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Protolytic equilibrium in lyophilic nanosized dispersions: Differentiating influence of the pseudophase and salt effects*

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Abstract: The so-called apparent ionization constants of various acids (mainly indicator dyes) in versatile organized solutions are analyzed. Aqueous micellar solutions of colloidal surfactants and related lyophilic colloidal systems display a strong *differentiating influence* on the acidic strength of indicators located in the dispersed pseudophase, i.e., non-uniform changes of pK_a on going from water to the given system. This concept allows the influence of such media on acid–base properties of dissolved reagents to be rationalized. It is demonstrated that the differentiating phenomenon is the main reason for limitation of the common electrostatic model of acid–base interactions, and is the principal hindrance to exact evaluations of the interfacial electrical potentials of ionic micelles by means of acid–base indicators. Salt effects, i.e., the influence of supporting electrolytes on the apparent ionization constants of acid–base indicators in the Stern region of ionic micelles, are considered. These salt effects can be conventionally divided into two kinds, namely, *general* (*normal*) and *special* (*specific*) effects. While the first type adds up to screening of the surface charge, the second one consists in micellar transitions caused by hydrophobic counterions.

Keywords: protolytic equilibrium; lyophilic dispersions; surfactant micelles; differentiating influence; salt effects.

INTRODUCTION

Protolytic equilibrium in surfactant micelles and related systems

Thermodynamically stable transparent ultramicro-heterogeneous systems, also called organized solutions, belong to solvent systems extensively applied in various fields of modern science and technology. Such traditional media as micellar solutions of colloidal surfactants (i.e., surfactants which are able to form aggregates of colloidal size) as well as their "derivatives", such as microemulsions, are widely used for equilibrium shifts and acceleration of a variety of reactions [1], as useful media for analytical processes [1a,d,e,j,2] including chromatography [3], for solubilization of various substances including drugs [4], in photophysical studies [5], in synthesis of nanoparticles [6], etc. Phospholipid vesicles, surfactant mono-, bi-, and multilayers on various interfaces, mixed micelles, and a number of other self-assembled systems are also intensively utilized in academic research and applied chemistry. Another kind of organized systems is exemplified by solutions of cyclodextrins, calixarenes, dendrimers, and other "Host" molecules. In fact, some of these systems are close to lyophilic nanosized dispersions.

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On the other hand, many problems of solution chemistry are centered on the acid–base equilibrium. Therefore, it is significant to rationalize the influence of the aforementioned media on acid–base and other protolytic reactions. The present report is devoted to protolytic equilibria in dispersions with aqueous bulk (continuous) phase.

The ionization of an acid with charge z in solution can be described by the following equation:

$$H_iB^z \rightleftarrows H_{i-1}B^{z-1} + H^+,\ K_{a(1-z)} \tag{1}$$

This style of numeration means that the constants K_{a0}, K_{a1}, and K_{a2} refer to the ionization of a cationic, neutral, and anionic acid, respectively. We use the term "ionization constants" with the understanding that ionic association of some species with surfactant ions or counterions in the dispersed phase cannot be excluded. In such a case, these constants, determined vis-spectroscopically, can be considered as more complicated "observed" ones [7].

The two main approaches to a description of such equilibria, the quasichemical model and the model of pseudophase, are probably of equal worth [8]. In particular, the concept of pseudophase [1b,c,f,l] allows the introduction of the ionization constant of an acid, K_a^m, in micelles, analogous to such quantities in other liquid media:

$$pK_a^m \equiv -\log K_a^m = -\log(a_{H^+}^m\, a_B^m / a_{HB}^m) \tag{2}$$

Here, $a_{H^+}^m$, a_B^m, and a_{HB}^m are activities of the corresponding species; in this paper, we use the molar scale of activities and concentrations. Thus, micellar pseudophase can be considered as a kind of organic solvent or water–organic mixture, where the state of acid–base and tautomeric equilibria of dissolved substances differs from that in water. Therefore, the influence of organic solvents on the protolytic equilibria must be briefly discussed.

Differentiating influence of organic solvents

The number of protolytic equilibrium constants determined in various liquid media is huge. Therefore, it appeared to be worthwhile to classify the solvents not only by numerous polarity parameters [9], but also reasoning from the solvents' influence on the state of acid–base equilibrium [9,10]. Now it is recognized that the chemical nature of the solvent determines its so-called *differentiating influence*. The last-named can be understood as *non-uniform changes of acid strength* on going from a standard solvent (water) to the given solvent [10]. In particular, Izmailov gave one of the earliest classifications of differentiating action in the 1940s to 1950s [10a,c,11].

In organic solvents with high enough relative permittivity, ε_r, where the nonspecific ion pairing is to the first approximation negligible, the difference between the indices of ionization constants in the given solvent, $K_a^s = a_{H^+}^s\, a_B^s / a_{HB}^s$, and in water, $K_a^w = a_{H^+}^w\, a_B^w / a_{HB}^w$, can be easily estimated and expressed in terms of transfer activity coefficients

$$\Delta pK_a^s = pK_a^s - pK_a^w = \log {}^w\gamma_{H^+}^s + \log {}^w\gamma_B^s - \log {}^w\gamma_{HB}^s \tag{3}$$

The ${}^w\gamma_i^s$ values can be converted into the Gibbs energies of transfer from water to the given solvent

$$\Delta G_i^{tr}\,(w \to s) = RT\ln {}^w\gamma_i^s \tag{4}$$

Here, R is the gas constant and T is absolute temperature. Based on the Born electrostatic theory for ion energy in a dielectric continuum, Brønsted explained the dependence of ΔpK_a^s values on the charge of the acid, z [9,10a,11c,d,12]. The concept of charge type of the acid–base couple utilized by Kolthoff appeared to be very useful [10a,11c,d,12]. In this paper, we use the designations HB^+/B^0, HB^0/B^-, HB^-/B^{2-}, and so on, for cationic, neutral, anionic, etc. acids. Shortly after the pioneering works of Brønsted, it appeared that not only the charge type, but also the "chemical type" is of significance [13].

The dependences ($\mathrm{p}K_\mathrm{a}^\mathrm{s}$ vs. $\mathrm{p}K_\mathrm{a}^\mathrm{w}$) appeared to be different not only for cationic and neutral acids, but also for carboxylic acids and phenols. This phenomenon was examined in detail by Izmailov [10a,11b–d], who explained it in terms of different solvation of molecular and ionic species in water and in organic solvents. A unified equation, which takes into account both dielectric properties of the solvent and solvation of reactants, which is given below in a somewhat simplified form, assuming the ions are spherical and disregarding dielectric saturation, can be named the Brønsted–Izmailov equation [1m,14]:

$$\Delta \mathrm{p}K_\mathrm{a}^\mathrm{s} = \frac{e^2 N_\mathrm{A}}{4.605\, RT \;\times 4\pi \times 8.854 \times 10^{-12}} \times \left[\frac{1}{r_{\mathrm{H}^+}} + \frac{z_\mathrm{B}^2}{r_\mathrm{B}} - \frac{z_\mathrm{HB}^2}{r_\mathrm{HB}}\right] \times \left[\frac{1}{\varepsilon_\mathrm{s}} - \frac{1}{\varepsilon_\mathrm{w}}\right] + \frac{\Delta G_{\mathrm{H}^+}^\mathrm{solv} + \Delta G_\mathrm{B}^\mathrm{solv} - \Delta G_\mathrm{HB}^\mathrm{solv}}{2.302 RT} \qquad (5)$$

Here, N_A is the Avogadro number, e is the elemental charge, ε_S and ε_W are ε_r values of the solvent and water, respectively, r_i are radii of i species, which are assumed to be unchanged on going from solvent to solvent. The $\Delta G_\mathrm{i}^\mathrm{solv}$ values, conventionally (but not exactly) named "non-electrostatic" contributions to Gibbs energies of transfer, reflect effects caused by specific solvation, ion–dipole interactions, etc. In the original works of Izmailov [10a,11b–d], the ΔG_i^solv values were deciphered in terms of stability constants of complexes formed by molecular species with solvent molecules, as well as constants of proton exchange between water and the given solvent.

Note that if we map out the last item, the $\Delta \mathrm{p}K_\mathrm{a}^\mathrm{s}$ value for couples of $\mathrm{HB}^+/\mathrm{B}^0$ type must be very small.

Water and, to considerable degree, alcohols are hydrogen-bond donor (HBD) solvents. They belong to the so-called "masking", or "levelling" solvents [10]. By contrast, those solvents with high molecular dipole moments and ε_r values, without OH groups, display strong a differentiating influence on the strength of different groups of acids; they also "resolve" the acid strength of acids belonging to the same chemical class [10b]. Typical representatives of this group are acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), nitromethane, propylene carbonate, acetone, etc. Izmailov called them "differentiating" solvents [10a,11]. After Parker, they are "dipolar aprotic" [10c,15], while Bordwell proposed a more precise term "polar non-HBD" solvents [9]. Mixtures of acetone, acetonitrile, and DMSO with water resemble to some degree the differentiating ability of pure solvents. In addition, in mixed solvents the differentiating can be caused by preferential solvation.

Along with comparing the $\Delta \mathrm{p}K_\mathrm{a}^\mathrm{s}$ values, other criteria of differentiating influence can be used [1m,10,11,13,14,16]. Namely, the acids of different ionizing group or charge type of acid–base couple give different plots of $\mathrm{p}K_\mathrm{a}^\mathrm{s}$ vs. $\mathrm{p}K_\mathrm{a}^\mathrm{w}$ [10a,11c,d,13]. Further, within one and the same chemical type of neutral or anionic acids, the $\Delta \mathrm{p}K_\mathrm{a}^\mathrm{s}$ values can be also different. Typically, in such cases the slope of eq. 6 exceeds unity [13,16]:

$$\mathrm{p}K_\mathrm{a}^\mathrm{s} = \mathrm{a}\ \mathrm{p}K_\mathrm{a}^\mathrm{w} + \mathrm{b} \qquad (6)$$

Taking into account eq. 5, it must be noted that the deviation of the slope from $a = 1$ can be explained by the stronger increase in the last item of eq. 5 for weaker acids. This is reasonable because organic acids with localized charge of anions are, in general, weaker ones, and in polar non-HBD solvents the $\mathrm{p}K_\mathrm{a}^\mathrm{s}$ s just of such acids increase particularly.

Now let us consider the picture of acid–base equilibrium in micellar solutions.

Acid–base equilibrium of an indicator dye located on the micelle/water interface

Acid–base [1d,11,17] and solvatochromic [8a,17g,h,18] indicators, including fluorescent dyes, and stable free radical probes [5,17g,19], are known to be a touchstone for examining micelles, microdroplets, and related nanosized particles, including biomolecules [17g,19c–e,20]. Indicator dyes serve as useful tools for estimating the solubilizing ability [8a,21], microviscosity, and interfacial polarity [18,22], for monitoring local acidity and electrical potentials [5b,17d–f,h,18,19c,e,20,23], etc. Colored and fluorescent dyes embedded in organized solutions are widely used in sensor devices [24]. Fluorescing molecular probes are of particular significance for medical studies [19h]. Hydrophobic species can be absorbed within the micellar core, [4a,8a,21,25]; in some papers, the (adsorption $\rightleftarrows$ absorption) equilibrium is discussed [4a,19c,21,26].

Acid–base indicators are generally believed to be located in the Stern region of ionic micelles [1b,17d,f,27]. As a rule, molar absorptivities of such dyes are of the order of magnitude of 10^5 dm^{-3} mole cm^{-1}, hence the working concentrations can be 10^{-5} M or even lower.* Typically, only a single indicator molecule (or ion) is situated in a micelle. Chart 1 shows a molecule of indicator located in the palisade of a cationic surfactant micelle.

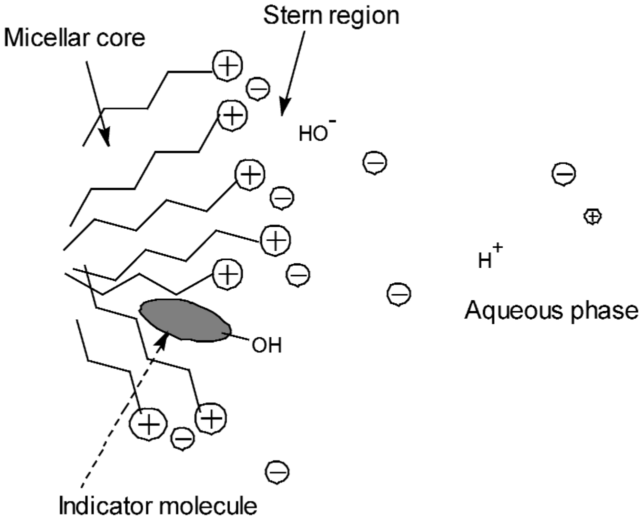

Chart 1 A schematic picture of a fragment of a cationic micelle with an embedded indicator.

Naturally, the value of $\Delta pK_a^m = pK_a^m - pK_a^w$ can be expressed as a combination of ${}^w\gamma_i^m$ values, analogous to eq. 3. However, since the experimental determination of pK_a^m is hindered, it appeared more practical to discuss and analyze the so-called "apparent" value, pK_a^a, which is the key characteristic of an indicator embedded in the micellar pseudophase.

$$pK_a^a = pH_w + \log\{[HB^z]_t/[B^{z-1}]_t\} \qquad (7)$$

The subscript t (total) denotes that the concentration is expressed in moles per dm^3 of the whole solution. The pH_w value characterizes the bulk phase and is determined as a rule using a glass electrode in a cell with liquid junction.** The ratio of equilibrium concentrations of indicator species can be obtained by means of UV/vis spectroscopy at extremely low indicator concentrations.

Hence, pK_a^a is an "instrumental" parameter which can be observed as a constant of two-phase equilibrium. In general, some fractions of B^{z-1} and HB^z species can stay in the bulk phase. To ensure

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*Hereafter, 1 M ≡ 1 mole dm^{-3}.

**Some complications caused by the presence of a surfactant in the buffer system are considered in supplementary electronic material to a recent publication [29k].

complete binding, ionic indicators with charge opposite to that of micellar surface can be used [17d,27a–d,28]. Alternatively, hydrophobic indicators, ordinarily with long hydrocarbon tails can be applied [17f,29]; such probes can be fixed in micelles despite the like charges of dye species and that of the interface. The pK_a^a value under conditions of *complete binding* of B^{z-1} and HB^z we designate as pK_a^{ac}.

Occupying even 0.1 to 1 % of the total volume of the aqueous solution, surfactant micelles can exert strong influence on acid–base equilibria of indicators.

In fact, the old-established "protein error" of indicators [12,30] reflects the modification of acid–base properties by the giant biomolecule, which acts as a pseudophase. Hartley explained the "protein" and "colloidal" errors of indicators [17a] and put forward rules which allowed micellar effects upon acid–base equilibria [17a,c,31] to be predicted. Specifically, cationic surfactants influence mainly anionic indicator dyes, decreasing their pK_a^a as compared with pK_a^w, while anionic surfactants first of all shift acid–base equilibria of cationic indicators, increasing their pK_a^a. Actually, these rules reflect both the phenomenon of dye binding to micelles caused by opposite charges attraction and acid–base equilibria shift of the bound dyes, also of electrostatic origin.

Starting from the Boltzmann distribution law, the concentration of H^+ ions nearby the positively charged interface must be lower as compared with the bulk aqueous phase, while that of OH^- ions must be higher. In the case of negatively charged surface, the situation is opposite. If we assume that K_a^m is equal to K_a^w, then decrease (increase) in H^+ concentration must just result in $\{[B^{z-1}]/[HB^z]\}$ increase (decrease). In many cases, this simplistic approach explains qualitatively the changes of indicator ratio in cationic and anionic micelles, respectively. However, little by little it became clear that micelles display some influence besides the electrostatic one [17d]. Note that in nonionic micelles, the pK_a^{ac} values of indicators often differ from their pK_a^ws distinctly.

Medium effects, i.e., the quantity $\Delta pK_a^{ac} = pK_a^{ac} - pK_a^w$, can reach 4 units by absolute value at low ionic strength of the bulk phase [1m,27e–h,32], while the introduction of electrolytes into the micellar solution can change these values to the extent of 3 units in the opposite direction [1m,28i–k,29i].

In the review published by El Seoud in 1989, ca. 400 pK_a^a values were collected [32b]. Since then, the number of published data has increased substantially. Despite a great deal of literature data on aqueous micellar solutions of colloidal surfactants, there is no generally accepted opinion about the impact of various factors, such as the length of the linear hydrocarbon tail, the nature of the ionic head-group, the counterion, and co-ion, as well as of the surfactants concentration and bulk ionic strength, on the pK_a^{ac} of acid–base indicators.

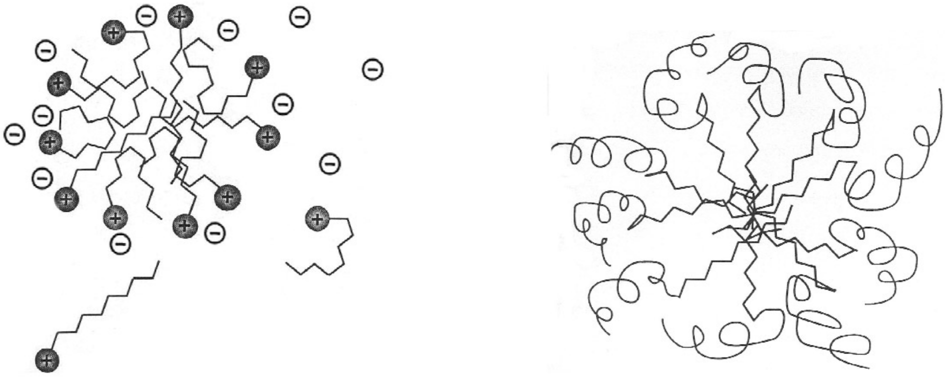
The aim of the present review is to consider the protolytic equilibria of indicators in self-assembled surfactant aggregates and related systems. Micellar solutions of over 20 surfactants are used, as well as mixed micellar systems. Effects caused by indifferent "supporting" electrolytes as well as specific effects of hydrophobic counterions are examined. Based on more than 1500 pK_a^a values determined in this laboratory, as well as on the data published by others, the main regularities governing the protolytic equilibria of substances dissolved in organized solutions are revealed.

The differentiating influence of the micellar pseudophase upon the acid–base properties of indicator couples of various charge types and chemical types, 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 counterions of different hydrophobicity. In addition to this "*true*" differentiating influence, "*trivial*" differentiating, originating from incomplete binding of some dye species, can take place.

CHARACTERIZATION OF MICELLAR PSEUDOPHASE

Peculiarities of micellar pseudophase

The structures of spherical micelles of an ionic (namely, cationic) and a nonionic surfactant are schematically depicted in Chart 2. The hydrophobic core is shielded from water by the hydrophilic palisade.



A **B**

Chart 2 A schematic sketch of the section of cationic (A) and nonionic (B) surfactant micelles.

The aggregation number of such micelles is of the order of magnitude of 10^2, the radius is within the range of ≈2 to ≈4 nm. It is common knowledge that increase in surfactant concentration and addition of electrolytes usually result in size increase and polymorphic conversions, i.e., "sphere to ellipsoid", "sphere to rod", etc., transitions of micelles, first of all of ionic ones. The number of publications devoted to detailed description of micellar size, shape, and other properties, is huge and permanently increasing.

The driving force of micelle formation in water is the hydrophobic interaction [9,33]. As a rule, micelles appearing in aqueous media when the surfactant concentration reaches the critical micelle concentration (cmc) are small and sphere-shaped. According to the generally recognized viewpoint, such micelles are highly porous, strongly hydrated, disordered clusters, being in the state of dynamic equilibrium with monomers in bulk phase [1b,j,2a,8,9,33,34]. Micellar solutions of colloidal surfactants are transparent, thermodynamically stable systems.

