T is the absolute temperature. Normally, the Stern layer of ionic micelles is expected to be the locus of the acid-base indicators. Hence, the Ψ value corresponds just to this region of micelles. The K_a^m constant refers to the acid-base equilibrium within the pseudophase, and K_a^i is the so-called intrinsic constant. For surfactant micelles these equations have been thoroughly considered by Hartley and Roe [19], Mukerjee and Banerjee [20], Funasaki [7-9], and Fernandez and Fromherz [10]. Similar equations can be found in the publications describing the ionization of polyelectrolytes [21-25], polyampholytes [26], and monolayers [28-32].

The values of the electrostatic potential may be estimated using the above equations. For example, the following relation is valid:

$$\Psi = RT\ln 10\,(\mathrm{p}K_\mathrm{a}^\mathrm{i} - \mathrm{p}K_\mathrm{a}^\mathrm{app})/F. \quad (3)$$

The Ψ value of the given micellar surface may vary along with changes of the bulk ionic strength and on introduction of non-ionic additives that penetrate the micelles.

State of the arts

At present, several approaches, more or less approximate, have been developed for Ψ determination starting from the experimental $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ value in the ionic micelle under study; they are discussed below. As a rule, they are based on eq. (3) and differ in methods of $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ estimation for ionic micelles [3].

First of all, the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value in an ionic micelle can be equated to $\mathrm{p}K_\mathrm{a}^\mathrm{w}$ [7]. However, neglecting the term $\log({}^\mathrm{w}\gamma_\mathrm{B}^\mathrm{m}/{}^\mathrm{w}\gamma_\mathrm{HB}^\mathrm{m})$ is in the general case not true [1, 4]. Some authors used two indicators with the charge types of the acid-base couples $\mathrm{HB}^+/\mathrm{B}^0$ and $\mathrm{HB}^0/\mathrm{B}^-$, for instance, two lipoid coumarins: 4-heptadecyl-4-dimethylaminocoumarin and 4-undecyl-7-hydroxycoumarin [10,33,34].

$$\mathrm{p}K_{\mathrm{a},0,\mathrm{I}}^\mathrm{app} - \mathrm{p}K_{\mathrm{a},0,\mathrm{I}}^\mathrm{w} + \mathrm{p}K_{\mathrm{a},1,\mathrm{II}}^\mathrm{app} - \mathrm{p}K_{\mathrm{a},1,\mathrm{II}}^\mathrm{w} = \log\frac{{}^\mathrm{w}\gamma_{\mathrm{B}_\mathrm{II}^-}^\mathrm{m}\;{}^\mathrm{w}\gamma_{\mathrm{HB}_\mathrm{I}}^\mathrm{m}}{{}^\mathrm{w}\gamma_{\mathrm{HB}_\mathrm{II}}^\mathrm{m}\;{}^\mathrm{w}\gamma_{\mathrm{H_2B_I}^+}^\mathrm{m}} - \frac{2\Psi F}{RT\ln 10}. \quad (4)$$

Normally, the $\mathrm{p}K_\mathrm{a}$ values of acids of $\mathrm{HB}^+/\mathrm{B}^0$ charge type decrease on going from water to water-organic mixtures, while in the case of $\mathrm{HB}^0/\mathrm{B}^-$ charge type the $\mathrm{p}K_\mathrm{a}$ increases [35]. Therefore, for semiquantitative estimates the first term of the RHS may be equated to zero [10,33,34,36]. Even more so it seems to be reasonable if $\mathrm{HB_I}$ and $\mathrm{HB_{II}}$ coincide, i.e., it deals with a monoprotic acid, that may be protonated: $\mathrm{H_2B^+} \rightarrow \mathrm{HB} \rightarrow \mathrm{B^-}$. For instance, *n*-decylfluorescein may be proposed as such a bifunctional indicator [4]. The pro and con were considered earlier [1,4]; in the general case the ${}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{m}$-containing term in eq. (4) can significantly differ from zero.

(2) Evaluation of $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ by shielding the surface charge of a high concentration of the background electrolyte. For the indicator chosen, $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ in ionic micelles can be equated to $\mathrm{p}K_\mathrm{a}^\mathrm{app}$ in the same micelles, but with extremely high (4–6 M) salt background [37-40]. It is not always possible, because the required relatively high concentrations of the background (supporting) electrolyte can cause precipitation of the surfactant. Moreover, in the case of micelles of a cationic surfactant even at concentrations

of the indifferent electrolyte about 4 M the completeness of the surface charge screening remains controversial [40-45]. The solutions with extremely high salt concentration, i.e., 6 M NaBr, became very viscous [39]. More accurate values may be registered for the difference between the Ψ values in one and the same colloidal system at two different salt concentrations in the bulk [46,47].

(3) Evaluation of pK_a^i by simulation of the micellar microenvironment by water-organic mixed solvents. The choice of the latter is usually made using a spectroscopic molecular probe, which indicates the same polarity as registered in micellar pseudophase. Then the equation ($pK_a^i = pK_a^m - \log {}^w\gamma_{H^+}^m$) can be used. In this case, the pK_a^m and ${}^w\gamma_{H^+}^m$ values are equated to the corresponding pK_a^s and ${}^w\gamma_{H^+}^s$ values of the indicator in a water–organic mixture [7,9,10,39,40-44,48,49]. Tahara and co-workers used this approach in the case of the indicator dye embedded into the monolayer of a cationic surfactant on the water/air interface, without using the Ψ value in an explicit form [50]. This algorithm has two major drawbacks. First, the choice of the organic solvent is ambiguous. Probably there is none solution that fully reproduces the specific properties of the micelle/water interface. Second, one needs to involve the extra-thermodynamic value ${}^w\gamma_{H^+}^m$ or ${}^w\gamma_{H^+}^s$. Indeed, the utilization of the tetraphenylborate assumption [51] instead of some archaic approaches leads to a dramatic re-evaluation of the model [9,39,45,52], which previously seemed quite successful and self-consistent. In addition, even if the pseudophase polarity or relative permittivity is estimated, it must be taken into account that the pK_a^s values of an acid in various isodielectric water–organic mixtures can differ markedly. Probably, strong differentiating influence of micellar pseudophase on protolytic equilibria of dissolved substances hinders modeling its properties with any water–organic mixture [1,4].

(4) Probably, most often the pK_a^i value in ionic micelles is equated to pK_a^{app} of the given indicator in non-ionic micelles with oxyethylene hydrophilic portion [1,9,45,49,52-55].

At first, no problems have been reported while using this approach. But along with the accumulation of data obtained with versatile indicators, an increasingly contradictory picture was observed. Utilization of a set of different indicators to determine the Ψ value of the fixed ionic micellar system leads to a strong scatter. The analysis of literature data demonstrate that the Ψ values determined in such a way may differ up to $\approx$ 200 mV [1-4, 54]. Probably, the interfacial regions of ionic and non-ionic micelles are quite dissimilar. According to some authors [39,40-45,52,53], the formation of ionic associates of indicator cations (anions) with anions (cations) surfactant may additionally contribute to the pK_a^{app} values. In some cases these assumptions seem to be unlikely [1]. The powerful and specific differentiating action of micellar pseudophases in respect to the strength of indicator acids is probably the main reason here [1, 4].

It should be pointed out, that the pK_a^{app} values of the given indicator dye never coincide exactly even in micelles of different non-ionic surfactants [1,3,4]. Hence, one should have some objective grounds for the selection of a certain non-ionic surfactant.

(5) Some authors considered the possibility of utilization of non-ionic surfactants with hydrophilic sugar group instead of ethylene oxide [45,56,57].

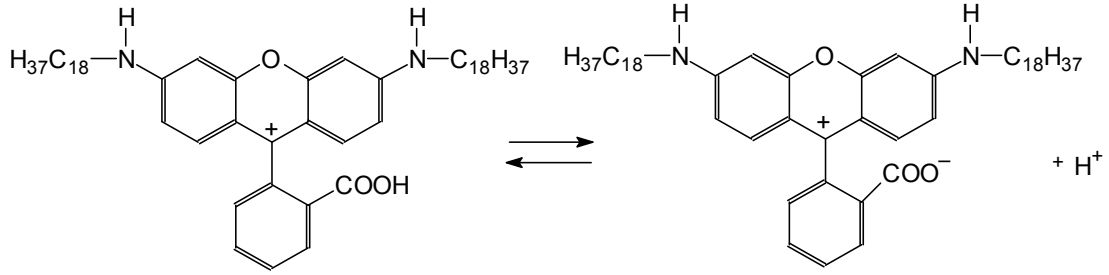
(6) The pK_a^i in ionic micelles can be equated to pK_a^{app} of the given indicator in micelles of zwitter-ionic surfactant, e.g., cetyldimethylammoniumpropanesulfonate, *n*-$C_{16}H_{33}N(CH_3)_2^+(CH_2)_3SO_3^-$ [1-4]. The palisade of zwitter-ionic micelles seems to be a more adequate model of the Stern layer of ionic ones. For instance, the utilization of the micelles of the above surfactant as a standard media for pK_a^i estimation leads to agreement between the Ψ values of cationic surfactant micelles, evaluated by using a set of six sulfonephthaleins: $\Psi = +99 \pm 7$ mV for cetylpyridinium chloride at bulk Cl^- concentration of 0.053 M Cl^- [1-3], while using the pK_a^{app}s of these dyes in non-ionic micelles as pK_a^i in cationic ones, the Ψ values vary from + 113 to + 179 mV. However, such approach appeared to be less favorable for more hydrophobic indicators, such as *n*-decylfluorescein and Reichardt's dye [1,3]. Drummond and Grieser [45] 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.