On discussing the regularities of micellar solubilization [4c,21], on considering the Krafft diagram in terms of Gibbs rule of phases [8b], and also on estimating the water content in ellipsoidal micelles [35], some authors recommend taking into account the additional Laplace pressure, Δp, caused by the curvature of micellar surface. However, the value of surface tension, σ, used for calculation of $\Delta p = 2\ \sigma\ r^{-1}$, was equated to the corresponding value for water/oil interface, ca. 20–40 mJ m^{-2} [8b,21,35], which results in Δp value of the order of magnitude of 10^7 Pa [8b,21]. Meanwhile, according to the Rehbinder–Shchukin criterion [36], the lyophilicity of the systems under consideration is provided by extremely low σ value, ca. 0.01–0.001 mJ m^{-2}. This explains the commensurability of the excess interfacial Gibbs energy of a colloidal particle, $4\pi r^2\sigma$, and the energy of Brownian motion of water molecules, k_BT. If we accept such a negligible σ value, the estimate of Δp will decrease at least by three orders of magnitude. Some authors report a higher σ value of 0.5 mJ m^{-2} [37], but it is still much lower than that for the water/oil interface.

Another significant characteristic of micellar pseudophase is microviscosity. On the whole, it is much higher than that of surrounding aqueous phase [22]. However, the estimates made using photophysical data are rather contradictory [38].

In the interfacial portion of ionic micelles (Stern layer, or "Stern region" [34c]), the charged head-groups are partly neutralized by counterions. The rest of the last-named are distributed within the diffuse part of the double electrical layer; together with co-ions they form the ionic atmosphere around the multicharged particle. The degree of dissociation of ionic surfactant in the micelle, α, as estimated for various surfactants and by different methods, varies within the range of 0.5–0.1. Another widely used parameter, the degree of neutralization of head-groups in the Stern layer, β, equals $(1 - \alpha)$. The equilibrium concentration of the counterion in the bulk phase can be calculated using the values of surfactant concentration, c_{surf}, and cmc and α values under given conditions [1b,c,27b–h,28a]. For example, for cationic surfactant

$$[\mathrm{X}^-_{\mathrm{w}}] = c_{\mathrm{X}^-} + \mathrm{cmc} + \alpha(c_{\mathrm{surf}} - \mathrm{cmc}) \tag{8}$$

Here, c_{X^-} is the initial concentration in the buffer mixture. The concentration of surfactants in the micellar pseudophase is within the range of ca. 3–7 M. The structural models of ionic micelles presume the entry of hydrocarbon chains, at least the first methylene group, into the Stern layer [1b,22,34c,d]. Therefore, *the Stern region is actually a mixture of water, hydrocarbon, and electrolyte. Such composition is unattainable in common homogeneous systems.* Probably, just this is the reason for difficulties in modeling the influence of the Stern region on the equilibria state of embedded substances through comparing with effects of water–organic mixtures.

Some authors [35,39] apply the principle of Donnan equilibrium to surfactant micelles, considering both the pseudophase (or the Stern region) and the bulk phase as two aqueous solutions. However, such an approach does not seem to be obvious, taking into account the essentially nonaqueous properties of micellar intefaces, or, more precisely, the absence of structurally "normal" water [40] even within the Stern region.

Probably, some analogies with ionic liquids containing admixtures of water (or other common solvents) can be found here [41]. Strong and Kraus [42] considered an extremely concentrated salt solution in a nonpolar solvent as organic liquid dissolved in fused salt; Pocker [43] described the reactivity in ionic clusters in solvents of low polarity.

On the other hand, the values of relative dielectric permittivity of micellar interfaces, ε_{m}, as estimated using versatile experimental approaches, are markedly higher than those of low-polarity solvents. Comparison of absorption spectra of different probes, from alkylpyridinium iodide to metal ion complexes, in micelles and in water–organic mixtures [18,44], leads to strong scatter of ε_{m} values [34a,38]. On the average, the ε_{m} values of interfaces of micelles of cationic tetraalkylammonium surfactants are within the range of 30–40, while those of anionic sulfate or sulfonate surfactants are somewhat higher. In the case of phospholipid bilayers organized in vesicles and biomembranes, the situation becomes even more complicated [45]. This can reflect both the multiplicity of location sites of probes within the pseudpohase, from hydrophobic interior to hydrophilic exterior regions, and selective solvation of the probes.

Solvatochromic parameters, such as $E_{\mathrm{T}}(30)$, $E_{\mathrm{T}}^{\mathrm{N}}$, π^*, etc., are probably more useful for characterization of micellar interfaces [9].

Examination of micelles using the standard Reichardt's solvatochromic dye

In order to examine and compare the polarity of different micelles, we used pyridinium *N*-phenolate zwitterionic indicators (Chart 3), which exhibit the largest range of solvatochromism among up-to-now known organic dyes [9].

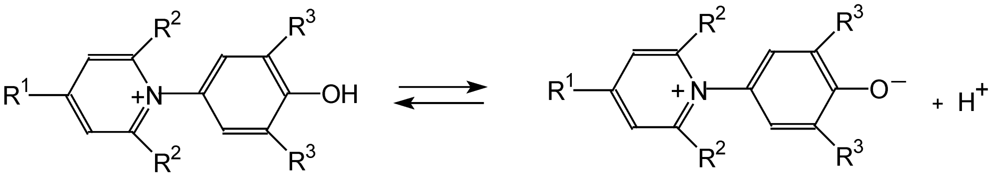


Chart 3 The colorless cationic pyridinium-*N*-phenol and the highly polar solvatochromic pyridinium-*N*-phenolate.

These dyes, also called Reichardt's dyes (RDs), appeared to be very useful for studying both homogeneous and microheterogeneous liquid systems [9,18b–d,28l,29j,41,44a,b,46]. Drummond, Grieser, and Healy were the first who proposed the standard 2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1) phenolate (Chart 3, $R^1 = R^2 = R^3 = C_6H_5$) as a single solvatochromic and acid–base probe for micelles [44a]. The values of the normalized polarity parameter, E_T^N, were determined by us using this dye [28l,29j,46m]. This parameter can be calculated from the absorption maximum value of the intramolecular charge transfer band, λ_{max}/nm, using the formula $E_T^N = [E_T(30) - 30.7]/32.4$, $E_T(30) = 28\,591/\lambda_{max}$. For water and tetramethylsilane, $E_T^N \equiv 1.00$ and 0.00, respectively. The data are collected in Table 1; they agree with the results reported by others in cases where the comparison is possible, e.g., in cetyltrimethylammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) solutions.

Likewise, the pK_a^{ac} values of the corresponding cationic acid ($HB^+ \rightleftarrows B^\pm + H^+$) are also compiled, as a rule, at ionic strength of $I = 0.05$ M.

Inspection of Table 1 leads to the conclusion that the locus of solvatochromic dye is less polar in the case of cationic and nonionic micelles and most polar in the case of anionic micelles. On the whole, the interfacial regions of micelles are strongly hydrated. So, even in 3.2 M aqueous solution of tetra-*n*-butylammonium bromide, the E_T^N value (= 0.48) [47] is much lower than in micellar pseudophase. The E_T^N values of least polar microenvironments (Table 1) correspond approximately to ethanol (E_T^N = 0.654), and thus markedly outnumber the values for acetonitrile, DMSO, and acetone (E_T^N = 0.460, 0.444, and 0.355, respectively [9]).

Both the sign of the micellar surface charge and its screening by supporting electrolytes manifest themselves in the pK_a^{ac} values (Table 1). However, there is no correlation between the equilibrium parameters of the dye and the length of the hydrophobic tail of surfactant. The reported strong dependence of pK_a^{ac} values on the size of the hydrocarbon chain as revealed in experiments without maintaining constant bulk ionic strength [44a] can be explained by the difference of counterion concentrations in the bulk phase, caused by different cmc values of surfactants [1m,29j]. The pK_a^{ac} value in phospholipid liposomes is in line with the general complicated character of their influence on indicator equilibria [48].

The total van der Waals volume of the RD molecule equals 0.83 nm^3 [46m]. According to AM1 calculations, this molecule goes in a cage of $1.26 \times 1.01 \times 0.81$ nm^3 = 1.03 nm^3 [49]. The volumes of SDS and CTAB spherical micelles are ≥24 nm^3 and ≥70 nm^3, respectively [29j].

Strictly speaking, the molecular probes give information not on the "pure" homomicelle, but rather on the micellar microenvironment disturbed by the dye itself. Even more so, it refers to the large-sized dipole of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1) phenolate, and the results can be considered, according to Fromherz, as investigation of physical chemistry of the chromophore rather than studying a true probe of the interface [50].

However, despite its relatively large size, the standard betaine dye is now extensively used for studying various colloidal systems both as acid–base and solvatochromic indicator. According to Healy [51], the legitimacy of such a procedure is the coincidence of Ψ and ε_{eff} values obtained with the betaine dye and with less "bulky" probes, such as coumarins, for micelles of cationic surfactants. Similar conclusions can be made by studying nitrophenols [29j,52].

Table 1 The data for the standard solvatochromic Reichardt's indicator, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1) phenolate, in micellar solutions of colloidal surfactants and related systems [28l,29j,46m]; c_{surf} = 0.01 M, I = 0.05 M (buffer + NaCl), and 25 °C, unless otherwise specified

Micellar system[a]	λ_{max}/nm (E_T^N)[b]	pK_a^{ac}	ΔpK_a^{ac}
None (water)	453 (1.000)	8.64 (lit.)[c]	0
SDS[d]	497 (0.828)	10.70 ± 0.01	2.06
SDS, 0.40 NaCl	497 (0.828)	10.20 ± 0.03	1.56
SDS, 0.003 M n-$C_{10}H_{21}N(C_2H_5)_3^+HSO_3^-$	503 (0.807)	–	–
SDS, 0.01 M $N(n\text{-}C_4H_9)_4I$[e]	505 (0.800)	9.89 ± 0.14	1.25
SDS – 1-pentanol – benzene (ME)[f]	502 (0.810)	10.35 ± 0.11	1.71
SDS, 50 °C	502 (0.810)	10.61 ± 0.04	1.97
n-$C_{13}H_{27}OSO_3Na$, 50 °C	511 (0.779)	10.29 ± 0.03	1.65
n-$C_{14}H_{29}OSO_3Na$, 50 °C	502 (0.810)	10.50 ± 0.01	1.86
n-$C_{16}H_{33}OSO_3Na$, 50 °C	510 (0.783)	10.47 ± 0.07	1.83
n-$C_{10}H_{21}SO_3Na$, 0.40 NaCl	501 (0.814)	9.57 ± 0.03	0.93
n-$C_{10}H_{21}SO_3Na$ (0.02 M)	496 (0.832)	9.67 ± 0.05	1.03
n-$C_{10}H_{21}SO_3Na$ (0.03 M)	507 (0.793)	10.27 ± 0.01	1.63
n-$C_{16}H_{33}SO_3Na$, 50 °C	505 (0.800)	10.12 ± 0.03	1.48
n-$C_{12}H_{25}C_6H_4SO_3Na$	495 (0.835)	10.34 ± 0.04	1.70
n-$C_{12}H_{25}C_6H_4SO_3Na$, 50 °C	495 (0.835)	–	–
n-$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	495 (0.835)	10.91 ± 0.03	2.27
Phospholipid liposomes (0.002 M)[g]	513 (0.773)	10.12 ± 0.09	1.48
$C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$	528 (0.724)	10.19 ± 0.04	1.55
SDS (0.01 M) + Nonyl phenol 12 (0.01 M)	520 (0.749)	10.47 ± 0.03	1.83
Nonyl phenol 12 (nonionic surf.)	538 (0.693)	9.10 ± 0.05	0.46
Tween 80 – 1-pentanol – n-hexane (ME)[i]	545 (0.672)	9.18 ± 0.05	0.54
Tween 80 – 1-butanol – n-hexane (ME)[i]	535 (0.702)	9.22 ± 0.05	0.58
Triton X 100 – 1-butanol – n-hexane (ME)[i]	543 (0.678)	8.98 ± 0.05	0.34
Brij 35 – 1-butanol – n-hexane (ME)[i]	554 (0.645)	8.42 ± 0.05	–0.22
Tween 80 – cyclohexanol – n-hexane (ME)[i]	544 (0.674)	9.10 ± 0.05	0.46
Tween 80 – 1-butanol – cyclohexane (ME)[i]	545 (0.672)	9.17 ± 0.05	0.53
n-$C_{16}H_{33}$ $N^+(CH_3)_2(CH_2)_3$ SO_3^- (0.001 M)	550 (0.657)	8.0 ± 0.08	–0.64
CTAB[h]	540 (0.687)	7.42 ± 0.02	–1.22
CTAB, 0.40 NaCl	543 (0.678)	8.09 ± 0.03	–0.55
CTAB, 0.01 M $C_7H_7SO_3Na$[e]	540 (0.687)	8.14 ± 0.02	–0.50
CTAB, 50 °C	542 (0.681)	7.22 ± 0.05	–1.42
CTAB (0.003 M), 4.00 KCl	562 (0.623)	8.60 ± 0.02	–0.04
n-$C_{16}H_{33}NC_5H_5Br$	535 (0.702)	7.18 ± 0.03	–1.46
CPC[j]	538 (0.693)	7.09 ± 0.01	–1.55
n-$C_{18}H_{37}N(CH_3)_3Cl$, 30 °C	543 (0.678)	7.30 ± 0.01	–1.34
CPC – 1-pentanol – n-hexane (ME)[i]	533 (0.708)	7.8 ± 0.3	–0.84

[a] Microemulsions are designed as "ME", volume fraction of the pseudophase φ = 1.3 %.

[b] $E_T^N = [E_T(30) - 30.7]/32.4$, $E_T(30)$, $= 28\,591/\lambda_{max}$, kcal mol^{-1}.

[c] From ref. [44a,b].

[d] SDS = n-$C_{12}H_{25}OSO_3Na$.

[e] Without NaCl.

[f] Molar ratio of organic components 1:7:4, however, at other ratios (1:3.5:2; 1:10.5:4, etc.) the pK_a^{ac} values are within ±0.1.

[g] Phosphatidylcholine + diphosphatidylglycerol (18:1, mol:mol).

[h] CTAB = n-$C_{16}H_{33}N(CH_3)_3Br$.

[i] Molar ratio 1:(2.5–6.5):(0.7–1.4).

[j] CPC = n-$C_{16}H_{33}NC_5H_5Cl$.

As a rule, only the standard betaine or, sometimes, the chlorinated dye (Chart 3, $R^1 = R^2 = C_6H_5$, $R^3 = Cl$) are used as such combined (solvatochromic/protolytic) indicators. However, betaine dyes of various structures can serve as both solvatochromic and acid–base probes. And today the question seems timely: Is the information on solvating properties, from both spectra and pK_a^{ac}, the same if obtained by using different indicators? Of course, the problem of different depth of penetration is to be discussed first of all. We have studied the spectra and acid–base equilibria of 11 betaine dyes in micelles and oil-in-water microemulsions of different kinds [46m,53]. Interestingly, the locus of the most lipophilic betaines, e.g., $R^1 = R^2 = C_6H_5$, $R^3 = C(CH_3)_3$, or $R^1 = R^2 = R^3 = 4\text{-}[C(CH_3)_3]\text{-}C_6H_4$, even in droplets of microemulsions corresponds to the E_T^N value of no less than 0.4, so that the occurrence of a “pure hydrocarbon core” is unlikely probable.

Electrostatic interfacial potential of ionic micelles

Along with polarity, another parameter, the electrostatic potential of the Stern region, Ψ, is of significance for the interpretation of equilibrium data in ionic micelles. There are four main approaches for Ψ estimation: (1) electrokinetic studies; (2) theoretical calculations based on the double electrical layer theory; (3) application of solvatochromic or solvatofluoric indicators [19c,e]; (4) use of pH-indicators (this approach will be considered later).

Direct electrokinetic measurements allow only the determination of the so-called zeta-potential, ζ, which is by absolute value knowingly lower than Ψ.

The theoretical Ψ calculations for nanosized charged particles can be made using versatile formulae, according to the shape of the interface. In the case of small spherical micelles, the curvature of surface is too large to use the equations of the flat double electrical layer [20b,28l,54] for exact calculations. Here, the most appropriate is the formula obtained by Oshima, Healy, and White for spherical colloidal particles with radius r, obtained by solving the nonlinear Poisson–Boltzman equation [29d,55]. It can be presented in the following form:

$$\frac{\alpha}{s_{\mathrm{i}}} - \frac{2\varepsilon\varepsilon_o kRT}{F}\sinh(Y/2)\left(1 + \frac{2}{kr\cosh^2(Y/4)} + \frac{8\ln\left[\cosh(Y/4)\right]}{(kr)^2\sinh^2(Y/2)}\right)^{\frac{1}{2}} = 0 \tag{9}$$

Here, s_{i} is the area of the charged head-group, $Y = \Psi F/RT$, F is the Faraday constant, k^{-1} is the Debye length, $\varepsilon_{\mathrm{o}} = 8.854 \times 10^{-12}$ F m^{-1}, $\varepsilon = 78.5$ at $T = 298.15$ K. Actually, α/s_{i} is the surface charge density. Some examples of calculations for SDS and CTAB micelles [1m,29j,k] are given in Table 2.

The calculations demonstrate that the uncertainty of Ψ values obtained by using eq. 9 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 from each other [29a,d,i,j,57]. So, for SDS micelles conductance measurements lead to $\alpha = 0.3–0.4$ [29a], or even higher, while pNa determination and analysis of salt effects upon cmc values result in 0.20–0.26 [57].

Even more so, such calculations are hindered for numerous colloidal systems, which are not so well defined as SDS or CTAB micelles are, because the complete set of parameters (r, α, and s_{i}) is as a rule unknown for them. Besides, we use the ε value for pure water, which may be also inexact. However, even if the possibility of exact calculations is doubtful, eq. 9 allows us to obtain plausible estimates of Ψ values. Other approaches to estimate the Ψ values for colloidal particles are also known [37,58].

Increase in surfactant concentration up to 0.1 M and/or addition of substantial amounts of electrolytes make the calculations uncertain, because under such conditions the micellar shape in general is known to deviate from spherical. In this case, the formula for cylindical particles is to be used [58b]. Treating micelle formation by small system thermodynamics, Gilányi suggested a diffuse monolayer structure instead of the idealized Goüy–Chapman model [58e].

Table 2 The Ψ values of SDS and CTAB, calculated by eq. 9; 25 °C [29j,56].[a]

$[\mathrm{Na}^+_\mathrm{w}]$/M	r/nm	s_i, nm^2	α	Ψ/mV
		SDS micelles		
0.01	1.8	0.500	1	–199
0.008	1.8	0.609	1	–193[b]
0.01	1.8	0.609	0.55	–148
0.01	1.8	0.609	0.20	–78
0.01	1.8	0.660	0.30	–100
0.01	2.0	0.900	0.20	–59
0.05	1.8	0.609	1	–147
0.05	1.8	0.609	0.55	–111
0.05	1.8	0.609	0.30	–75
0.05	1.8	0.384	0.55	–140
0.05	1.8	0.384	0.20	–78
0.05	2.0	0.600	0.20	–57
0.05	1.8	0.459	0.20	–68
0.05	1.8	0.506	0.20	–63
0.05	1.8	0.663	0.20	–50
0.05	1.8	0.660	0.35	–79
		CTAB micelles		
0.053	2.56	0.474	0.27	+88
0.019	2.56	0.474	0.27	+110
0.019	2.56	0.675	0.27	+87
0.005	2.56	0.474	0.19	+101
0.019	3.5	0.474	0.27	+113

[a] As a rule, c_surf = 0.01 M.