Concluding, one can state, that the differentiating influence of micelles seems to be the main hindrance to exact evaluations of the Ψ values of micelles via acid-base indicators. 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, non-ionic (with oxyethylene chains), and zwitter-ionic surfactants.

(7) Bissell et al. reported the creation of a special kind of indicators with targeting/anchoring modules called "molecular versions of submarine periscopes" for mapping membrane-bounded protons; the complete binding is observed at proper hydrophobicity of the anchoring tail group [58]. Some indicators fixed at a long spacer were used to monitor the electrostatic potential in the diffuse part of the double electrical layer, outside of the Stern region [59]. In several cases, the large-sized substrates involved into the surfactant micelles may alter the structure of the latter [60, 61].

(8) Recently, the rhodamine dye *N,N'*-di-*n*-octadecylrhodamine was proposed for monitoring interfacial electrostatic potentials [4,62,63]. Owing to the peculiarities of the structure of this hydrophobic indicator it should be probably fixed in a similar way in any ionic or non-ionic micelle. The existence of two long hydrocarbon chains allows expecting similar orientation of its cation and zwitter-ion on the micelle/water interface, with the dissociating group (COOH $\rightarrow$ COO^-) directed toward the aqueous phase.



Another reason for recommendation of this indicator is as follows: for acid-base couples with the charge type $HB^+/B^{\pm}$, the deviations of pK_a^i from pK_a^w are expected to be relatively small. In non-ionic micelles $\Delta pK_a^{app} \approx 1.0$, close to that for hydrophobic coumarins with charge type HB^0/B^- [10,45], while indicators with charge type HB^+/B^0 demonstrate sharp decrease in pK_a^{app}, up to $\Delta pK_a^{app} = -2.1$ for methyl yellow [54]. Therefore, it is reasonable to expect that variations in the pK_a^i value of *N,N'*-di-*n*-octadecylrhodamine are small and therefore more similar in non-ionic and ionic micelles than those for common cationic indicators.

On the other hand, if the COO^- group with localized charge undergoes some additional specific interactions with head-groups of cationic surfactants or with Na^+ ions of SDS, the true Ψ values must be less positive in cationic micelles and more negative in anionic ones.

The pK_a^{app} values of *N,N'*-di-*n*-octadecylrhodamine have been determined in various micelles, droplets of microemulsions, and in Langmuir–Blodgett films soaked into aqueous media [4,62,63]. Both absorption and fluorescence of the dye can be used for monitoring interfacial properties. The Ψ values were calculated using the average value of pK_a^{app} in non-ionic micelles, 4.21, as pK_a^i in ionic ones.

Results and discussion

The experimental section of the present paper is devoted to the determination of the Ψ values in cetyltrimethylammonium bromide (CTAB) micellar solutions with 4-methylbenzenesulfonate, or tosylate (Tos^-), as a counter-ion.

The procedure has been described in previous publications [37,38,54,55,62,63]. The dye concentrations in working solutions were 1×10^{-5} M or lower; pH values were checked by glass electrodes. The important feature of CTAB – tosylate system is its high viscosity [64,64]. The latter is caused by sphere-to-rod transition of the micelles and even by formation of worm-like colloidal species [66, 67]. This counter-ion induced transformation may significantly influence the state of indicator dyes appended to the micelles. Namely, displacing solvatochromic pyridinium *N*-phenolate towards outlying areas of rod–like micelles was observed in solutions of cationic surfactants in the presence of tosylate and some other aromatic counter-ions [66, 67].

Figure 1 demonstrates the specificity of the tosylate ion. The relative location of this anion and the surfactant chain in the adsorption monolayer on water/air interface is presented as obtained by neutron reflection [68].

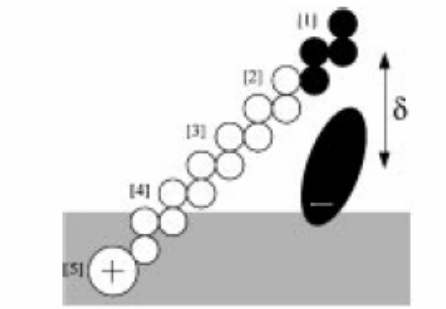


Figure 1. Labeling scheme used to determine the position of the tosylate ions in the surfactant monolayer by neutron reflection. The surfactant is subdivided into five blocks: four blocks containing four carbons each and the head group. One block is deuterated (black) and the remainder (white) are contrast matched to water. The tosylate ion (black) is fully deuterated. The figure is schematic and should not be taken to imply that the chains are all-trans or uniformly tilted. From ref. [68] with permission of the American Chemical Society.

Such a position of the counter-ion is unusual; as a rule, Br^- or Cl^- ions are located in the water environment close to the head groups. Thus, the tosylate ion behaves itself rather like a surface-active agent. Such a finding is significant for understanding the structure and nature of the palisade of the CTATos micelles studied below.

The selectivity parameter $S_i = 23$ for the $C_7H_7SO_3^-$ ion was estimated by using the pK_a^{app} values of bromophenol blue within the framework of ion-exchange model (for Br^- the S_i value is equated to unity) [4]. This parameter is close to the corresponding ion-exchange constant. However, some other methods that does not use the acid-base equilibria, result in 4- to 5-fold lower values of the last-named parameter [69]. The ion-exchange constants for other aromatic counter-ions derived from the critical micelle concentrations are also substantially lower as compared with those calculated using the pK_a^{app} s. Therefore, it is worthwhile to reveal if the pK_a^{app} of indicators and thus the Ψ values are additionally influenced by the so-called "special" salt effect [4]. The change of the locus of indicators on going from CTAB to CTATos micelles may result both in the pK_a^i value and the electrostatic potential around the ionizing group.

First, let us consider the results obtained with bromophenol blue (Figure 2, Table 1). Tosylate was introduced into the working solutions in the form of the *p*-toluenesulfonic acid, with or without adding of NaOH. Utilization of higher concentrations of tosylate is hindered by sharply increasing viscosity of solutions.

These results are in line with the data obtained earlier [4, 37, 66]. However, taking into account the displacing of the solvatochromic pyridinium *N*-phenolate dipole caused by the micellar transitions [65,66], the effects in CTAB–tosylate system should be verified using another indicator.

One may expect that in the case of *N,N'*-di-*n*-octadecylrhodamine, two long hydrocarbon tails strongly hold the indicator in the micelles. The ionizing COOH group probably stays within the Stern

region irrespective of sphere-to-rod transitions, and thus the pK_a^{app} values provide more correct information concerning the Ψ value. However, it should be taken into account that the spectra of the limiting forms of the indicator are poorly resolved (Figure 3).

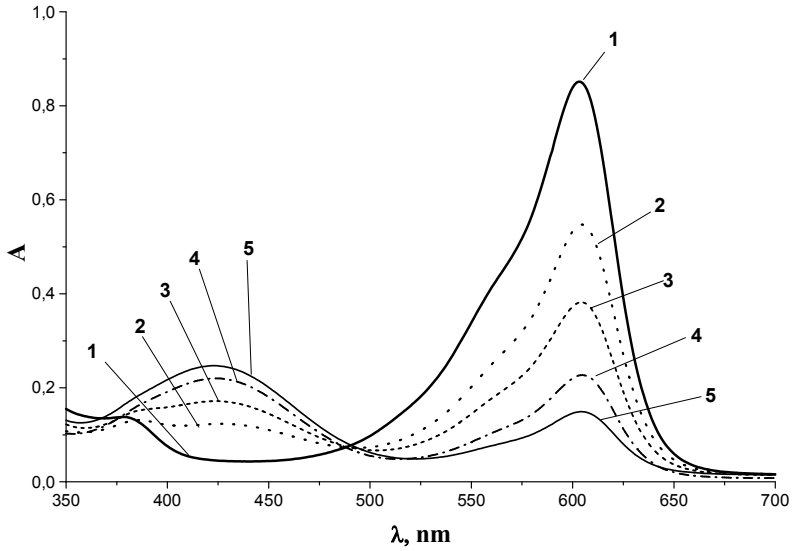


Figure 2. Absorption spectra of bromophenol blue in 0.01 M CTAB + 0.01 M tosylate solution; 1 – pH ≈ 9 (B^{2-} species); 2 – pH 3.17; 3 – pH 2.69; 4 – pH 2.43; 5 – pH 2.03.