[b] Close to the Ψ = –195 mV value reported in ref. [29d].

Sometimes, the micelles of nonionic surfactants are supposed to have a charged interface owing to the charge of indicator species [29f] or to complexation of metal cations with polyoxyethylene chains [59]. Additional reasons for appearance of interfacial potential may be preferential adsorption of one kind of ions, orientation of water dipoles, or even different mobility of cations and anions of the supporting electrolyte within the voluminous polyoxyethylene mantle, analogous to the mechanism characteristic for cells with liquid junction. However, reliable evidences for the existence of interfacial electrostatic potential in the case of nonionic surfactant micelles are absent.

PRINCIPAL RELATIONS AND ADAPTABILITY OF THE ELECTROSTATIC MODEL

The electrostatic model is mostly used for the description of protolytic equilibria in micellar media and related systems. It is based on the concept of pseudophase and on taking into account (i) the electrostatic potential of the interface and (ii) solvation effects [17d–f,25,27a–d,28a,c–l,29,46m,48,60]. The detailed consideration can be found in a set of reviews [1c,f,17h,61].

Within the framework of the electrostatic model, key relations can be derived, assuming that the partition of any ion or molecule, including the species HB^z and B^{z-1}, between the bulk aqueous phase and the pseudophase can be described by eq. 10

$$P_\mathrm{i} = a_\mathrm{i}^\mathrm{m}/a_\mathrm{i}^\mathrm{w} = P_\mathrm{i}^\mathrm{o}\exp(-z_\mathrm{i}\Psi F/RT) = ({}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{m})^{-1}\exp(-z_\mathrm{i}\Psi F/RT) \tag{10}$$

Here, P_i is partition constant of *i*-species with charge z_i; a_i^m and a_i^w are activities in micellar and aqueous phases, respectively; ${}^w\gamma_i^m$ is the activity coefficient of transfer from water to the pseudophase. The quantity $P_i^o = ({}^w\gamma_i^m)^{-1}$ reflects the ability of the species to go from water to pseudophase, apart from electrostatic attraction or repulsion. Equation 10 follows from the equality of the electrochemical potentials of the *i*-species in the two phases under equilibrium conditions. Actually, the Stern layer (or Stern region) is considered as a pseudophase. For Gibbs energy of transfer from water to pseudophase, eq. 11 is valid:

$$\Delta G_i^{tr}(w \rightarrow m) = -RT \ln P_i = RT \ln {}^w\gamma_i^m + z_i\Psi F \tag{11}$$

In particular, applying eq. 10 to the proton (hydronium ion), the expression for interfacial pH, pH_m, can be obtained:

$$pH_m \equiv -\log a_{H^+}^m = pH_w + \log {}^w\gamma_{H^+}^m + \Psi F/RT \ln 10 \tag{12}$$

Hence, the difference between pH_m and pH_w is caused both by the electrical charge of the interface and by its solvation properties.

For the indicator, *completely bound by the interface*, the deviations of pK_a^m and pK_a^{ac} from the pK_a^w value can be represented using the partition constants

$$\Delta pK_a^m = pK_a^m - pK_a^w = \log P_{HB} - \log P_B - \log P_{H^+} \tag{13}$$

$$\Delta pK_a^{ac} = pK_a^{ac} - pK_a^w = \log P_{HB} - \log P_B \tag{14}$$

The last equation is more common, because it is just the pK_a^{ac} value, which is determined experimentally. The agreed notation of the first two items in the expression for pK_a^{ac} is pK_a^i:

$$pK_a^{ac} = pK_a^w + \log({}^w\gamma_B^m/{}^w\gamma_{HB}^m) - \Psi F/(2.302RT) = pK_a^i - \Psi F/(2.302RT) \tag{15}$$

Here, K_a^i is called "intrinsic" constant. It can be easily shown that $pK_a^i = pK_a^m - {}^w\gamma_{H^+}^m$. Note that the spectroscopic method gives the ratio of equilibrium concentrations of HB^z and B^{z-1} species, not activities. However, because the Stern region is actually a concentrated (ca. 3–7 M) electrolyte solution, the f_B^m/f_{HB}^m ratio of concentration activity coefficients is expected to be close to unity, and the corresponding logarithmic term is as a rule supposed to be negligible [44a], taking into account the character of the dependence of ionization constants of indicators in aqueous media on ionic strength [44a,62]. Moreover, since the Stern region can be also considered as a kind of ionic liquid or a solution of water and hydrocarbon in fused salt, the standardization "to infinite diluted indicator solution" still means the ionic environment. Therefore, it is more practical to suppose that the interaction energy of dye species with surrounding ions in Stern region is included in the ${}^w\gamma_i^m$ values.

In fact, K_a^{ac} is a constant of two-phase equilibrium. Contrary to the case of transfer of the acid–base equilibrium from water to homogeneous water–organic mixtures of nonaqueous solvents, the ΔpK_a^{ac} value does not include the log ${}^w\gamma_{H^+}^m$ quantity, but contains the electrostatic contribution ($-\Psi F/RT \ln 10$).

Equation 15 is of key character. Hartley and Roe were the first who used such an approach to describe apparent ionization constants as early as 1940; they utilized the ζ-potential instead of Ψ [17b]. In posterior years, Mukerjee and Banerjee [17d], Fromherz and coworkers [17f,20b,63], and Funasaki [17e,28a,60a] developed the electrostatic model. Therefore, though the considering approach results from effort of many authors, we find it justified calling eq. 15 the "HMFF equation" according to the names of Hartley (1934, 1940, 1948), Mukerjee (1964), Fromherz (1973, 1974, 1977), and Funasaki (1976, 1979). Somewhat later, Gaboriaud and associates [27a–d] and then Drummond, Grieser, and Healy [17h,28c–f,29b–e,44a,60c,d,61b,64] contributed a lot to the electrostatic model of equilibria.

Similar equations were used to describe the ionization of polyelectrolytes [65] and monolayers [20b,54,63]. The HMFF equation can be transformed into the formula for Ψ/mV estimation:

$$\Psi = 59.16\ (\mathrm{p}K_\mathrm{a}^\mathrm{i} - \mathrm{p}K_\mathrm{a}^\mathrm{ac});\ 25\ °\mathrm{C} \quad (16)$$

The $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value in ionic micelles is often equated to the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ value of the same indicator bound by micelles of nonionic surfactants [17e,h,28l,29c,d,i,60e]. For example, with Reichardt's indicator (Table 1), one can estimate the Ψ values of –95 and +99 mV for SDS and CTAB micelles at $I = 0.05$ M, using the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value of 9.10.

Based on an equation similar to eq. 16, Tokiwa and Ohki [65b] developed a method, which allowed estimating of the Ψ values of dimethyl dodecylamine oxide micelles during potentiometric titration of this amphiphilic base with HCl. Funasaki successfully utilized these data in his studies with indicators [60a]. Note that the degree of binding of counterions, Cl^-, can vary along the titration curve. Therefore, the relation between the degree of protonation of dimethyl dodecylamine oxide and the Ψ value can be complicated.

In the classical version of the electrostatic model, the constancy of (i) the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value of the given indicator in any micellar system on the one hand, and of (ii) the value of electrostatic potential of the Stern layer of the given micellar surface as obtained by using any indicator, on the other hand, is assumed. Consequently, the change in $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ on going from one kind of micelles to another must be equal for all the indicators.

The common electrostatic model of acid–base indicators equilibria in micelles, based on the HMFF equation, is certainly adequate in outline. However, the two aforementioned assumptions are proved to be justified only approximately, and sometimes are even invalid. In the cited papers, sulfonephthaleins, phenols, azo dyes, coumarines, hydroxyxanthenes, antraquinones, imidazoles, azines, triarylcarbinols, and some other dyes were studied. *The more number of indicator dyes are involved in the determination of Ψ, the stronger discrepancies becomes evident.*

Of course, the limited validity of the simple model can reflect the peculiar of dye location within the pseudophase. Indeed, some relatively large-sized dye molecules (ions) cannot completely come into the Stern region. On the other hand, some extremely hydrophobic dyes can penetrate even into the micellar or microdroplet core [25,46m]. In the context of the approach under discussion, all these peculiarities are included in the ${}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{m}$ values. The electrical potential within the charged uniform sphere stays constant; however, the existence of local charges and complicated potential profiles in the interfacial regions (micelles of zwitterionic surfactants, phospholipid vesicles, etc.) also results in different medium effects ($\Delta\mathrm{p}K_\mathrm{a}^\mathrm{ac}$) for various indicator dyes.

A rather distinct illustration of the limited validity of the simple electrostatic model can be obtained by comparing the indices of apparent ionization constants of a two-step (or bifunctional) indicator *n*-decylfluorescein (Chart 4, X = COO-*n*-$\mathrm{C_{10}H_{21}}$):

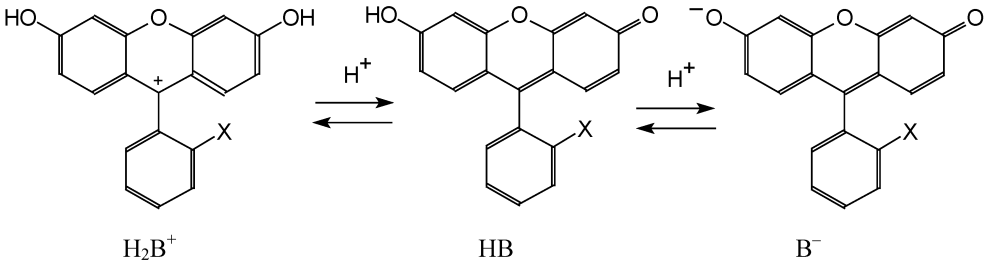


Chart 4 Stepwise protolytic equilibria of fluorescein esters.

The neutral molecule, HB, participates in the both equilibria. The presence of a long hydrocarbon tail allows one to expect identical or at least similar character of location of cation and anion within micelles, with ionizing groups situated in the Stern region.

Therefore, it can be anticipated that the difference between pK^{ac}_{a1} and pK^{ac}_{a0} will stay constant in versatile ultramicroheterogeneous systems. However, the data obtained in this laboratory [1m,29j,66] and compiled in Table 3 demonstrate that this is not the case.

Table 3 The indices of apparent ionization constants of *n*-decylfluorescein in micellar solutions of colloidal surfactants and related systems; $c_{surf} = 0.01$ M, $I = 0.05$ M (buffer + NaCl) and 25 °C, unless otherwise specified.[a]

Micellar system[b]	pK^a_{a0}	pK^a_{a1}	$pK^a_{a1} - pK^a_{a0}$	$-\dfrac{10^3 RT(\Delta pK^a_{a0} + pK^a_{a1})}{0.8686F}$
n-$C_{16}H_{33}SO_3Na$, 50 °C	5.16 ± 0.02	8.66 ± 0.04	3.50	–146
SDS[c]	5.17 ± 0.01	8.96 ± 0.04	3.79	–144
SDS, 0.4 M NaCl	4.55 ± 0.03	8.18 ± 0.04	3.63	–103
n-$C_{13}H_{27}OSO_3Na$, 50 °C	4.92 ± 0.05	8.68 ± 0.03	3.76	–139
n-$C_{14}H_{29}OSO_3Na$, 50 °C	4.87 ± 0.03	8.64 ± 0.09	3.77	–136
n-$C_{16}H_{33}OSO_3Na$, 50 °C	5.03 ± 0.05	8.78 ± 0.08	3.75	–146
n-$C_{10}H_{21}SO_3Na$ (0.03 M)	4.47 ± 0.02	8.77 ± 0.05	4.30	–118
n-$C_{10}H_{21}SO_3Na$ (0.01 M), 0.4 M NaCl	4.05 ± 0.08	7.89 ± 0.05	3.84	–80
n-$C_{12}H_{25}C_6H_4SO_3Na$	5.19 ± 0.04	8.78 ± 0.04	3.59	–142
n-$C_{12}H_{25}C_6H_4SO_3Na$, 50 °C	5.10 ± 0.04	8.64 ± 0.03	3.54	–144
SDS, 0.01 M $N(n\text{-}C_4H_9)_4I$[d]	4.25 ± 0.03	8.38 ± 0.01	4.13	–100
SDS, 0.003 M n-$C_{10}H_{21}N(C_2H_5)_3HSO_4$	4.89 ± 0.06	8.38 ± 0.02	3.49	–119
SDS – 1-pentanol – benzene (ME)[e]	4.69 ± 0.11	8.52 ± 0.04	3.83	–117
n-$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	4.77 ± 0.03	8.58 ± 0.06	3.81	–121
n-$C_{12}H_{25}C_6H_4(OC_2H_4)_{12}OSO_3Na$	3.62 ± 0.02	7.72 ± 0.04	4.10	–62
SDS (0.01 M) + Tween 80 (0.01 M)	3.83 ± 0.04	8.49 ± 0.02	4.66	–91
Tween 80	2.12 ± 0.05	7.20 ± 0.04	5.08	–2
$C_{16}E_{16}$ (0.005 M)[f]	1.92 ± 0.01	7.14 ± 0.02	5.22	+6
$C_{16}E_8$ (0.005 M)	2.30 ± 0.05	6.90 ± 0.01	4.60	+1
$C_{11}E_{10}$ (0.005 M)	2.22 ± 0.01	6.88 ± 0.01	4.66	+4
$C_{12}E_{12}$ (0.005 M)	2.13 ± 0.02	6.91 ± 0.01	4.78	+6
$C_{12}E_{15}$ (0.005 M)	2.17 ± 0.02	6.96 ± 0.04	4.79	+4
CDAPS[g] (0.001 M)	1.63 ± 0.05	6.07 ± 0.02	4.44	+46
Phospholipid liposomes (0.002 M)	–	8.42 ± 0.05	–	–
CTAB[h]	0.82 ± 0.02	4.94 ± 0.02	4.12	+103
n-$C_{16}H_{33}N(CH_3)_3Cl$, 0.4 M NaCl	1.62 ± 0.08	5.43 ± 0.01	3.81	+65
CTAB (0.003 M), 4 M KCl	2.13 ± 0.01	6.61 ± 0.07[i]	4.48	+15
n-$C_{16}H_{33}NC_5H_5Br$	–	4.91 ± 0.02	–	–
CPC[j]	0.79 ± 0.10	4.92 ± 0.07	4.13	+105
CPC, 0.4 M NaCl	1.32 ± 0.01	5.52 ± 0.02	4.20	+71
CPC + Tween 80 (1:4)	1.50 ± 0.05	6.87 ± 0.04	5.37	+26
CTAB, 0.01 M $C_7H_7SO_3Na$[d]	1.43 ± 0.04	5.67 ± 0.01	4.24	+64
CPC – 1-pentanol – benzene (ME)[k]	0.94 ± 0.02	5.28 ± 0.20[l]	4.34	+90

[a] The values for ethylfluorescein: $pK^w_{a0} = 2.94$, $pK^w_{a1} = 6.31$.

[b] Microemulsions are designed as "ME", volume fraction of the pseudophase $\varphi = 1.3$ %.

[c] SDS = n-$C_{12}H_{25}OSO_3Na$.

[d] Without NaCl.

[e] Molar ratio of organic components 1:7:4.

[f] $C_{16}E_{16}$ = n-$C_{16}H_{33}O(CH_2CH_2O)_{16}H$, etc.

[g] CDAPS = n-$C_{16}H_{33}N(CH_3)_2^+(CH_2)_3SO_3^-$.

[h] CTAB = n-$C_{16}H_{33}N(CH_3)_3Br$.

[i] The value for ethylfluorescein equals 6.59 ± 0.03.

[j] CPC = n-$C_{16}H_{33}NC_5H_5Cl$.

[k] Molar ratio of organic components 1:4:1.

[l] The value for ethylfluorescein equals 5.15 ± 0.18.

Assuming that the Ψ value is the same for the both ionization steps, this difference can be expressed in the following way:

$$\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a1}} - \mathrm{p}K^{\mathrm{ac}}_{\mathrm{a0}} = \mathrm{p}K^{\mathrm{i}}_{\mathrm{a1}} - \mathrm{p}K^{\mathrm{i}}_{\mathrm{a0}} = \mathrm{p}K^{\mathrm{w}}_{\mathrm{a1}} - \mathrm{p}K^{\mathrm{w}}_{\mathrm{a0}} + \log\{{}^{\mathrm{w}}\gamma^{\mathrm{m}}_{\mathrm{B^-}}\ {}^{\mathrm{w}}\gamma^{\mathrm{m}}_{\mathrm{H_2B^+}}\ ({}^{\mathrm{w}}\gamma^{\mathrm{m}}_{\mathrm{HB}})^{-2}\} \quad (17)$$

Here, the imperfection of the model manifests itself quite essentially. The scatter of the mentioned difference is substantial: from 3.49 to 5.37. Hence, at least one of the $K^{\mathrm{i}}_{\mathrm{a}}$ constants is varying along with variation of micellar type or, more probably, both of them. An additional reason may be the inequality of the electrostatic potentials in the regions of H_2B^+ and B^- location. However, even in nonionic systems (surfactants with oligomeric oxyethylene hydrophilic portion) the value of ($\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a1}} - \mathrm{p}K^{\mathrm{ac}}_{\mathrm{a0}}$) varies within 0.3 units.

But for all that, the substantial increase and decrease in $\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a}}$ values on going from water to anionic and cationic surfactant systems, respectively, was observed at low bulk ionic strength. Instead of experimentally unavailable $\mathrm{p}K^{\mathrm{w}}_{\mathrm{a}}$s of *n*-decylfluorescein, the corresponding values for its water-soluble analogs, 6-hydroxy-9-phenyl fluorone and ethylfluorescein (Chart 4, X = H and $COOC_2H_5$), can be used: $\mathrm{p}K^{\mathrm{w}}_{\mathrm{a1}} = 6.28–6.31$ and $\mathrm{p}K^{\mathrm{w}}_{\mathrm{a0}} = 2.94–3.10$ [1m,29j,67]. Using these values, we can see that in the case of nonionic micelles, $\Delta\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a1}}$ is positive, while $\Delta\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a0}}$ is negative. The increasing and U-shaped curves are typical for the acid–base couples with charge types HB^0/B^- and HB^+/B^0, respectively [1m,9,11c,12,17e,17f,28c–f]. It is also in line with the data for 6-hydroxy-9-phenyl fluorone in water–organic solvents (Fig. 1), though for strict comparison of $\Delta\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a}}$ in nonionic micelles with $\Delta\mathrm{p}K^{\mathrm{s}}_{\mathrm{a}}$, the extrathermodynamic ${}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{H^+}}$ values for the given water–organic mixtures must be known.

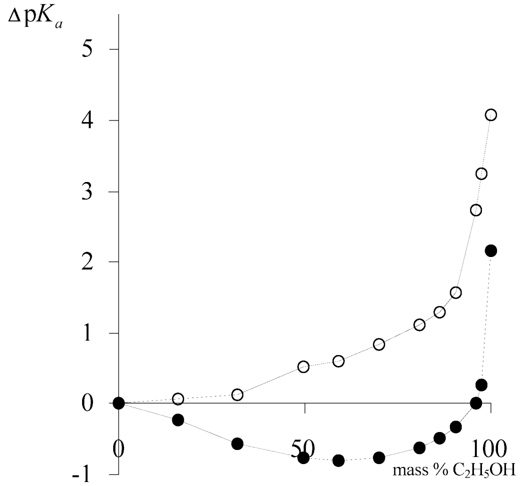


Fig. 1 The dependences of $\Delta\mathrm{p}K^{\mathrm{s}}_{\mathrm{a0}}$ (●) and $\Delta\mathrm{p}K^{\mathrm{s}}_{\mathrm{a1}}$ (○) of 6-hydroxy-9-phenylfluorone on the composition of water-ethanol mixture; 25 °C (data from ref. [67]).

Interestingly, the $\mathrm{p}K^{\mathrm{ac}}_{\mathrm{a}}$ values of of *n*-decylfluorescein in some cases markedly differ even from those of its homolog *n*-hexadecylfluorescein (X = COO-*n*-$C_{16}H_{33}$), determined in the same colloidal systems [68]. Meanwhile, the role of the hydrophobic tail length for an acid–base indicator once bound by the micelle, is as a rule not discussed [17f], though it can be of significance in photophysical studies [5a].

*On the whole, the data presented in Table 3 confirm the limited applicability of the elecrostatic model in its classical form.**

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*The last column of Table 3 will be discussed later.

Allied indicator systems, with a fluorescing dye (e.g., fluorescein) conjugated to a biomolecule, are often used in biochemical studies and related fields [23c,d,69]. The $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ alterations are usually ascribed to conformational or some other changes, or local electrical potentials. However, in case the whole difference between the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ and $\mathrm{p}K_\mathrm{a}^\mathrm{w}$ values is attributed to the $(-\Psi F/RT\ \ln 10)$ term, the contribution of the $\log({}^\mathrm{w}\gamma_\mathrm{B}^\mathrm{m}/{}^\mathrm{w}\gamma_\mathrm{HB}^\mathrm{m})$ item is underestimated.

It is appropriate to mention here another kindred branch of papers devoted to optical pH-responding sensors. Such dye-based devices are widely used for different purposes, from physiological research to monitoring of seawater [24]. As a rule, the colored and/or fluorescing indicator is covalently or noncovalently embedded in a polymeric or sol-gel matrix. The quantitative description is similar to the above equations, but in some cases an attempt is made to take into account the activity of water in the media surrounding the indicator. However, in expressions analogous to eq. 12, the term $\log {}^\mathrm{w}\gamma_{\mathrm{H}^+}^\mathrm{m}$ was not taken into account; this also refers to some other publications [17f,h].

Finally, water-insoluble long-tailed indicators have been developed, which can be used for determination of pH in an inaccessable aqueous phase, which is of significance for understanding biocatalysis in organic media [70]. Such systems are closer to common two-phase (extraction) systems and reversed (water-in-oil) microemulsions, which are beyond the shape of the present paper.

Now let us consider other models used for quantitative description of acid–base equilibria in micellar solutions of colloidal surfactants.

OTHER APPROACHES FOR DESCRIPTION OF MICELLAR EFFECTS

Though the surface of micelles formed by ionic surfactants is charged, the micellar effects can be described without using the Ψ values [26,28b,32a,71]. Some authors used only the equilibrium constants of partition between the aqueous and micellar phases, or of binding of the indicators or other reactants by the micelles, or of reactants' association with surfactants [32a,52a,72]. In general case, such binding (association) constants can be recalculated to the P_i constants (eq. 10) and thus (in the case of ionic surfactants) implicitly include the Ψ values. Similar approaches can be used for processing the micellar liquid chromatography data [3a,b,e–h].

The constants of HB^z and B^{z-1} binding by micelles (or droplets of microemulsions) can be obtained using the dependences of $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ on surfactant concentrations (or volume fraction of dispersed phase) [72a,b,73]; the corresponding equations will be considered somewhat later. However, this is impossible in the case of very hydrophobic, water-insoluble indicators, which are practically completely bound by micelles.

Alternatively, Berezin, Bunton, Romsted, and some other authors developed another model for equilibria in solutions of ionic surfactants. This model is based on the concept of pseudophase ion exchange, or PIE [1b,27e–h,34a,74]. Namely, it is supposed that the increase in $\mathrm{pH_w}$ leads to the decrease in H_m^+ concentration and to the increase in that of OH_m^- in the Stern layer, as a sequent of ion exchange. In the case of $\mathrm{pH_w}$ decrease, the result is opposite. The aforementioned β parameter of ionic micelles ($\beta = 1 - \alpha$) is assumed to be constant; more detailed consideration and perfection of the PIE model is available in literature [1c,d,f,61a,75].

The principal equations of PIE model are based on a special concentration scale [1b,c,k,27e–h,75]. Turning to the molar concentration scale, the relations between the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ and $\mathrm{p}K_\mathrm{a}^\mathrm{m}$ values can be rewritten for micelles of cationic [28a] and anionic surfactants, respectively, in the following manner:

$$\mathrm{p}K_\mathrm{a}^\mathrm{ac} = \mathrm{p}K_\mathrm{a}^\mathrm{m} + \log\{(K_{\mathrm{OH}^-}^{\mathrm{X}^-}\ K_\mathrm{W}^\mathrm{m})\ (\beta s K_\mathrm{W}^\mathrm{w})^{-1}\} + \log[\mathrm{X}_\mathrm{w}^-] \tag{18}$$

$$\mathrm{p}K_\mathrm{a}^\mathrm{ac} = \mathrm{p}K_\mathrm{a}^\mathrm{m} + \log(\beta s/K_{\mathrm{H}^+}^{\mathrm{M}^+}) - \log[\mathrm{M}_\mathrm{w}^+] \tag{19}$$

Here, $K_{\mathrm{OH}^-}^{\mathrm{X}^-}$ is a constant of OH^- ion exchange for X^- ions ($\mathrm{X}^- = \mathrm{Cl}^-$, Br^-, $\mathrm{NO_3}^-$, etc.) in the Stern layer of cationic surfactant micelle, $K_{\mathrm{H}^+}^{\mathrm{M}^+}$ is the constant of H^+ (hydronium) ion exchange for M^+ ions

($M^+ = Li^+$, Na^+, $N(CH_3)_4{}^+$, etc.) in the Stern layer of anionic surfactant micelle, $[X^-_w]$ and $[M^+_w]$ are equilibrium ionic concentrations in the bulk phase, K^w_W and K^m_W are ionic products of water in aqueous and interfacial phases, respectively, s is the surfactant concentration in the pseudophase and varies within the range of 3–7 M [27e,f,28a,i,73m].

In a vast series of publications, the PIE model is used for processing equilibrium and kinetic data. Even more so, the papers are of interest, where this model was confronted with the electrostatic one [1c,28a,61a,c].

In particular, the unification of electrostatic and PIE models leads to the following expressions for activity coefficients of proton (hydronium) transfer from water to micellar peusdophase of cationic and anionic surfactants, respectively:

$$ {}^{w}\gamma^{m}_{H^+} = \beta s K^{w}_{W} \{K^{X^-}_{OH^-}[X^-_w]K^{m}_{W}\}^{-1} \exp(-\Psi F/RT) \tag{20} $$

$$ {}^{w}\gamma^{m}_{H^+} = K^{M^+}_{H^+}[M^+_w](\beta s)^{-1} \exp(-\Psi F/RT) \tag{21} $$

Combining the Ψ values for SDS micelles in aqueous NaCl solutions, determined by Hartland, Grieser, and White by using 4-heptadecyl-7-hydroxycoumarin [29d], with the PIE parameters for (SDS + NaCl) system reported by Romsted and Zanette, we obtained the estimate $\log {}^{w}\gamma^{m}_{H^+} = -0.2 \pm 0.1$ for SDS system [29j]. Besides, the value of $-\log P_{0,OH^-} = \log {}^{w}\gamma^{m}_{OH^-} = 0.76$ was reported for CTAB micelles [28a]. The estimation of $\log {}^{w}\gamma^{m}_{H^+}$ values in micelles of cationic surfactants is hindered by uncertainty of the pK^m_W values. For example, Funasaki [28a] used the value of 15.65, which leads to $\log {}^{w}\gamma^{m}_{H^+} = 1.0 \pm 0.1$. On the contrary, Romsted [27e] supposed that $K^m_W \approx K^w_W$; in this case, eq. 20 gives the value $\log {}^{w}\gamma^{m}_{H^+} \approx -0.6$.

Before considering the peculiarities of the influence of different surfactant systems on the apparent ionization constants of indicators, some comments are to be made on possible ionic pairing within the Stern layer.

In general case, the coexistence of oppositely charged ions within the Stern layer is favorable for interionic interactions. Basing upon spectral data, the association between dye ions and oppositely charged surfactant head-groups is supposed by numerous researchers [28b,32a,71a,b,72a,b,73h]. In such terms, the protolytic reactions of the dye species in ionic micelles can be regarded as competition with ion association, e.g., $H\,B_m + surf^+_m \rightleftarrows (B^-\ surf^+)_m + H^+_w$. Then the apparent pK^a_a contains an additional contribution [29j], e.g.,

$$ pK^a_a = pK^a_a\ (\text{“true”}) - \log(1 + K_{ass}[surf^+_m]) \tag{22} $$

Here, K_{ass} is a constant of ion association in the pseudophase. The “true” apparent pK^a_a value describes the equilibria without ion association. On the other hand, there is good reason to believe that the possible association of the sulfonate or carboxylate groups of sulfonephthalein and fluorescein dyes with cationic surfactant head-groups cannot be regarded as a neutralization of their negative charge [28j]. In other words, even if such ion pairs exist, they can be regarded as rather solvent-separated than intimate ones.

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

On the whole, taking into account the peculiarities of the discussed systems, it is worthwhile just to include all these effects into ${}^{w}\gamma^{m}_{i}$.

PECULIARITIES OF VARIOUS LYOPHILIC NANOSIZED DISPERSIONS

Differentiating influence of lyophilic nanosized dispersions

The analysis of vast body of $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ data allows us to reveal the strong differentiating influence of micellar media.* The most ample evidence is essential non-uniformity of the $\Delta\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ values of different indicator dyes in the same media. Some of our data are given in Table 4 [1m,28g–l,29i–k,46m,48,73m,n,76]. In several cases, for example, for bromothymol blue in SDS micelles, the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ values were obtained by extrapolation, using the binding constants of equilibrium species [73m].

Table 4 The medium effects, $\Delta\mathrm{p}K_\mathrm{a}^\mathrm{ac} = \mathrm{p}K_\mathrm{a}^\mathrm{ac} - \mathrm{p}K_\mathrm{a}^\mathrm{w}$, of indicators in various ultramicroheterogeneous systems, 20–25 °C; bulk ionic strength 0.05 M, unless otherwise specified.[a]

Dye, acid–base couple	CDAPS	CPC	SDS	Nonionic[b]	Nonionic ME[b,c]	Liposomes	CTAC, 4 M KCl
Bromophenol blue, HB^-/B^{2-}	–0.40	–2.16	–	0.61	1.23	–	–0.34
Bromocresol green, HB^-/B^{2-}	–0.04	–1.68	–	1.03	1.72	–	0.23
Bromocresol purple, HB^-/B^{2-}	(0.22)[d]	–1.32	–	0.91	1.28	–	0.62
Bromothymol blue, HB^-/B^{2-}	0.90	–0.94	3.1	1.64	1.95	(1.6)	0.96
Phenol red, HB^-/B^{2-}	(0.54)	–0.92	–	0.7	0.8	–	0.71
ortho-Cresol red, HB^-/B^{2-}	–	–0.94	–	–	–	–	1.00
meta-Cresol purple, HB^-/B^{2-}	–	–0.70	–	–	–	–	1.02
Thymol blue, HB^-/B^{2-}	1.28	–0.37	–	1.07	1.8	–	1.27
n-Decyleosin, HB/B^-	–0.62	≈–1.9	2.63	0.71	–	–	–0.72
n-Decylfluorescein, HB/B^-	–0.24	–1.39	2.65	0.69	–	2.11	0.30
n-Decylfluorescein, H_2B^+/HB	–1.31	–2.15	2.23	–0.80	–	–	–0.81
Reichardt's betaine, $HB^+/B^\pm$	–0.6	–1.55	2.06	0.46	0.37	1.48	0.0
Rhodamine B, $HB^+/B^\pm$	0.36	–	2.10	1.0	–	–	–
DODR[e], $HB^+/B^\pm$	0.36	–0.76	1.97	0.97	–	–	0.70
Methyl yellow, HB^+/B	–1.45	–	1.56	–2.13	(–2.6)	–2.0[f]	–
Neutral red, HB^+/B	–0.68	–	≈2.3	≈–0.8	(–1.1)	0.65[f]	–
Hexamethoxy red, B^+/BOH	–0.5	–	2.14	–0.9	–1.0	–1.0[f]	–
Quinaldine red, HB^{2+}/B^+	0.62	–	0.56	–	–0.57	–0.06[f]	–
Pinacyanol, HB^{2+}/B^+	–	–	–1.60	–	–	–	–
Pseudoisocyanine, HB^{2+}/B^+	–	–	–1.20	–	–	–	–

[a] From refs. [1l,28g–l,29i–k,46m,48,73m,n]; as a rule, the dye:micelle ratio is less than unity.
[b] In some cases, the average values are given for nonionic systems.
[c] Microemulsions.
[d] These ($\Delta\mathrm{p}K_\mathrm{a}^\mathrm{a}$) values are close to $\Delta\mathrm{p}K_\mathrm{a}^\mathrm{ac}$.
[e] *N*,*N*'-di-*n*-octadecyl rhodamine.
[f] $I = 0.005$ M [48].

The second sign of differentiating influence is the essential inconstancy of variations in $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ on going from one lyophilic nanosized dispersion to another, as registered for different indicator dyes. For example, the transfer from CPC to SDS micelles at $I = 0.05$ M increases the $\mathrm{p}K_\mathrm{a2}^\mathrm{ac}$ value of bromothymol blue by 4.05 units, the $\mathrm{p}K_\mathrm{a1}^\mathrm{ac}$ of *n*-decyleosin – by 4.53, $\mathrm{p}K_\mathrm{a0}^\mathrm{ac}$ of Reichardt's dye and *N*,*N*'-di-*n*-octadecylrhodamine by 3.46 and 2.73, respectively. For methyl yellow and hexamethoxy red, on going from nonionic to SDS micelles, the $\mathrm{p}K_\mathrm{a0}^\mathrm{ac}$ values increase by 3.69 and 3.0 units, respectively. On going from cetyldimethylammonium propanesulfonate (CDAPS) micelles to micelles of nonionic surfactants, the

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*Here we discuss only the *true* differentiating influence, which is caused by the peculiarity of the pseudophase and not by selective binding of different dye species (see Introduction).

$\mathrm{p}K_{\mathrm{a2}}^{\mathrm{ac}}$ value of bromocresol green increases by 1.07, while the $\mathrm{p}K_{\mathrm{a0}}^{\mathrm{ac}}$ of *n*-decylfluorescein only by 0.37 units. The $\mathrm{p}K_{\mathrm{a1}}^{\mathrm{ac}}$ value of the latter indicator on going from SDS micelles to phospholipid liposomes decreases by 0.54 units, while the $\mathrm{p}K_{\mathrm{a0}}^{\mathrm{ac}}$ value of hexamethoxy red by 3.14, and so on.

The HMFF equation can be rearranged, utilizing for the ${}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{m}}$ values the same approach which was used for the ${}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}}$. Then, eq. 23 can be derived, similar to eq. 5

$$\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}} = \frac{e^2 N_{\mathrm{A}}}{4.605\,RT \ \times 4\pi \times 8.854 \times 10^{-12}} \times \left[\frac{z_{\mathrm{B}}^2}{r_{\mathrm{B}}} - \frac{z_{\mathrm{HB}}^2}{r_{\mathrm{HB}}} \right] \times \left[\frac{1}{\varepsilon_{\mathrm{m}}} - \frac{1}{\varepsilon_{\mathrm{w}}} \right] + \frac{\Delta G_{\mathrm{B}}^{\mathrm{solv}} - \Delta G_{\mathrm{HB}}^{\mathrm{solv}}}{2.302RT} - \frac{\Psi F}{2.302RT} \tag{23}$$

The differentiating influence of micellar pseudophase upon the acid–base properties of indicator couples of various charge types and nature, i.e., the disparity in their $\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{a}}$ values, *manifests itself distinctly, depending on the nature of the surfactant.* For instance, the miscellaneous character of the surface of ionic micelles likely causes their specific action. Indeed, the Stern region is a unique mixture of electrolyte, water, and hydrocarbon.

Cationic micelles

A rather extensive set of $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ values in micelles of cationic surfactants is available in the modern literature [1b,d,17d–f,h,25,27e,28a–j,l,29b,c,e,f,h,j,k,44a,46j,52,60a–d,64,71a,b,h,72a,b,73e–h,j,74g, 77,78]. However, the results often refer to surfactants with different hydrocarbon tail length, head-group, counterion, etc. Therefore, it is difficult to compare the data and to rationalize the influence of the above factors on the ionization of indicators.

We carried out a study of acid–base equilibria using cationic surfactants of alkylammonium and *N*-alkylpyridinium series with varying length of hydrocarbon chain, C_{11} to C_{18}, and 27 counterions [1m,46j,79]; the specificity of the last-named will be considered in the section “Salt effects”. As indicators, five sulfonephthaleins (Chart 5), the standard solvatochromic Reichardt’s dye, and *n*-decylfluorescein were used; the $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$s for these two substances have been already presented in Tables 1 and 3. Our results for sulfonephthaleins agree with the available numerical data reported by others [1d,77,80].

The strong differentiating influence of micellar pseudophase in respect to the strength of the indicator acids is practically independent of the hydrocarbon tail length, of the structure of the cationic head-group, counterion nature (Cl^-, Br^-, and $\mathrm{NO_3}^-$) and, in first approximation, of the bulk ionic strength.

The effect of the surfactant concentration on the $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ values within the micellar region at fixed ionic strength of the bulk (aqueous) phase is shown to be negligible. For example, at KBr concentration of 0.1 M, the $\mathrm{p}K_{\mathrm{a2}}^{\mathrm{ac}}$ values of bromophenol blue remain constant (3.16 ± 0.03) within the $n\text{-}\mathrm{C_{16}H_{33}N(CH_3)_3}$ Br concentration range from 1.0×10^{-4} to 0.005 M. This agrees with the data for thymol blue [28a].

The variation of the tail length of the surfactant at a given head-group and fixed ionic strength displays practically no effect on the $\mathrm{p}K_{\mathrm{a2}}^{\mathrm{ac}}$ value of a dye, bound by the micelles. However, this conclusion is reached principally by using the $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$s at medium ionic strengths, ca. (0.1–0.2) M Br^- or Cl^-. As the slopes $\{b = \mathrm{d}(\mathrm{p}K_{\mathrm{a}}^{\mathrm{a}})/\mathrm{d}\log[\mathrm{X}_{\mathrm{w}}^-]\}$ somewhat vary along with the variations of the tail length [17d], some deviations may occur both at very low and very high ionic strengths.