Table 1. The pK_a^{app} values of bromophenol blue in CTAB micellar solutions in the presence of Br^- and Tos^- as counter-ions.

CTAB/M	X^-/M	pK_a^{app}
Br^- [a]		
0.003	0.006	2.09 [b]
0.003	0.011	2.26 [b]
0.003	0.021	2.48 [b]
0.003	0.10	3.08 [b]
Tos^- [c,d]		
0.01	0.001	2.30 ± 0.13
0.001	0.001	2.78 ± 0.12
0.01	0.01	2.82 ± 0.06
0.001	0.01	3.40 ± 0.12
0.001	0.10	4.33 ± 0.03 [e]

[a] The equilibrium bulk concentration as calculated using the cmc value at the corresponding salt background and the degree of counter-ion binding. [b] From ref. [37]. [c] The total concentration of the tosylate ion. [d] The total concentration of Br^- ions in the system is equal to the initial CTAB concentration. [e] From ref. [4, 66].

According to the earlier described procedure [62,63], a linear combination of absorbances at different wavelengths, ΔA, was used instead of A in the calculations (Figure 4).

This dependence, being in fact a kind of "titration curve", reveals another problem. The abnormal stretching of the curve is probably caused by some additional increase in the ΔA value of the dye cation beyond the equilibrium region. This effect may be caused by some electrolyte-induced micellar transitions. In this case HCl and HTos act not only as acidic agents but also as electrolytes, which

screen the interfacial micellar charge and thus influence the Ψ value. This, in turn, may alter the position of the cationic dye species within the Stern region as compared with that at higher pH, where the Ψ value is not reduced to such an extent.

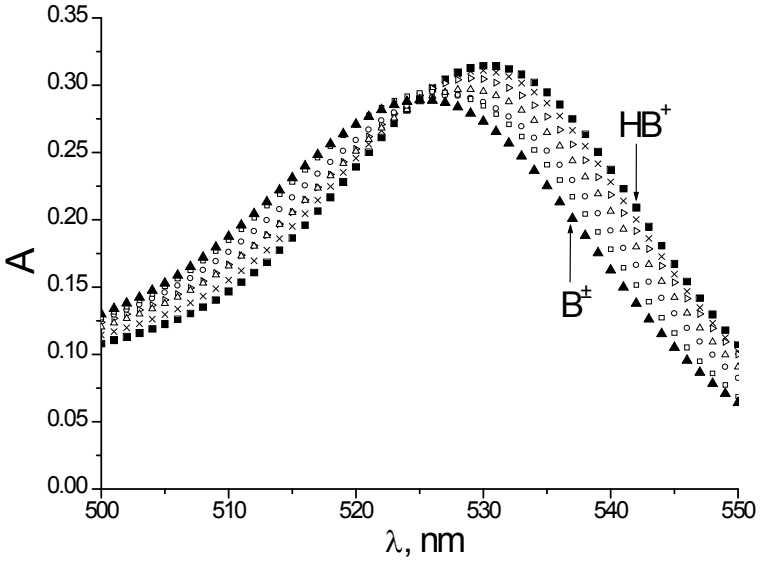


Figure 3. Absorption spectra of *N,N′*-di-*n*-octadecylrhodamine at different pH values in the micellar solution of CTAB (0.001 M); the pH values were created by mixtures of *p*-toluenesulfonic acid (0.01 M) with NaOH. The spectrum of $B^{\pm}$ species was obtained in phosphate buffer solution (pH ≈ 6.9). Absorption in 0.1 M HTos solution may be ascribed to the dye cation, HB^+ (see the text). Acidities: ■ – pH~1.1, HB^+, c(HTos) = 0.1 M; × – pH 2.07; ▷ – pH 2.66; Δ – pH 2.83; ○ – pH 3.32; □ – pH 3.92; ▲ – pH~6.9, $B^{\pm}$, phosphate buffer.