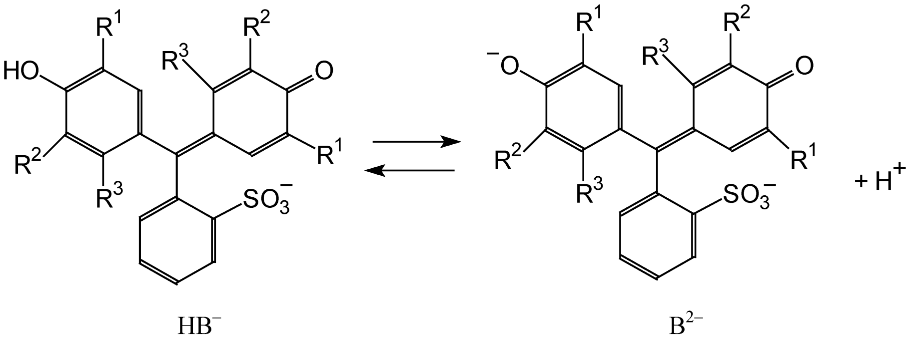

Chart 5 Acid–base equilibrium of sulfonephthalein dyes. Phenol red (phenolsulfonephthalein): $R^1 = R^2 = R^3 = H$; *ortho*-cresol red (3,3'-dimethylphenolsulphonephthalein): $R^1 = CH_3$, $R^2 = R^3 = H$; *meta*-cresol purple (2,2'-dimethylphenolsulphonephthalein): $R^1 = R^2 = H$, $R^3 = CH_3$; thymol blue (3,3'-di-*iso*-propyl-6,6'-dimethylphenolsulfonephthalein): $R^1 = CH(CH_3)_2$, $R^2 = H$, $R^3 = CH_3$; bromophenol blue: (3,3',5,5'-tetrabromophenolsulphonephthalein) $R^1 = R^2 = Br$, $R^3 = H$; bromocresol green (2,2'-dimethyl-3,3',5,5'-tetrabromophenolsulphonephthalein): $R^1 = R^2 = Br$, $R^3 = CH_3$); bromocresol purple (3,3'-dimethyl-5,5'-dibromophenolsulphonephthalein): $R^1 = Br$, $R^2 = CH_3$, $R^3 = H$; bromothymol blue (3,3'-di-*iso*-propyl-6,6'-dimethyl-5,5'-dibromophenolsulfonephthalein): $R^1 = CH(CH_3)_2$, $R^2 = Br$, $R^3 = CH_3$.

The surfactants with different cationic head-groups can be arranged in a sequence according to the pK_a^{ac} values of a given dye at fixed bulk ionic strength: $-NH_3^+ < -NC_5H_5^+ < -N(CH_3)_3^+ \approx -N(C_2H_5)_3^+$. This effect, being in line with the data for 4-heptadecyl-7-hydroxycoumarin [29g], can be explained by the decrease in surface charge density and hence in Ψ and/or in pK_a^i increase of the sulfonephthalein or coumarin dye due to hydrophobization of micelle/water interface.

The most powerful tool for the variation of the pK_a^{ac} value of an indicator in cationic micelles is the total bulk concentration and the nature of the anion; such effects will be considered in a separate section. However, even the variation of the co-ion nature displays some influence on the equilibria state. So, the replacement of Na^+ ions (0.1–0.5 M) by $N(C_2H_5)_4^+$ markedly (by 0.3–0.2 units) decreases the pK_{a2}^{ac} values of bromophenol blue, the effect being probably connected with the character of micellar surface hydration.

The differentiating influence of cationic micelles is similar to that of mixtures of water with non-HBD solvents, such as acetone, CH_3CN, DMSO [1m,28g–j,29j,76b,79,81]. In particular, eight sulfonephthaleins (Table 4) are arranged in the same sequence according to their ΔpK_{a2}^{ac} values in cetylpyridinium chloride and other cationic micelles and to their ΔpK_{a2}^{s} in acetonitrile, water–acetone, and water–DMSO mixtures [1m,28g,h,29j]. The similarity of cationic micellar interfaces and mixtures of water with non-HBD solvents follows also from the analysis of π^* values and other Kamlet–Taft parameters [18b].

The above effects manifest themselves against the background of pK_a^{ac} decrease. However, the differentiating influence of CTA^+-based micelles can be demonstrated even at such high bulk counterion concentrations, where the ΔpK_a^{ac} values are often positive. So, for a set of pK_a^{ac}s referring to hydroxy groups (sulfonephthaleins, hydroxyxanthenes, etc.) the slope of the below correlation is higher than unity [1m,28j,29j]:

$$pK_a^{ac}\,(4.00\text{ M Cl}^-) = -1.36 + 1.26\,pK_a^{w} \qquad (24)$$

$$n = 17,\ r = 0.993$$

The differentiating influence under such conditions corresponds to that of (1:1) water–acetone mixture (Fig. 2) [1m,29j].

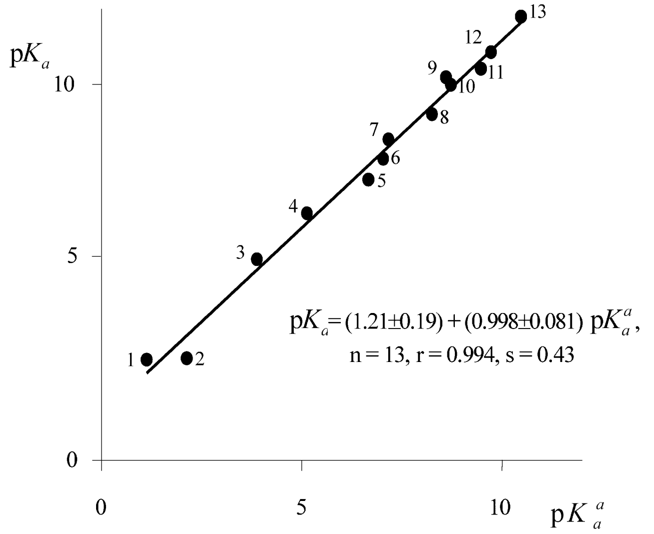

Fig. 2 The dependence of p$K^{\mathrm{s}}_{\mathrm{a}}$ in 52 mass % $(CH_3)_2CO$ vs. p$K^{\mathrm{a}}_{\mathrm{a}}$ in cetyltrimethylammonium chloride micelles, 4.0 M Cl^-: p$K^{\mathrm{a}}_{\mathrm{a1}}$ of ethyl eosin (1), p$K^{\mathrm{a}}_{\mathrm{a0}}$ of 6-hydroxy-9-phenyl fluorone (2), p$K^{\mathrm{a}}_{\mathrm{a2}}$ of bromophenol blue and bromocresol green (3, 4), p$K^{\mathrm{a}}_{\mathrm{a1}}$ of 6-hydroxy-9-phenyl fluorone (5), p$K^{\mathrm{a}}_{\mathrm{a2}}$ of bromocresol purple, fluorescein, and bromothymol blue (6–8), p$K^{\mathrm{a}}_{\mathrm{a0}}$ of Reichardt's betaine (9), p$K^{\mathrm{a}}_{\mathrm{a2}}$ of phenol red, *o*-cresol red, *m*-cresol purple, and thymol blue (10–13) [29j].

The Δp$K^{\mathrm{ac}}_{\mathrm{a}}$ values corresponding to COOH groups are as a rule higher as compared with those of phenolic ones [17f,28g,h,j,29k,52,60c,78,82]; as an exception, see the value for thymol blue in CPC solutions, Table 4. High bulk ionic strength induces "drying" of the micellar surface and other kind of pseudophase modification, which make the micellar effects even more similar to effects of organic solvents [28j].

On going from water to pure organic solvents and water–organic mixtures, the Δp$K^{\mathrm{s}}_{\mathrm{a}}$ values for anionic acids are higher than for neutral ones, in the case of dianionic acids they are even more, etc. This follows from eq. 5. The same uptrend is typical for the Δp$K^{\mathrm{ac}}_{\mathrm{a}}$ s for indicator couples of different charge types in cationic micelles (eq. 23). As a result, for such complicated indicators as bromopyrogallole red, chromazurole, eriochrome black, gallein, and other trihydroxyfluorones, the p$K^{\mathrm{ac}}_{\mathrm{a}}$ values corresponding to the formation of polycharged anions (z = –2, –3, etc.) are higher than p$K^{\mathrm{w}}_{\mathrm{a}}$s even in cationic micelles at low bulk ionic strength [82], *despite the Hartley rules* [17a,31]. Hence, the increase in p$K^{\mathrm{i}}_{\mathrm{a}}$ overcomes the item $-\Psi F/RT \ln 10$.

Finally, the shift of the state of tautomeric equilibria of conjugated species can also contribute to the Δp$K^{\mathrm{ac}}_{\mathrm{a}}$ values. For example, it takes place for hydroxyxanthenes in micellar solutions [28g,h,j,83], analogous to the changes observed on going from water to true organic solvents [1m,7,84].

Anionic micelles

Judging from the $E^{\mathrm{N}}_{\mathrm{T}}$ values (Table 1; [18b–d,44a,46]), micelles of SDS and other anionic surfactants are more hydrated and their Stern layers are less polar as compared with cationic ones. In the case of 4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Chart 3, $R^1 = R^2 = C_6H_5$, R^3 = H), the orientation of the dye in anionic and cationic micelles is likely of opposite character [46a,b]. The shift of tautomeric equilibrium of both lipoid fluorescein and rose bengal B molecules toward the colorless lactone is less expressed in SDS micelles than in cationic and nonionic ones [29e,81], the fluorescence lifetime of rose bengal B, depending on microviscosity, is in CTAB micelles ca. twice that of SDS micelles [22].

While the affinity of the surface of cationic micelles to OH^- anion is much higher than Cl^- [27e,28a,i,61c], the constant of Na^+/H^+ exchange on SDS micelles is close to unity [27a–d,f,29i]. Some other probes also give evidence for a more hydrated surface in the case of SDS micelles [18b,19c,d].

Despite the well-hydrated state of SDS micellar interface, the latter displays powerful differentiating influence on ionization of embedded indicators. The variations in ΔpK_a^{ac} on going from one indicator to another reach 4.7 units (Table 4). At that, the medium effects for different types of indicators are as a rule increasing in the sequence: $(HB^-/B^{2-}) > (HB^0/B^-) > (HB^+/B^0)$. This is typical for ΔpK_a^s s on going from water to water–organic mixtures [9,10a,11c,d,12,16a,28c–f,86]. Moreover, a *contradiction with Hartley's rules* is registered, namely, some $\Delta pK_{a(-1)}^{ac}$ values are even negative (Table 4). In other words, deprotonation of dications is revealed.

$$HB^{2+} \rightleftarrows B^+ + H^+ \tag{25}$$

The shift of the equilibrium 25 toward the right on going from water both to SDS micellar solutions and water–organic mixtures was observed for rhodamines B, 6G, 19, and 110, for pyronine B, methylene blue, phenosafranine, neutral red, acridine orange, pseudoisocyanine, pinacyanole, astraphloxine, and indotricarbocyanine at HCl concentrations of 0.1–1.0 M [1m]. Under such conditions, the SDS micelles become actually HDS ones; the dyes stay in the pseudophase, judging from vis spectra.

This effect is hardly being explained in terms of ion pair formation, because DS^- associates with HB^{2+} cations would be more stable than those with B^+. It is more probable that the contribution of the first item in the right side of eq. 23 overcomes that of the last quantity.

This effect can be used for protection of rhodamine fluorophore from protonation in acidic media, etc.

Experiments made in this laboratory [1m,29j] demonstrate that the impact of micelles of different anionic surfactants on the state of acid–base equilibria is similar to those of SDS. The reported monotonic influence of the hydrocarbon tail length of alkylsulfates [27a–d,29a] was not confirmed by indicators studied by us, including triarylcarbinols.

The pK_a^{ac} values given in Tables 1 and 3, together with the data for rose bengal B [81] demonstrate that micelles of oxyethylated anionic surfactants exert an influence intermediate between those of SDS and nonionic surfactants.

Nonionic micelles

The influence of nonionic micelles with polyoxyethylene hydrophilic portion resembles that of water–organic mixtures. As a rule, the strength of carboxylic functions decreases more obvious as compared with hydroxylic groups; the ΔpK_a^{ac} values are positive for neutral and anionic acids and distinctly negative for cationic ones [17e,f,25,28c–f,l,29c,f,j,32b,44a,c,52a,60c,72c–e,73a,l,87].

Here, the depth of penetration of indicator species into the voluminous oxyethylene mantle (Chart 2B) is of significance [17e,76a,88]. For sulfonephthalein and xanthene dyes, the medium effects, ΔpK_a^{ac}, in nonionic micelles and microemulsions rise along with an increase in their hydrophobicity; the measure of the latter is the total molecular volume or the equilibrium constants of extraction of anion associates with $As(C_6H_5)_4^+$ cation from water to trichloromethane [1m]. Interestingly, the pK_a^{ac} values of a series of bioactive diarylamines in micellar solutions of a surfactant n-$C_{12}H_{25}O(C_2H_4O)_8H$ correlate with pK_a^s s in aqueous ethanol only if the steric parameters of substituents are taken into account [72c–e]. Bulky substituents provide more "nonaqueous" microenvironment in the hydrophilic oxyethylene portion of nonionic micelles.

Additions of indifferent salts such as NaCl display relatively small influence on the pK_a^{ac} values in nonionic surfactant solutions, contrary to the case of ionic micelles (see below).

Despite the similarity of surfactant molecules, the pK_a^{ac} values of a fixed indicator in different nonionic systems systems as a rule do not coincide [1m,29j]; see also Table 3. For example, the pK_{a2}^{ac} values of bromothymol blue in micellar solutions of 16 nonionic surfactants, including block-copolymers of ethylene oxide and propylene oxide, determined at $c_{surf} = 0.005$ M, $I = 0.05$ M (NaCl) and 25 °C with accuracy ±0.03, varied from 8.96 to 9.41 [1m,76]. Though these values differ markedly from that in water under the same conditions (7.21), such spread of pK_{a2}^{ac} values in different nonionic surfactant solutions must be taken into account by using one of such micellar systems as a reference media with $\Psi = 0$. It must be noted that the commercial samples of nonionic surfactants are as a rule mixtures of molecules with different oxyethylation degree. Finally, a rise in surfactant concentration in the region $c_{surf} >>$ cmc can also influence the pK_a^{ac} values, which reflects the structural transitions of micelles. Therefore, the data compiled in Table 4 for nonionic micelles demonstrates only the most general features of these colloidal systems.

Zwitterionic and some other surfactants

Until recently, the information on pK_a^a and pK_a^{ac} values in zwitterionic surfactant micelles was desultory. The data obtained with 15 indicator dyes in CDAPS solutions [1m,29j,89] reveal the strong differentiating influence of such kinds of micelles (Table 4). This influence differs sharply from that of nonionic surfactants. But at the same time, the sequence of indicators according to their ΔpK_a^{ac} values in CDAPS micelles is similar to that in cationic surfactant ones. Zwitterionic micelles possess a lot of interesting properties [90]; for example, they allow realization of a kind of micellar-enzymatic catalysis, namely, the cholinesterase hydrolysis of fluorogeneous substrates [91]. Alkyl dimethylamine oxide surfactants are also very interesting and promising. Naturally, their behavior is pH-dependent [58,60a,65b,92]. A new class of ionic surfactants, the so-called gemini surfactants, was intensively studied in recent decades [93]. The well-known substance ethonium [1d] can be also regarded as such a gemini cationic surfactant; the behavior of eosin dyes in micellar solutions of ethonium (in form of dichloride) strongly resembles that in solutions of CTAB or CPC [94].

DETERMINATION OF INTERFACIAL ELECTROSTATIC POTENTIALS USING ACID–BASE INDICATORS: RESULTS AND LIMITATIONS

At present, several approaches, more or less approximate, have been developed for Ψ determination starting from the experimental pK_a^{ac} value in the ionic micelle under study; they are discussed below. As a rule, they are based on eq. 16 and differ in methods of pK_a^i estimation for ionic micelles. Usually, the pK_a^{ac} values are determined using molecular spectroscopy; some other techniques have also been reported [61b].

1. For the indicator chosen, pK_a^i in ionic micelles can be equated to pK_a^{ac} in the same micelles, but with extremely high (4–6 M) salt background [28i,j,29j,44a,76b]. However, even screening of the interfacial charge with 4 M of indifferent electrolyte can be still incomplete [28c–f,29c,j]. Moreover, the solutions with extremely high salt concentration, i.e., 6 M NaBr, became very viscous [44a]; on the other hand, some surfactants (SDS, CPC) can be salted out from aqueous media.
2. The pK_a^i value in ionic micelles can be equated to pK_a^w [17e]; the approach can be modified by utilizing two indicators, for example, lipoid coumarins with acid–base couples HB^+/B^0 and HB^0/B^- [17f,29a]. However, in general, the ${}^w\gamma_i^m$-containing item in eq. 15 can significantly differ from zero [1m,29j].
3. 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 corresponding pK_a^s and ${}^w\gamma_{H^+}^s$ values of the indicator in a water–organic mixture [17e,f,28a,c–f,44a,60e,d]. The choice of the latter is usually made using a spectroscopic molecu-

lar probe, which indicates the same polarity as registered in micellar pseudophase. However, the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ estimation by using water–organic mixtures for mimicking micellar interfacial regions has also some disadvantages. For instance, we have demonstrated [1m,29j], that the satisfactory fitting of the model, reported by several research groups, is reached by using the old-fashioned ${}^\mathrm{w}\gamma_{\mathrm{H}^+}^\mathrm{s}$ values, while the use of the log ${}^\mathrm{w}\gamma_{\mathrm{H}^+}^\mathrm{s}$ values, obtained by means of the most recognized tetraphenylborate assumption [95], leads to essentially different $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ values. The Ψ values can differ up to ca. 100 mV, depending on the chosen log ${}^\mathrm{w}\gamma_{\mathrm{H}^+}^\mathrm{s}$ values [29j]. In addition, even if we know the pseudophase polarity or dielectric constant, it must be taken into account that the $\mathrm{p}K_\mathrm{a}^\mathrm{s}$ 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 of its properties with any water–organic mixture.*

4. Probably, the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value in ionic micelles is most often equated to $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ of the given indicator in nonionic micelles with oxyethylene hydrophilic portion [17e,f,h,28a,l,29c,d,i,60e]. However, it must be pointed out that the $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ values of the given indicator dye in different nonionic micelles never coincide exactly [29j] (see the previous section). From this viewpoint, the data given in Tables 1 and 3 are rather typical. Moreover, 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 demonstrated that the Ψ values determined in such a way can differ up to ≈200 mV [1m,28l,29j]. This conclusion can also be reached from the data given in Table 4. Probably, the interfacial regions of ionic and nonionic micelles are quite dissimilar (Chart 2).

   If cationic indicator dyes ($\mathrm{HB}^+/\mathrm{B}^0$) are used, than the Ψ values of SDS micelles thus obtained are unlikely low [28c–f,l]; the coincidence of the results obtained using indicator couples of ($\mathrm{HB}^+/\mathrm{B}^0$) and ($\mathrm{HB}^0/\mathrm{B}^-$) type [17f] is rather an exception to this rule. Sometimes the Ψ values of ca. –240 mV can be obtained, which is even more negative than the calculated value for the "bare" micelle without counterions in the Stern layer (Table 2). This effect was explained by ion pairing between DS^- and dye cation [17h,28c–f,29c,d,44a].

   Another explanation is based on (expected) strong difference between $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ in SDS micelles and $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ in nonionic ones for the charge type of acid–base couple $\mathrm{HB}^+/\mathrm{B}^0$ [28l,29i,j,48,66]. And really, the micelle/water interface of anionic micelles is hydrated to a much higher degree than those of nonionic and cationic ones (see Table 1, the corresponding text, and the subsection "Anionic micelles"). Therefore, the decrease in $\mathrm{p}K_\mathrm{a}$, typical for cationic acids on going from water to water–organic mixtures [12] (as example, see Fig. 1), must be less expressed just in SDS dispersions.

   In any case, application of indicators of ($\mathrm{HB}^0/\mathrm{B}^-$) type, such as 4-heptadecyl-7-hydroxycoumarin [29d], *n*-decyleosin [29i], or *n*-decylfluorescein ($\mathrm{p}K_\mathrm{a1}^\mathrm{ac}$ values, Table 3) allows us to obtain more reliable Ψ values for SDS micelles.