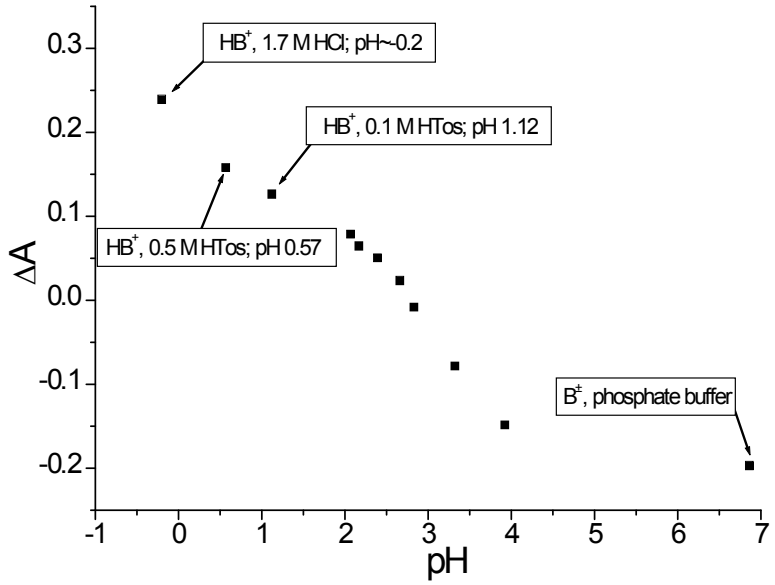


Figure 4. The dependence of the ΔA function of *N,N′*-di-*n*-octadecylrhodamine on pH; 0.001 M CTAB, the pH values created by 0.01 M HTos with addition of varying amounts of NaOH (exceptions are shown on the graph). Here ΔA = A (535 nm) + A (540 nm) + A (545 nm) – A (510) – A (515 nm) – A (520 nm).

In Table 2, the data for *N,N*'-di-*n*-octadecylrhodamine are gathered. These results shed light upon the influence of the choice of the cationic absorption spectrum. As more probable, the values obtained at pH 1.1 or at least 0.6 should be used. In the last case, the pK_a^{app} drift in the CTAB–tosylate system is rather expressed. Figure 5 also reflects the corresponding differences in the indices of the apparent

ionization constants, but the general regularity stays unaffected: the increase in the pK_a^{app} begins when the CTAB : Tos^- ratio is around 1.5. Note, that just under such conditions the completeness of tosylate binding is reached [70].

Table 2. The pK_a^{app} values of *N,N'*-di-*n*-octadecylrhodamine in CTAB micellar solutions in the presence of Br^- and Tos^- as counter-ions.

CTAB/M	X^- [a]	pK_a^{app}		Ψ /mV
0.05	0.019 (Br^-)	2.24 [b]		116
0.01	0.012 (Br^-)	2.47 ± 0.07 [c]		103
0.01	0.052	2.53 ± 0.04 [b]		99
0.01	0.052 ($Br^- + Cl^-$) [d]	2.60 ± 0.06 [e]		95
0.01	0.052 ($Br^- + Cl^-$) [d]	2.66 ± 0.05 [f]		92
0.01	0.052 ($Br^- + Cl^-$) [d]	2.71 ± 0.03 [g]		89
	Tos^- [h]	pK_a^{app}		Ψ /mV
0.01	0.001	2.36 ± 0.05 [i]	2.32 ± 0.05 [j]	109–112
0.01	0.01	2.88 ± 0.04 [i]	2.77 ± 0.07 [j]	79–85
0.001	0.01	2.96 ± 0.12 [i]	2.88 ± 0.25 [j,k]	74–79
0.001	0.05	3.7 ± 0.3 [i,l]		30

[a] The equilibrium bulk concentration as calculated using the cmc value at the corresponding salt background and the degree of counter-ion binding. [b] From ref. [62]. [c] The spectrum of the cation HB^+ is obtained at pH = 0.61; in case if 1.71 M HCl solution (pH = –0.2) was used for this purpose, pK_a^{app} equals 2.44 ± 0.08. [d] NaBr + HCl. [e] The spectrum of the cation HB^+ is obtained at pH = –0.2. [f] The spectrum of the cation HB^+ is obtained at pH = 0.61. [g] The spectrum of the cation HB^+ is obtained at pH = 1.12. [h] The total concentration of Br^- ions in the system is equal to the initial CTAB concentration. [i] The spectrum of the cation HB^+ is obtained at pH = 1.12 (HTos solution). [j] The spectrum of the cation HB^+ is obtained at pH = 0.57 (0.3 M HTos solution). [k] The values are drifting from 2.61 to 3.12. [l] From 3.46 to 3.97.

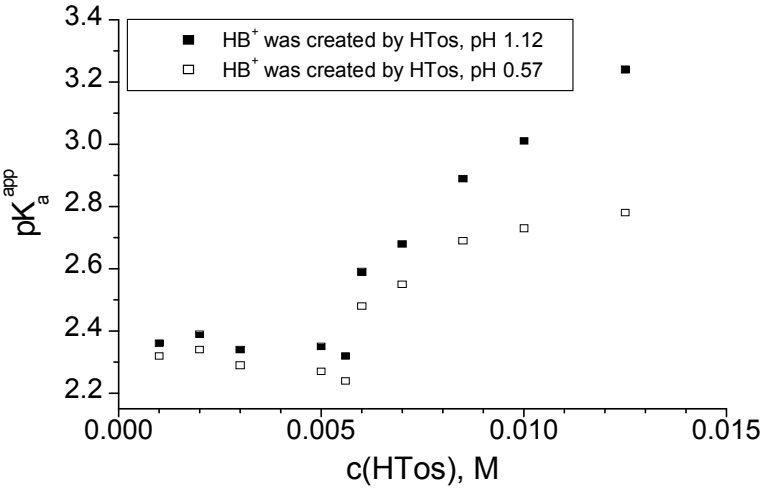


Figure 5. The dependence of the pK_a^{app} of *N,N'*-di-*n*-octadecylrhodamine on HTos concentration; c(CTAB) = 0.01 M, the spectra of the limiting cationic dye forms were created by 0.3 M HTos (pH 0.57) in 0.001 M CTAB solution (cation) and in phosphate buffer at pH 6.9, 0.01 M CTAB (neutral species).

In any case, the comparison of the pK_a^{app} values in bromide and tosylate systems determined using the same spectrum of the HB^+ species reveals somewhat smaller differences as compared with those registered using bromophenol blue as indicator (see above). However, the increase in pK_a^{app}s is also higher than it might be expected from the ion exchange data obtained via independent methods [69]. This is in line with the concept of the "specific" character of salt effects upon the acid-base equilibrium in the Stern layer, caused by aromatic counter-ions.

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Н. О. Мчедлов-Петросян, Н. Н. Камнева, А. Ю. Харченко, Н. А. Водолазкая, В. И. Алексеева. Определение поверхностных потенциалов мицелл ПАВ с использованием кислотно-основных индикаторов. Результаты и ограничения.

В статье рассмотрены и сопоставлены различные методы оценки электростатического потенциала Ψ мицелл ПАВ при помощи кислотно-основных индикаторов. Все эти методы основаны на определении показателей так называемых «кажущихся» констант ионизации, pK_a^{app}. Развитый авторами подход, основанный на использовании индикатора *N,N′*-ди-*н*-октадецилродамина, использован для определения значения Ψ слоя Штерна в мицеллах на основе цетилтриметиламмония в присутствии иона тозилата.

Ключевые слова: мицелла ПАВ, электростатический потенциал, индикаторный краситель, кажущаяся константа ионизации, цетилтриметиламмоний, тозилат.

М. О. Мчедлов-Петросян, Н. М. Камнєва, А. Ю. Харченко, Н. О. Водолазкая, В. І. Алексєєва. Визначення поверхневих потенціалів міцел ПАР з використанням кислотно-основних індикаторів. Результати та обмеження.

В статті розглянуті та співставлені різні методи оцінки електростатичного потенціалу Ψ міцел ПАР за допомогою кислотно-основних індикаторів. Всі ці методи ґрунтуються на визначенні показників так званих «уявних» констант іонізації, pK_a^{app}. Розвинутий аторами підхід, пов'язаний з використанням індикатора *N,N′*-ди-*н*-октадецилродаміна, використаний для визначення потенціалу Ψ шару Штерна в міцелах на основі цетилтриметиламонію в присутності іону тозилату.

Ключові слова: міцела ПАР, електростатичний потенціал, індикаторний барвник, уявна константа іонізації, цетилтриметиламоній, тозилат.