5. Equating the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ value of myristic acid in ionic micelles to the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ value in sugar-derived nonionic surfactants was proposed recently [78b]; in this case, potentiometric titration was used. It must be noted that some results with acid–base indicators in such surfactant systems have been already published earlier [96], and the possibility of specific interactions between the carboxylic group and hydrophilic alkylglucoside portion of the surfactant was supposed [29b].

6. The $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ in ionic micelles can be equated to $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ of the given indicator in micelles of zwitterionic surfactant, e.g., CDAPS, $n\text{-}\mathrm{C}_{16}\mathrm{H}_{33}\mathrm{N(CH_3)_2}^+\mathrm{(CH_2)_3SO_3}^-$ [1m,29j]. The palisade of zwitterionic micelles seems to be a more adequate model of the Stern layer of ionic ones. For instance, the application of CDAPS as a standard media for $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ 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 CPC at bulk Cl^- concentration of 0.053 M Cl^- [1m,29j], while using the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$s of these dyes in nonionic micelles as $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ in cationic ones, the Ψ values vary from +113 to +179 mV. However, such application of CDAPS appeared to be less favorable just for more hydrophobic indicators, such as *n*-decylfluorescein and Reichardt's dye [29j].

7. A method, based on utilization of a hydrophobic bifunctional indicator, is developed [1m,29j]. For this purpose, we propose *n*-decylfluorescein, considered above. We have already seen that the difference ($\mathrm{p}K_{\mathrm{a1}}^{\mathrm{ac}} - \mathrm{p}K_{\mathrm{a0}}^{\mathrm{ac}}$) in the organized solutions studied varies within two logarithmic units. Another combination of the two constants is as follows:

$$\Delta \mathrm{p}K_{\mathrm{a1}}^{\mathrm{ac}} + \Delta \mathrm{p}K_{\mathrm{a0}}^{\mathrm{ac}} = \log {}^{\mathrm{w}}\gamma_{\mathrm{B^-}}^{\mathrm{m}} - \log {}^{\mathrm{w}}\gamma_{\mathrm{H_2B^+}}^{\mathrm{m}} - 0.8686\ \Psi\ F/RT \qquad (26)$$

The negative and positive charge is strongly delocalized within the xanthene moiety of the anion and cation, respectively. If we assume that in a given micellar system ${}^{\mathrm{w}}\gamma_{\mathrm{B^-}}^{\mathrm{m}} = {}^{\mathrm{w}}\gamma_{\mathrm{H_2B^+}}^{\mathrm{m}}$, analogous to the tetraphenylborate–tetraphenylarsonium hypothesis [95], then the Ψ value can be easily calculated (see the last column in Table 3; the $\mathrm{p}K_{\mathrm{a1}}^{\mathrm{w}}$ and $\mathrm{p}K_{\mathrm{a0}}^{\mathrm{w}}$ values are equated to the corresponding values of ethylfluorescein, Chart 4, X = $\mathrm{COOC_2H_5}$). Indeed, thus-estimated Ψ values for nonionic micelles are close to zero. In fact, this is a modification of the method proposed by Fernandez and Fromherz, who utilized the $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ values of two different dyes, namely, 4-heptadecyl-4-dimethylaminocoumarin and 4-undecyl-7-hydroxycoumarin [17f].

However, the combination of data presented in Fig. 1 for the chainless analog of *n*-decylfluorescein with the ${}^{\mathrm{w}}\gamma_{\mathrm{H^+}}^{\mathrm{s}}$ values based on $\mathrm{B(C_6H_5)_4^-}$ assumption [95] demonstrates that the difference ($\log {}^{\mathrm{w}}\gamma_{\mathrm{B^-}}^{\mathrm{s}} - \log {}^{\mathrm{w}}\gamma_{\mathrm{H_2B^+}}^{\mathrm{s}}$) is substantially positive, somewhat higher than unity at 30 to 60 mass % of ethanol [1m,29j]. This indicates a stronger hydration of the anion (hydrogen bonds) as compared with the cation. If the same is valid for ionic micelles, then the true Ψ values must be up to ≈40 mV less negative for anionic surfactant micelles and more positive for cationic ones.

8. Recently, a rhodamine dye *N*,*N*′-di-*n*-octadecylrhodamine was proposed for monitoring interfacial electrostatic potentials [1m,29k,97]. The existence of two long hydrocarbon chains allows expecting similar orientation of its cation and zwitterion on the surface of any ionic micelle, with the dissociating group ($\mathrm{COOH} \rightarrow \mathrm{COO^-}$) directed toward the aqueous phase, as shown in Chart 6.

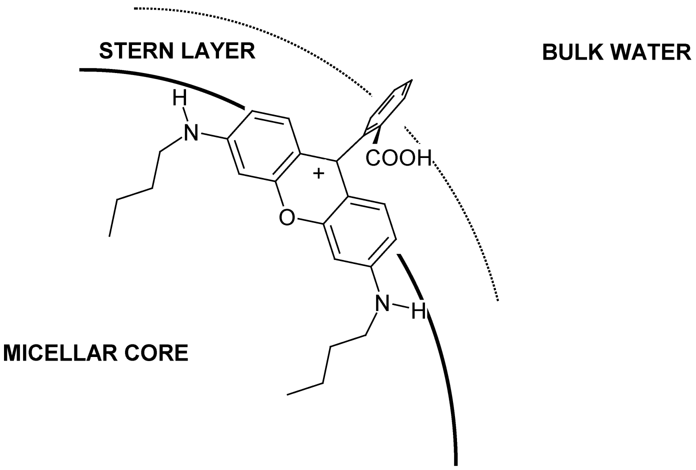

Chart 6 Presumable arrangement of *N*,*N*′-dioctadecylrhodamine in the Stern region gegion of an ionic micelle (This has been reproduced from ref. [97] with permission of the author).

The $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ values in micelles, droplets of microemulsions, and in Langmuir–Blodgett films soaked into aqueous media are compiled in Table 5. Both absorption and fluorescence of the dye can be used for monitoring interfacial properties. The Ψ values were calculated using the average value of $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ in nonionic micelles, 4.21, as $\mathrm{p}K_{\mathrm{a}}^{\mathrm{i}}$ in ionic ones.

Table 5 The pK_a^{ac} values of HR$^+$ cation of *N,N'*-di-*n*-octadecylrhodamine in various micellar systems; c_{surf} = 0.01 M and 25 °C, unless otherwise specified.[a,b]

Micellar system[c]	Salt background, M[d]	pK_a^{ac}	ΔpK_a^{ac}	59.16 (4.21 – pK_a^{ac})/mV
n-$C_{16}H_{33}OSO_3Na$, 50 °C	0.05	5.48 ± 0.06	2.24	–75[e]
SDS[f], 0.05 M	0.005[g]	5.52 ± 0.07	2.28	–77
SDS	0.05	5.21 ± 0.09	1.97	–59
SDS, 0.10 M	0.05[h]	5.06 ± 0.06	1.82	–50
SDS	0.20	4.68 ± 0.01	1.44	–28
SDS	0.30	4.46 ± 0.06	1.22	–15
SDS	0.40	4.41 ± 0.05	1.17	–12
SDS, 0.001 M + 0.01 M N(*n*-$C_4H_9)_4^+$	0.011[g]	5.16 ± 0.05	1.92	–56
SDS, 0.02 M + 0.05 M N(*n*-$C_4H_9)_4^+$	0.05[g]	5.27 ± 0.05	2.03	–63
SDS – 1-pentanol – benzene (ME)[i]	0.05	5.00 ± 0.02	1.76	–47
n-$C_{12}H_{25}(OC_2H_4)_3OSO_3Na$	0.05	5.22 ± 0.03	1.98	–60
SDS (0.01 M) + Tween 80 (0.01 M)	0.05	5.35 ± 0.02	2.11	–67
Tween 80	0.05	4.32 ± 0.02	1.08	–
Triton X 100	0.05	4.25 ± 0.02	1.01	–
Brij 35	0.05	4.12 ± 0.02	0.88	–
n-$C_{12}H_{25}(OC_2H_4)_{12}OH$	0.05	4.15 ± 0.02	0.91	–
n-$C_{16}H_{33}N^+(CH_3)_2(CH_2)_3\ SO_3^-$, 0.001 M	0.05	3.60 ± 0.09	0.36	+36
CTAB[j], 0.05 M	0.005[k]	2.24 ± 0.02	–1.00	+116
CTAB	0.05	2.50 ± 0.08	–0.74	+101
CTAB	0.05[k]	2.53 ± 0.04	–0.71	+99
CTAB	0.40[k]	3.32 ± 0.01	0.08	+53
CTAB	4.00[l]	3.94 ± 0.09	0.70	+16
n-$C_{18}H_{37}N(CH_3)_3Cl$, 30 °C	0.05	2.14 ± 0.07	–1.1	+122[e]
n-$C_{18}H_{37}\ NC_5H_5Cl$, 0.003 M, 30 °C	0.05	2.40 ± 0.02	–0.84	+108[e]
CPC [m]	0.05	2.48 ± 0.14	–0.76	+102
CPC	0.40	3.06 ± 0.02	–0.18	+68
CPC – 1-pentanol – benzene (ME)[n]	0.05	2.53 ± 0.07	–0.71	+99
n-$C_{18}H_{37}\ NC_5H_5Br$ film[o]	0.003–0.03[p]	2.4 ± 0.2	–0.8	+107[e]

[a] From refs. [29k,97].
[b] pK_a^w = 3.24, an average value for water-soluble rhodamines.
[c] Microemulsions are designed as "ME", φ = 1.0 %.
[d] Created by addition of NaCl to acetate buffers or HCl solutions, unless otherwise specified.
[e] Conventional values, calculated assuming that the pK_a^{ac} value at 20 °C is the same.
[f] SDS = *n*-$C_{12}H_{25}OSO_3Na$.
[g] Acetate buffer mixtures, without NaCl.
[h] Taking into account the dissociation of micellized SDS, [Na_w^+] = 0.077 M.
[i] Molar ratio of organic components 1:7:4.
[j] CTAB = *n*-$C_{16}H_{33}N(CH_3)_3Br$.
[k] HBr + KBr.
[l] KCl.
[m] CPC = *n*-$C_{16}H_{33}NC_5H_5Cl$.
[n] Molar ratio of organic components 1:4:1.
[o] Langmuir–Blodgett film, 80 monolayers, molar fraction of the dye 5.6 %, 20 °C.
[p] HCl solutions.

The charge type of the acid–base couple is HB$^+$/B$^\pm$. In nonionic micelles ΔpK_a^{ac} ≈ 1.0, close to that for hydrophobic coumarins with charge type HB^0/B$^-$ [17f,29c], while indicators with charge type HB$^+$/B^0 demonstrate a sharp decrease in pK_a^{ac}, up to ΔpK_a^{ac} = –2.1 for methyl yellow [28l]. 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 nonionic 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 (eq. 22) or with Na$^+$ ions of SDS, the true Ψ values must be less positive in cationic micelles and more negative in anionic ones.

The value Ψ = +37 mV calculated using the pK_a^{ac} value of 3.60 in CDAPS micelles may reflect the local electrical potential near the phenylcarboxylic moiety of the dye in zwitterionic micelles. Interestingly, Drummond and Grieser [29c] 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.

Concluding this section, we can state that *the differentiating inluence 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, nonionic (with oxyethylene chains), and zwitterionic surfactants.

Recently, some new approaches were made, based on determination of pK_a^a of lauric acid [78a] and a set of salicylic acid derivatives [58g].

SALT EFFECTS IN IONIC MICELLES: SCREENING OF THE INTERFACIAL CHARGE AND MICELLAR TRANSITIONS

Normal salt effects: Ion exchange and screening of the surface charge

The introduction of salts (supporting electrolytes, following the biophysical terminology) into aqueous solutions of cationic surfactants as a rule results in pK_a^{ac} increase of indicators. In the case of anionic surfactants, the effects are of opposite sign. If the difference between the pK_a^{ac} and pK_a^w values is ascribed to association of ionic dye species with oppositely charged surfactant head-groups, the aforementioned salt effects can be considered in terms of decomposition of such associates by electrolytes added [28b,71b,72a,b,98]. Using the PIE model, the salt effects are described by eqs. 18 and 19. Our data for methyl orange and sulfonephthalein dyes demonstrate that the pK_a^m values in cationic micelles calculated at $[\mathrm{Br}_w^-]$ up to 1.0 M stay constant with accuracy within ±(0.03–0.07) units [28i]. In the case of hydroxyxanthenes, the constancy is somewhat poorer [28g]. Probably, the micellar "sphere-to-rod" transitions, which take place on addition of inorganic salts, do not lead to essential changes in microenvironments of the dyes.

Finally, in terms of electrostatic theory, the salt effects can be explained by surface charge screening and thus by decrease in $|\Psi|$ (eq. 15). Both our data and numerous publications of others demonstrate, that the dependences of pK_a^{ac} vs. logarithm of counterion activity or concentration can be successfully fitted by eqs. 27 and 28 for cationic and anionic micelles, respectively [1m]:

$$\mathrm{p}K_a^{ac} = B + b\log[\mathrm{X}_w^-] = B' + b'\log a_{\mathrm{X}_w^-} \tag{27}$$

$$\mathrm{p}K_a^{ac} = B - b\log[\mathrm{M}_w^+] = B' - b'\log a_{\mathrm{M}_w^+} \tag{28}$$

As a rule, the plots are linear (with $r \approx 0.99$) up to salt concentrations of several moles per dm^3. Such dependences can be considered as *general*, or *normal salt effects*. A representative picture is given in Fig. 3.

The utilization of ionic activities is sometimes hindered by the lack of information on activity coefficients. Equations 27 and 28 can be utilized for recalculation of the pK_a^{ac} values from one salt concentration to another. The "micelle + indicator" complex can be considered as a nanodevice with response to counterion bulk concentration [99].

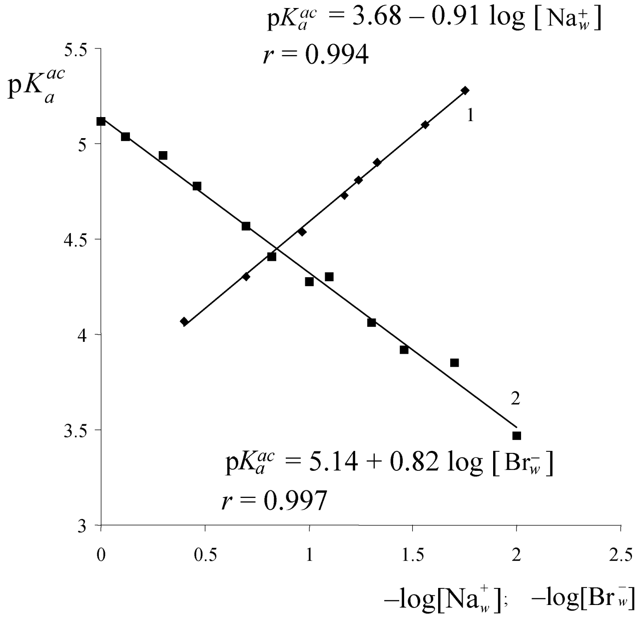

Fig. 3 The dependences of methyl yellow pK_{a0}^{ac} in SDS micelles (1) and bromocresol green pK_{a2}^{ac} in CTAB micelles (2) on logarithm of Na^+ and Br^- bulk concentrations, respectively [1m].

Such equations can be derived in various ways. For instance, proceeding from the quasichemical model of CTAB micelles formation [8,100] (eq. 29)

$$_{\nu+}\,CTA^+ + {}_{\nu-}Br^- \rightleftarrows (CTA^+{}_{\nu+}Br^-{}_{\nu-})^{\nu+ - \nu-},\ K_M \tag{29}$$

and using the mass action law, the Nernst equation and eq. 15, we obtained the following expression for pK_a^{ac} as a function of counterions activity, $a_{Br_w^-}$ [28i]:

$$pK_a^{ac} = pK_a^{i} - \Psi_0 F/(2.302RT) - (1/\nu_+)\log\frac{a_M}{K_M} + (\nu_-/\nu_+)\log a_{Br_w^-} \tag{30}$$

Here, Ψ_0 is Ψ at $a_{CTA_w^+} = 1$, a_M is activity of micelles; $\nu_-/\nu_+ = \beta$. However, it must be noted that the slopes of eqs. 27 and 28 in a fixed colloidal system are somewhat different as obtained with different indicators. For example, in CTAB + KBr system, utilization of a set of sulfonephthalein dyes at $0.005 \le [Br_w^-] \le 1.0$ M and 20 °C resulted in b values from 0.77 to 0.88 and b' values from 0.83 to 0.96 [28i]. A set of indicators studied in SDS micelles, at $[Na_w^+]$ up to 0.4–1.0 M and 25 °C, gave the following b values [28k,l,29i,k,101]: 0.73 ± 0.04 (decyleosin, HB^0/B^-), 0.84 ± 0.04 (hexamethoxy red, B^+/BOH^0), 0.91 ± 0.03 (methyl yellow, HB^+/B^0), 0.92 ± 0.07 (quinaldine red, HB^{2+}/B^+), 0.83 ± 0.09 (rhodamine B, $HB^+/B^\pm$), 0.89 ± 0.05 (*N*,*N'*-di-*n*-octadecyl rhodamine, $HB^+/B^\pm$). Processing the data for the lipoid hydroxycoumarin published by Hartland et al. [29d] gives the value 0.77 ± 0.05.

The β value of SDS micelles as determined with DS^--selective electrode by Loginova et al. [29i,102] is equal to 0.74 ± 0.04. Some examples of detailed consideration of ionic equilibria in micellar solutions are available in the literature [103]. In these publications, the approaches to β estimation are refined, as well as methods of calculation of true ionic strength of the bulk, etc.

In a particular case of carboxylic group ionization of eosin dyes, the b value is higher than unity [28g]. This can be a result of some specific interactions of COO^- with cationic surfactant head-groups at low $[X^-_w]$ values, or additional increase in pK_a^i of carboxylic groups at high ionic strengths, due to hydrophobization of micellar surface [28j].

The items *B* in eqs. 27 and 28 also depend on the counterions' nature. Strictly speaking, such a specificity likely caused by different pK_a^i values already reflects the peculiarities of counterions. But until the counterions are similar and the differences are moderate, for example, on going from Br^- to Cl^- in CTA^+-based systems [28i], the salt effects can be still regarded as normal ones.

Mixed supporting electrolytes

In practice, salt backgrounds are often of mixed character. Within the framework of the PIE model, the inequality of effects displayed by different counterions, including organic ones, are described by the $K_{OH^-}^{X^-}$ and $K_{H^+}^{M^+}$ values in cationic and anionic micelles, respectively. The differences of β values for different counterions can be also taken into account in a refined model [1f,61a].

Gaboriaud and coworkers proposed a combination of electrostatic and ion-exchange models [27a–d]. Using the dependence of cmc on the concentration and nature of counterions, they obtained the following expression for the pK_a^{ac} value of an indicator in anionic surfactant micelles in the presence of a mixture of counterions $M^{z+}_{i,w}$:

$$pK_a^{ac} = const - \log \sum_i S_i \, [M^{z+}_{i,w}]^{b_i} \tag{31}$$

Here, S_i are selectivity parameters. For the standard counterion, S_i is equated to unity: $S_{Na^+} \equiv 1$. The S_i values are close to ion-exchange constants [28i], while b_i parameters to the β values used in PIE model. For mixed salt background in micellar solutions of cationic surfactants, an analogous equation can be used [28i]:

$$pK_a^{ac} = B + \log \sum_i S_i \, [X^{z-}_{i,w}]^{b_i} = B' + \log \sum_i S_i \, (a^{z-}_{i,w})^{b'_i} \tag{32}$$

The S_i values can be determined by a combination of eqs. 27 or 28, obtained with one and the same indicator and different counterions [28i]. The S_i and b_i values compiled in Table 6 are obtained chiefly with bromophenol blue.

Thus-estimated parameters allow fitting the variation in pK_a^{ac} values in mixed salt backgrounds. For instance, eq. 33 is valid for bromophenol blue in CTA^+-based micelles [1m].

$$pK_{a2}^{ac} = 3.95 + \log\{0.32[Cl^-_w]^{0.73} + [Br^-_w]^{0.83} + 1.45[NO^-_{3,w}]^{0.78} + 23[C_7H_7SO^-_{3,w}]\} \tag{33}$$

The value $S_{Cl^-} = 0.32$ agrees with the $K_{Br^-}^{Cl^-}$ values available in literature and obtained by other methods [28i]. Equation 34 describes the equilibrium of methyl yellow in DS^--based systems [102]:

$$pK_{a0}^{ac} = 3.68 - \log\{[Na^+_w]^{0.91} + 0.9[Cu^{2+}_w]^{0.32}\} \tag{34}$$

The deviations of calculated pK_a^{ac} s from experimental ones do not exceed 0.2 units. Note that the b_i values for double-charged counterions are ca. two times lower as compared with those of single-charged ones. In $Mg(DS)_2 + MgSO_4$ system, the $b_{Mg^{2+}}$ value obtained with *n*-decyleosin at 30 °C is equal to 0.24 ± 0.03 [29i]. See also the $b_{SO_4^{2-}}$ value (Table 6).

Table 6 The selectivity parameters of counterions as determined using the indicator bromophenol blue in surfactant micelles, 25 °C [1m,28i].

Surfactant	Anion	B	b	r	S_i
CTAB	NO_3^-	4.12 ± 0.02	0.78 ± 0.05	0.996	1.45 ± 0.04
CTAB	Br^{-a}	3.95 ± 0.03	0.83 ± 0.03	0.996	1.00
CTAB	Cl^-	3.45 ± 0.08	0.73 ± 0.08	0.995	0.32 ± 0.02[b]
n-$C_{16}H_{33}NC_5H_5Br$	NO_3^-	3.61 ± 0.02	0.64 ± 0.03	0.994	1.6 ± 0.2
n-$C_{16}H_{33}NC_5H_5Br$	Br^-	3.51 ± 0.02	0.71 ± 0.02	0.969	1.00
CPC	Cl^-	2.96 ± 0.05	0.54 ± 0.09	0.997	0.28 ± 0.03
CPC	SO_4^{2-}	2.73 ± 0.02	0.26 ± 0.07	0.997	0.17 ± 0.01
CTAB	n-$C_5H_{11}SO_3^-$	4.80 ± 0.07	0.92 ± 0.08	0.999	5.5 ± 0.8
CTAB	n-$C_6H_{13}SO_3^-$	5.16 ± 0.07	0.89 ± 0.08	0.998	14 ± 2
CTAB	$H_7C_7SO_3^-$	5.33 ± 0.02	1.00 ± 0.02	0.992	23 ± 5

[a] Processing of literature data [17d], at KBr concentrations from 0.0077 to 1.05 M result in: $B = 3.91$, $b = 0.85$, $r = 0.9998$.
[b] In activity scale: = 0.29 ± 0.02.

Special (or specific) salt effects: Counterions cause micellar transitions

Very often, the influence caused by organic counterions is much larger than that of inorganic ones. Two examples of such *special* (or *specific*) *salt effects* are given below.

Methyl yellow (HB^+/B^0) in 0.02 M SDS solutions. In diluted acetate buffers with NaCl addition, at $[Na_w^+] = 0.05$ M, the pK_a^{ac} value equals 4.81, whereas in the presence of 0.05 M $N(n\text{-}C_4H_9)_4^+$ in diluted HCl solutions $pK_a^{ac} = 1.61$.

Bromophenol blue in CTAB micellar solutions. At $[Cl_w^-] = 0.1$ M, the pK_a^{ac} value is 2.68, while at the same concentration of tosylate, $pK_a^{ac} = 4.33$.

Equations presented in two previous subsections are derived with understanding that the parameters β, b, b', S_i, B, pK_a^i, and pK_a^m stay unchanged in the given (indicator + micelle + salt) system. Meanwhile, the rearrangement of micelles, dehydration of their surface, and decrease in α values along with increase in surfactant and salt concentrations is well documented. For example, at KCl concentration as high as 4 M, the change in E_T^N value of CTAB micellar solution is marked (Table 1); under such conditions, *not only surface charge screening, but also* pK_a^i *alteration can be expected* [28j]. The CTAB micelles in the presence of NaBr and SDS micelles on NaCl addition can lengthen up to ca. 50 and 70 nm, respectively [104]. However, effects of variation of Cl^-, Br^-, and NO_3^- concentrations in CTA^+-based systems and that of Na^+ in SDS solutions were satisfactorily explained using the PIE model [1b,27e–h,28a]. The $K_{Br^-}^{X^-}$ and S_i values for several inorganic anions in micellar solutions of CTAB and other cationic surfactants are available in literature.

It can be expected that organic counterions display principal changes in micellar structure. For example, it is proved using electron spin resonance (ESR) and NMR spectroscopy, small-angle neutron scattering (SANS), and rheological methods, that the entry of aromatic anions into cationic micelles [46j,n,104,105] and involving ammonium and alkylammonium cations in DS^--based micelles [28k,106] results in principal changes of micellar structure and micelle/water interface. Such rearrangement of the Stern layer can lead to reduction of surface charge density and thus to $|\Psi|$ decrease. *Degeneration of the pseudophase can readily reflect itself in the intrinsic acidity of acid–base indicators (*pK_a^i *values).*

We studied the influence of a set of counterions, including 8 inorganic, 5 aliphatic carboxylates, 5 benzoates, 2 nitrophenolates, and 7 sulfonates, on the pK_a^{ac} s of indicators [1m,46j,79]. For instance, at initial X^- concentrations of 0.1 and 0.01 M, the anions can be arranged in the following row:

$SO_4^{2-} < Cl^- < BrO_3^- < Br^- \leq ClO_3^- < NO_3^- < I^- < SCN^- <$ benzoate$^-$ ≤ tosylate$^-$ ≤
n-$C_6H_{13}SO_3^-$ < m-nitrobenzoate$^-$ < o-hydrophthalate$^-$ < hydrosalicylate$^-$, n-$C_6H_{13}CO_2^-$.

Similar sequences have been obtained also at 0.001 M of organic counterions. The S_i values presented in Table 6 can be compared with Gibbs energies of hydration or of transfer from water to organic solvents [9,107], with the so-called hydration parameters [108], ion-exchange constants on water–air interface [105e,109] and on anion-exchange resins [110]. The latter correlation, as well as that with ionic refraction, appeared to be most successful [1m].

For inorganic anions in cationic surfactant micelles, the above lyotropic series are in line with the corresponding cmc values [1d,111]. This is natural, because eqs. 27, 29, 30, and 32 are derived from equations describing dependences of cmc values on counterions' nature.

But for organic anions, the S_i values obtained using acid–base indicators are much higher than those calculated using the cmc data. For example, the S_i values for n-$C_6H_{13}SO_3^-$, $H_7C_7SO_3^-$, and hydrosalicylate in CTA^+-based micelles are 14 ± 2, 23 ± 5, and ≈60, respectively [1m,46j,79], while the cmc values of a set of several cetyltrimethylammonium benzoates are only 5 times lower as compared with that of CTAB [46j].

Application of the Gaboriaud equation to the pK_a^{ac} values of methyl yellow (HB^+/B^0) and hexamethoxy red (B^+/BOH^0) in DS^--based systems resulted in following S_i values against Na^+ as a reference cation [28k]:

Cation	$N(CH_3)_4^+$	$N(C_2H_5)_3H^+$	$N(C_2H_5)_4^+$	$N(n\text{-}C_4H_9)_4^+$
S_i	5 ± 1	15 ± 2	22 ± 3	125 ± 5

Again, the estimates of ion-exchange constants as obtained by processing cmc data [106a–d] are sometimes lower by an order of magnitude. *This gives evidence for changes of the* pK_a^i *values of indicators along with micellar transitions.*

The value $S_i = 110$ for tetraethylammonium reported by Gaboriaud et al. [27a–d] is much higher than our value and that obtained by fluorescence technique [106h], 6–6.5. In turn, the last-named procedure [106h] leads to an unlikely high value of 180 for triethylammonium [106h].

Interestingly, the aforementioned effect of deprotonation of indicator dications in SDS micelles is less expressed in tetraalkylammonium-modified DS^- aggregates [1m]. Moreover, the pK_a^{ac} s of some dyes, e.g., rhodamines ($HB^+/B^{\pm}$), are not so strong affected by such kind of counterions (see ref. [101] and Table 4).

The high affinity of organic cations to the adsorbent phase is also typical for ion-exchange resins [11c,110b–e,112]. In the last-named systems, the equilibrium constants of replacing inorganic ions by organic ones often depend on the ionic concentrations.

The inconstancy of concentration "constants" for cation exchange on resins and glasses is well known; according to Izmailov, the reason is the inconstancy of activity coefficients in the phase of adsorbent [11c,112a,b].

Contrary to solid ion exchangers with rigid matrixes, surfactant micelles are flexible systems inclined to polymorphism, and gradual saturating of the Stern layer with organic counterions can induce deeper structural changes.

Indeed, our data demonstrate that the S_i values of counterions often essentially depend on the concentration range used in calculations. For example, the S_{M^+} value of tetra-n-propylammonium, obtained in 0.001 M SDS solutions at $[Na_w^+] = 0.031$ M, using the pK_a^{ac} value of hexamethoxy red, decreases from 66 to 36 on going from $[M_w^+] = 0.019$ M to $[M_w^+] = 0.199$ M, etc. This appeared to be a general trend: increase in working concentration of organic counterion results in decrease of the S_i estimate.

The pK_a^{ac} values of hexamethoxy red 0.01 M SDS solution at 25 °C, determined with accuracy ±(0.01–0.03), reflect the extreme influence first of all of small additives of organic counterions. The pK_a^{ac} value, as obtained in acetate buffers at $[Na_w^+] = 0.016$ M, equals 5.93, while adding of only 0.003 M of C_6H_5–CH_2–$N(C_2H_5)_3^+$, n-C_4H_9–$NC_5H_5^+$, or n-C_nH_{2n+1}–$N(C_2H_5)_3^+$, n = 5, 6, 9, 10, and 11, decreases pK_a^{ac} up to 5.24–5.02 [89].

At low concentrations of OH^- and F^- in the bulk phase, these hydrophilic anions are retained in cationic micelles stronger that it could be expected judging from the ion-exchange constants determined by higher concentrations [113].

The excess adsorption of organic counterions in the Stern region is also probable; the possibility of recharging of cationic micelles is open to question [29h,105c]. Decrease in $|\Psi|$ value due to both decrease in surface charge density and excess adsorption leads to pK_a^{ac} increase in micelles of cationic surfactants, while in DS^--based micelles the effect is opposite. On the other hand, hydrophobization of the Stern region is expected to increase the pK_a^i values for the HB^-/B^{2-}, HB^0/B^-, and $HB^+/B^{\pm}$ couples and to decrease those for HB^+/B^0 ones. Hence, the resulting effect of hydrophobic counterions introduction in CTAB micelles is exclusively the increase in pK_{a1}^{ac} and pK_{a2}^{ac} (n-decylfluorescein, bromophenol blue, etc.). In the case of SDS micelles, pK_a^{ac} decrease on addition of tetraalkylammonium cations is the greatest for cationic dyes (HB^+/B^0, pK_{a0}^{ac}).

Gradual hydrophobization of CTAB micelles on adding tosylate or similar counterions results in additional increase in pK_a^i values of bromophenol blue, and thus in S_i and b increase (up to $b \to 1$, Table 6).

Concluding, we can stress that the S_i and b values as obtained with indicators can be somewhat noisy in the case of hydrophobic counterions.

Transformations of cationic surfactant micelles into rod-like, worm-like ones, etc., under addition of hydrosalicylate, tosylate, and other organic anions is proved by examining the viscosity and using electron microscopy and other methods [29h,104,105,114]. In (CTAB + hydrosalicylate) system, the micelles can lengthen up to 137 nm [104].

Introduction of tosylate, hydrosalicylate, benzoate, and some other organic anions leads to micellar transitions of cationic surfactants; the micelles become anisometric, sometimes even "worm-like". In the case of Reichardt's dyes, this results in changes of pK_a^{ac} and in expressed spectral effects [46j,n]. In the case of counterions with long hydrocarbon tail, e.g., n-$C_7H_{15}SO_3^-$, n-$C_8H_{17}SO_3^-$, n-$C_{10}H_{21}SO_3^-$, and especially of "pseudospherical" hydrophobic anions $B(C_6H_5)_4^-$ and ClO_4^-, micellar solutions of cationic surfactants transform into lyophobic unstable suspensions [1m,115]. Tetraphenylborate anion is used for precipitation of cationic surfactants in analytical chemistry [115a]. In the case of SDS solutions, the cation $N(n\text{-}C_7H_{15})_4^+$ displays similar influence.

Association of anionic surfactants at c_{surf} below cmc of homomicelles with hydrophobic cations is well documented [106e,f,116].

In the case of the zwitterionic surfactant CDAPS, only hydrophobic anions, not cations, display marked effects on the pK_a^{ac} s of acid–base indicators [29j]. It is reasonable to expect the adsorption of such anions in the region of quaternary nitrogen atom; see also [90b–d].

MODIFICATION OF IONIC MICELLES BY NONIONIC ADDITIVES

Noncolloidal additives

Small amounts of alcohols, amides, and other organic substances are known to decrease the cmc values of colloidal surfactants owing to mixed micelles formation [8a,117]. However, high concentrations of methanol, ethanol, acetone, DMSO, 1,4-dioxane, etc., favor decay of micelles as a result of increase in solubility of monomers [8a,117c]. The mostly used nonionic additives, which modify the structure of ionic micelles, are 1-butanol, 1-pentanol, and some other substances, which are limitedly soluble in water. They are located in the Stern region [29d,64b,117c,118], and this results in α increase [117a,b]. The thermodynamics of such systems and the composition of the mixed micelles are studied in detail [4c,29d,64b,117a,b,118,119]. Thus-modified micelles strongly influence rates of some chemical, photochemical, and photophysical processes. The addition of proper amounts of the third component, such as benzene, hexane, etc., results in the formation of thermodynamically stable microemulsions. The structure of mixed monolayers on the water–air interface was also examined [117c]. Crown ethers and cryptands can be used for peculiar modification of anionic micelles and vesicles [29i,101,120], because they are able to form "Host + Guest" complexes with Li^+, Na^+, and other cations. The counterions thus enlarged become more hydrophobic.

The pK_a^{ac} values of indicators "sense" the addition of organic solvents to micellar solutions [29d,i,l,73m,101]. In the case of cationic and anionic micelles, the addition of nonionic species leads to increase and decrease in pK_a^{ac}, respectively [1m,29i,l,83]. These effects are evidently caused by drop in interfacial charge density and thus in $|\Psi|$ of micelles. However, such "dilution" of the surface charge can be (partly) compensated by the increase in the α values.

The alterations of apparent ionization constants are especially expressed in the case of anionic micelles, e.g., of SDS ones [1m,28l]. Note that well-ordered structures of (SDS + alcohol) monolayers are formed on water–air interface owing to interaction between $O–SO_3^-$ and HO groups [117c]. The strongest decrease in pK_a^{ac} values was registered for indicators of HB^+/B^0 type [1m,28l]. Some authors explain the large difference between the pK_a^{ac} values of cationic acids in anionic and nonionic micelles by $(O–SO_3^- + HB^+)$ ion pairing [17h,28c–f,29c,d,44a,60d,e]. On the one hand, the penetration of nonionic molecules into the SDS micellar palisade reduces the local concentration of anionic head-groups; on the other hand, the α value increases and the effective dielectric constant of the Stern region decreases. The first effect must destroy the associates while the other two stabilize them.

Marked decrease in pK_a^{ac} of an indicator embedded in SDS micelles on addition of 1-pentanol was also reported for 4-heptadecyl-7-hydroxycoumarin [29d] and *n*-decyleosin [29i], indicators of HB^0/B^- type, and for rhodamine B, which belongs to $HB^+/B^\pm$ type [101].

In any case, the strongly hydrated surface of anionic micelles (see Table 1) seems to be "dried" by organic solvents. Indeed, the decrease in E_T^N value of 0.05 M SDS solution from 0.840 to 0.796, as well as the strong shift of the tautomeric equilibrium of methyl yellow protonated HB^+ species from red (azonium) to colorless (ammonium) on introduction of 0.3 M n-$C_5H_{11}OH$ also confirm the principal rearrangement of anionic micelles [28l]. The mentioned conversion is typical for azo dye cations docked into hydrophobic cages of cyclodextrins [121].

Colloidal additives

The addition of nonionic colloidal surfactants displays most expressed influence on the pK_a^{ac} values of indicators embedded in ionic micelles. In systems containing two hydrocarbon-tailed surfactants, ionic and nonionic ones, mixed micelles appear (Chart 7).

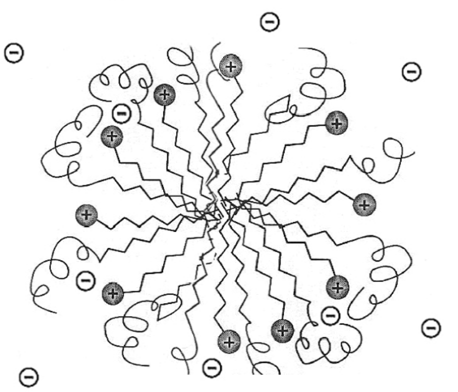

Chart 7 A schematic sketch of the section of a spherical (cationic + nonionic) mixed surfactant micelle.

In general, the molar fractions of ionic and nonionic surfactants, x and $(1 - x)$, respectively, do not coincide with their fractions in mixed micelles, y and $(1 - y)$, respectively. Many papers and reviews have been published on the thermodynamics of mixed micelles formation; at small surfactant concentrations, the formula of Rubingh [122] is valid, based on the theory of regular solutions

$$y^2 \ln(\mathrm{cmc}^* x/\mathrm{cmc}_{\mathrm{ionic}} y) = (1 - y)^2 \ln[\mathrm{cmc}^*(1 - x)/\mathrm{cmc}_{\mathrm{nonionic}}(1 - y)] \tag{35}$$

Here, cmc* is the experimentally available cmc value of mixed micelles. However, at high enough surfactant concentrations: $x \to y$.

In mixtures of ionic and nonionic surfactants, the stepless variation of polarity, solubilizing capacity, and of many other properties of the pseudophase becomes possible [4b,58d,117d,e,128e,i]. For example, gradual adjustment of interfacial charge density and hence of Ψ can easily be realized [1m,58d,128e]. Some reactions, such as photofading of azo dyes, are known to occur in mixed anionic + nonionic surfactant mixed micelles, but not in individual micelles of both kinds [123].

We have studied the dependence of pK_a^{ac} s of acid–base indicators on x in mixed micellar solutions [1m,28l,29i–k,81,83,99]. Forty-two mixed (cationic + nonionic) surfactant systems were examined. As a rule, the total surfactant concentration was maintained constant and high enough to equate x to y. Five cationic and six nonionic surfactants were involved in the study, surfactant concentrations and ionic strengths were within the ranges (0.0004–0.03 M) and (0.01–0.6 M), respectively. The character of differentiating influence of (cationic + nonionic) systems even at $x = 0.2$ is closer to that of pure cationic micelles [28l].

Thirty (SDS + nonionic surfactant) systems were also studied, with total surfactant concentration of 0.005 to 0.10 M, and [Na$_w^+$] within the range of 0.01–0.4 M. At $x = 0$, extrapolation to complete binding (p$K_a^a \to$ pK_a^{ac}) was made, as described in one of the below sections. Some representative curves are depicted in Fig. 4. Naturally, the strengthening of salt background always makes the dependences more flat.

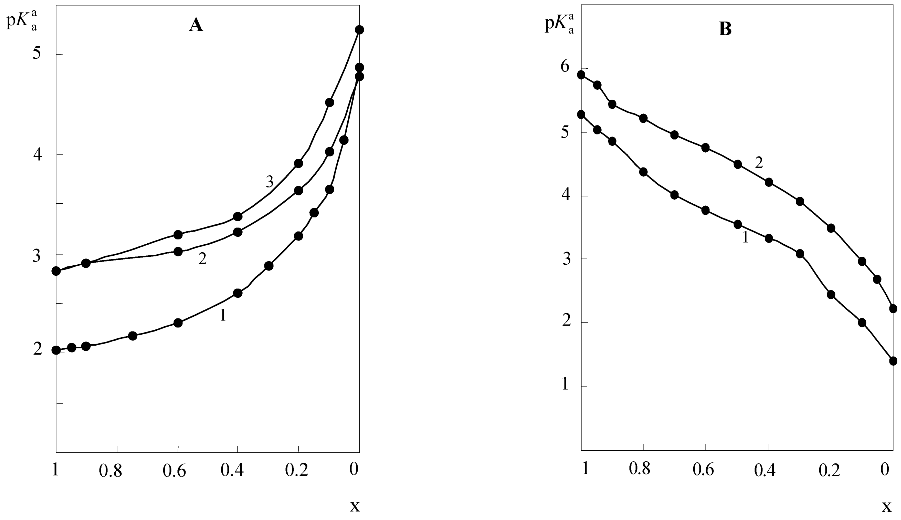

Fig. 4 (A) pK_{a2}^{ac} of bromophenol blue as a function of the molar fraction of CTAB in its mixtures with Nonylphenol-12 (*1*, *2*) and Tween-60 (*3*) at total concentration of surfactants of 0.003 M and $I = 0.01$ M (NaCl + buffer) (*1*) and 0.05 M (NaBr + buffer) (*2,3*). (B) pK_{a0}^{ac} of methyl yellow (*1*) and hexamethoxy red (*2*) as a function of the molar fraction of SDS in its mixtures with Nonylphenol-12 at total concentration of surfactants of 0.02 M and $I = 0.01$ M (NaCl + buffer); 25 °C (Data from ref. [28l]).

As demonstrated above, the differences between the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ values in given ionic and nonionic surfactants strongly vary from one indicator to another (Table 4), and this predestines the lack of coincidence of the curves obtained for a set of indicators. However, some typical features are to be underlined. The dependence of Ψ on interfacial surface charge density (e.g., see eq. 9) is of such a nature, that even if we take into account the increase in α on addition of nonionic component, the "dilution" of ionic surfactant head-groups results in sharp decrease in $|\Psi|$ and in corresponding changes of $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ only at $y <$ 0.5. As a rule, this is the case with cationic + nonionic systems (Fig. 4A).

In contrast, in (SDS + nonionic surfactant) systems the first additives of the second component already change the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ values markedly (Fig. 4B). But this takes place first of all for acid–base couples of $\mathrm{HB}^+/\mathrm{B}^0$ type [28l,29i], whereas for 1-hexadecyl-5-hydroxyquinoline [124] and *n*-decyleosin, the effect is not expressed so distinctly. Finally, the $\mathrm{p}K_\mathrm{a0}^\mathrm{ac}$ values of rhodamine 19 and *N*,*N*′-di-*n*-octadecylrhodamine, indicators with charge type $\mathrm{HB}^+/\mathrm{B}^\pm$, are insensitive to first additions of Tween 80 (Fig. 5).

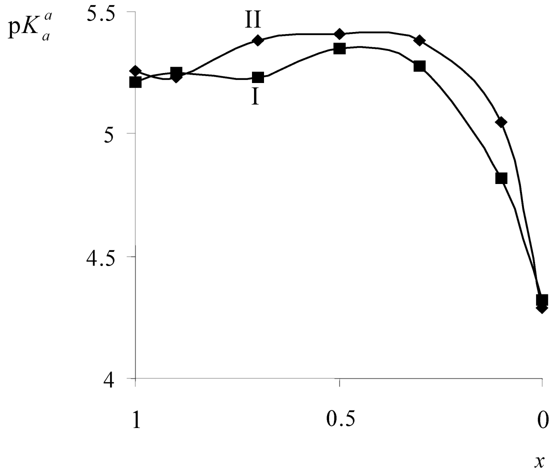

Fig. 5 The dependence of $\mathrm{p}K_\mathrm{a0}^\mathrm{a}$ on molar fraction of SDS in SDS – Tween 80 mixture; I – *N*,*N*′-di-*n*-octadecylrhodamine, II – rhodamine 19; total surfactant concentration of 0.02 M and I = 0.05 M (NaCl + acetate buffer), 25 °C [68].

The NaCl concentration is in this case somewhat higher than that in Fig. 4B; a small increase in $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ at medium x values is evidently caused by α increase of SDS in mixed micelles.

Such peculiarities of indicator behavior can readily be ascribed to the variations of $\mathrm{p}K_\mathrm{a}^\mathrm{i}$. In line with the concept of stronger hydration of SDS micelles as compared with nonionic ones, the first molecules of the latter display "drying", analogous to the effect caused by alcohol addition. As substantiated above, the most expressed differences in $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ values are expected for $(\mathrm{HB}^+/\mathrm{B}^0)$-indicators, while smaller ones are expected for HB/B^- and $\mathrm{HB}^+/\mathrm{B}^\pm$ acid–base couples. In addition, the dehydration ("drying") of the Stern region must increase the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ s of the last two types of indicators and decrease the $\mathrm{p}K_\mathrm{a}^\mathrm{i}$ values of traditional cationic acids of $\mathrm{HB}^+/\mathrm{B}^0$ type. This model allows us to rationalize the ($\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ vs. x) dependences typified in the current section.

Though cationic and anionic surfactants can in some cases also form stable micellar mixtures [125], such systems are less studied.

Salt effects in mixed (ionic + nonionic) micelles

The slopes b of the (pK_a^{ac} vs. logarithm of counterion bulk concentration) dependences decrease along with addition of 1-pentanol or nonionic surfactants to SDS micelles. The data for hexamethoxy red (eqs. 36 and 37) are typical [28l]:

$$\mathrm{p}K_{a0}^{ac} = (4.40 \pm 0.02) - (0.84 \pm 0.02)\log[\mathrm{Na}_w^+], \quad 0.02\ \mathrm{M\ SDS} \tag{36}$$

$$\mathrm{p}K_{a0}^{ac} = (3.82 \pm 0.04) - (0.43 \pm 0.08)\log[\mathrm{Na}_w^+], \quad 0.02\ \mathrm{M\ SDS} + 0.2\ \mathrm{M}\ n\text{-}\mathrm{C_5H_{11}OH} \tag{37}$$

As the b values are close to $(1 - \alpha)$, this confirms the increase in SDS dissociation degree in micelles obtained by conductivity and potentiometry. It must be noted that transitions of SDS micelles caused by addition of 1-pentanol and other alcohols are expressed in NaCl brines [126].

In (SDS + Brij 35) system, the effects of NaCl upon the pK_{a0}^{ac} values of methyl yellow and hexamethoxy red allowed us to make similar conclusions [1m,127]. For example, at $x = y = 0.1$ the estimate of α value is 0.62, against 0.08–0.16 in pure SDS micelles, as obtained with the same indicators. The examination of salt effects up to 0.6 M of Br$^-$ on the pK_{a2}^{ac} values of bromophenol blue in (CTAB + Brij 35) system [1m,127] demonstrated a gradual decrease in b and thus an increase in α:

$x \to y$	1.00	0.50	0.40	0.30	0.20	0.10	0.05
α	0.16	0.26	0.30	0.34	0.38	0.51	0.64

These data confirm the increase in α *values for mixed (ionic + nonionic) surfactant micelles, earlier obtained by conductivity, electrophoresis, potentiometry, and other methods* [8a,58d,128].

Though the ion-exchange constant $K_{\mathrm{Br}^-}^{\mathrm{Cl}^-}$ in mixed micelles was approximately the same as in pure cationic surfactant systems, the tosylate anion does not display such strong effects on pK_a^{ac}. Analogously, tetra-n-butyl ammonium cation influences the equilibria of acid–base indicators in mixed (SDS + nonionic surfactant) micelles much weaker as compared with its action in pure SDS systems. This illuminates *the origin of the special salt effects*: introduction of large organic counterions favors the dehydration of micellar surface and structural transformations of ionic surfactant micelles, but in the case of mixed (ionic + nonionic) micelles, *the initial properties of ionic micelles are already altered.*

It is assumed that the increase in α values in mixed (ionic + nonionic) micelles is caused by "dilution" of the ionic component, and that a critical micellar surface charge exists, below which the counterion binding is absent at all [128c,h], in agreement with Manning's theory developed for polyelectrolytes [58b,129]. In the latter case, hydration of uniformly charged area overcomes electrostatic repulsion beginning from some critical interfacial charge. Surfactant micelles, however, are able to easily change their size and shape, and some fraction of counterions can be fixed even at extremely low y values.

INCOMPLETE BINDING OF INDICATORS TO IONIC MICELLES

Up to this point, we have considered primarily the pK_a^{ac} values, i.e., the pK_a^a values under conditions of complete binding of the indicator by the pseudophase. As a rule, this takes place in the case of water-insoluble indicators, or if the electrical charge of ionic species and that of micellar interface are opposite, or if the dye is covalently bound, e.g., as fluorescein isothiocyanate to proteins and other biomolecules with NH$_2$ groups. In general, the binding can be incomplete.

Actually, the aforementioned partition constants, P_i (eq. 10), allow us to evaluate the degree of binding. In practice, however, the so-called binding constants, $K_{b,i}$, are more suitable. Such constants refer to the quasichemical equilibrium {(substrate i in bulk water) + (surfactant head-group situated in micelle) $\rightleftarrows$ (substrate in bound state)}. In micellar solutions, if the inequality $[i_m]_t \ll (c_{surf} - \mathrm{cmc})$ is valid, the $K_{b,i}$ value can be calculated using eq. 38

$$K_{b,i} = \frac{[i_m]_t}{[i_w]_t} \times \frac{1}{c_{surf} - cmc} \tag{38}$$

Indeed, such constants can be used if the precise value of the pseudophase volume is unknown. But if it is available, and the concentration activity coefficient of the i species in the aqueous phase, f_i^w, can be estimated, the $K_{b,i}$ values can be converted into P_i

$$P_i = K_{b,i}\,(c_{surf} - \mathrm{cmc})V_w(V_m f_i^w)^{-1} = K_{b,i}\, s/f_i^w \tag{39}$$

Here, V_w and V_m are volumes of the bulk and micellar phases, respectively [1m]. A vast number of $K_{b,i}$ and P_i values are accumulated in the literature for various substances, from noble gases to dyes and metal complexes [4c,6,71e–g,73a,74b,118a,b,d,130]. The $K_{b,i}$ values can be used as criteria of hydrophobicity of compounds; correlations are known between logarithms of water–micelle and water–octanol-1 partition coefficients [73a,131].

To estimate the degree of binding of various molecules and ions by surfactant micelles, a number of methods are developed, for example, spectroscopic, chromatographic, diffusion ones, etc. For acid–base reactions, the analysis of the pK_a^a plots vs. surfactant concentration in the region above cmc [1a,f,1l,72a,b,73] is most helpful and universal, because the alteration of electronic absorption spectra along with binding is sometimes not distinct enough.

The relation between the pK_a^a value of the acid ($HB^z \rightleftarrows B^{z-1} + H^+$) in micellar solutions at fixed ionic strength and the indices of ionization constant in water, pK_a^{w*}, determined at the same ionic strength, is as follows:

$$pK_a^a = pK_a^{w*} + \log\{[1 + K_{b,HB}(c_{surf} - \mathrm{cmc})][1 + K_{b,B}(c_{surf} - \mathrm{cmc})]^{-1}\} \tag{40}$$

Evidently, if the binding constants of the HB^z and B^{z-1} species, $K_{b,HB}$ and $K_{b,B}$, are large enough, the pK_a^a completely coincides with pK_a^{ac}. On the contrary, if both binding constants are so small that $K_{b,i}\,(c_{surf} - \mathrm{cmc}) << 1$, then pK_a^a is equal to pK_a^{w*}, and the pseudophase does not influence the acid–base equilibrium state at all. At last, in case either or both species are bound incompletely, eq. 40 can be used for $K_{b,i}$ determination, using the increasing or decreasing sigmoid (pK_a^a vs. c_{surf}) curve [1m,72a,b,73]. The equation can be linearized, but the nonlinear fitting is also possible [48].

Such processing of data appeared to be proper for micellar solutions of colloidal surfactants [73a,b,e–m], phospholipid liposomes [48], and microemulsions [66,73d,n]. In the last case, the V_m/V_w ratio or the volume fraction of the pseudophase, $\varphi = V_m/(V_m + V_w)$, can be used as argument [66]

$$pK_a^a = pK_a^{w*} + \log[(1 + P_{HB}^* V_m/V_w)(1 + P_B^* V_m/V_w)^{-1}] \tag{41}$$

Here, the P_i^* values refer to the given ionic strength of the bulk. Finally, having the $K_{b,i}$ or P_i^* values, it is possible to calculate the pK_a^{ac} value

$$pK_a^{ac} = pK_a^a + \log\frac{K_{b,B}^{\ \ -1} + c_{surf} - cmc}{K_{b,HB}^{\ \ -1} + c_{surf} - cmc}; \qquad pK_a^{ac} = pK_a^a + \log\frac{1 + (P_B^*)^{-1}(\varphi^{-1} - 1)}{1 + (P_{HB}^*)^{-1}(\varphi^{-1} - 1)} \tag{42}$$

Some representative data are compiled in Table 7.

Hence, the partition model seems to be capable. However, there are some aspects to be considered. First of all, the $K_{b,i}$ or P_i values are often dependent on the working concentration range [66,73f,m,n]. Therefore, the data precision is low; the accuracy can reach 30 %, and in the case of microemulsions can be even worse. Note that alterations of pK_a^{ac} values along with variations in surfactant concentration are reported even for completely bound indicators [29j]. The evident reasons are changes in micellar size and shape.

Table 7 The binding constants, K_b, of indicators as obtained using the dependences of $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ vs. c_surf, as a rule at 25 °C [1m,48,66,73m,n,101].

Indicator system	Colloidal system	I, M	$K_\mathrm{b,HB}$, M^{-1}	$K_{b,\mathrm{B}}$, M^{-1}	$\mathrm{p}K_\mathrm{a}^\mathrm{ac}$
Methyl yellow, $\mathrm{HB}^+ \rightleftarrows \mathrm{B} + \mathrm{H}^+$	Brij 35 micelles	0.05	65	5.8×10^3	1.12 ± 0.06
Rhodamine B, $\mathrm{HB}^+ \rightleftarrows \mathrm{B} + \mathrm{H}^+$	Brij 35 micelles	0.05	4.0×10^3	5.9×10^2	4.08 ± 0.04
Bromophenol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Brij 35 micelles	0.01	1.2×10^4	1.25×10^3	5.10 ± 0.03
Bromophenol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Triton X 100 micelles	0.01	11	1.7	5.00 ± 0.02
Bromophenol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Triton X 305 micelles	0.01	2.4	0.13	4.88 ± 0.03
Bromophenol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Nonylphenol 12 micelles	0.05	20	2.7	4.80 ± 0.03
Bromophenol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Tween 80 micelles	0.05	13	0.90	5.09 ± 0.03
Phenol red, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Brij 35 micelles	0.01	285	32	8.73 ± 0.03
Phenol red, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	CTAB micelles	0.4 (KBr)	2.5×10^3	2.6×10^2	8.72
Phenol red, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	n-$\mathrm{C_6H_{14}}$ – Tween 80 – n-$\mathrm{C_5H_{11}OH}$ microemulsion[a]	0.05	17	77	8.6 ± 0.3
Bromothymol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	n-$\mathrm{C_6H_{14}}$ – Tween 80 – n-$\mathrm{C_5H_{11}OH}$ microemulsion[a]	0.05	37	2.4×10^4	10.0 ± 0.10
Bromothymol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	$\mathrm{C_6H_6}$ – SDS – n-$\mathrm{C_5H_{11}OH}$ microemulsion[a]	0.05	10	1.0×10^3	9.24 ± 0.10
Bromothymol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	SDS micelles	0.2 (NaCl)	16	1.3×10^4	9.90 ± 0.06
Bromothymol blue, $\mathrm{HB}^- \rightleftarrows \mathrm{B}^{2-} + \mathrm{H}^+$	Phospholipid liposomes	2.0	2.4×10^5	8.4×10^2	9.63 ± 0.07
Neutral red, $\mathrm{HB}^+ \rightleftarrows \mathrm{B} + \mathrm{H}^+$	Phospholipid liposomes	0.005	9.6×10^3	2.2×10^3	7.15 ± 0.06
Acridine orange, $\mathrm{HB}^+ \rightleftarrows \mathrm{B} + \mathrm{H}^+$	Phospholipid liposomes	0.05	8.3×10^2	6.8×10^3	9.74 ± 0.08

[a] The P_i^* values as determined as obtained using the dependences of $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ vs. φ.

In the case of nonionic surfactant micelles, both $\mathrm{p}K_\mathrm{a}^\mathrm{a}$ analysis and spectral data allow us to obtain directly the P_i^o and ${}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{m}$ values for ionic species. In the case of transfer from one bulk phase to another, these quantities are unavailable without extrathermodynamic assumptions. In the case under consideration, the introduction of the pseudophase concept itself serves as such an assumption.

The anions are known to be bound by liposomes better than cations of the same hydrophobicity; for example, for $\mathrm{B(C_6H_5)_4^-}$ and $\mathrm{As(C_6H_5)_4^+}$ the difference amounts to 19 kJ mol^{-1} [132]; see also [133]. This is in qualitative agreement with the $K_\mathrm{b,i}$ values of cationic and anionic dyes, notwithstanding the negative interfacial charge of the liposomes used by us [48] (Table 7).

Whereas the HB^- and B^{2-} anions of the most hydrophobic sulfonephthalein, bromothymol blue, are bound to SDS micelles in the presence of 0.2 M NaCl, the relatively hydrophilic phenol red is incompletely bound even to cationic micelles, if the concentration of bromides or nitrates in the system is high enough to reduce partly the interfacial electrical potential. Interestingly, this is not the case in chloride-containing solutions, up to 4 M of KCl [1m].

Diverse degree of binding of indicators or other substrates, as well as of equilibrium species of one and the same reagent can evidently result in differentiating their acid–base properties. This can be considered as a "trivial" differentiating influence of the pseudophase. Such phenomena manifest themselves distinctly in the protolytic equilibria of fluorescein and its derivatives in aqueous solutions of nonionic surfactants [88]. At the same time, it is a model of selective solvation, typical for mixed solvents.

In the case of ionic surfactants, the ($\mathrm{p}K_\mathrm{a}^\mathrm{a}$ vs. c_surf) curves sometimes possess a turning point [73a,b]. The most probable reason for appearance of a minimum in the case of cationic surfactants and a maximum in the case of anionic ones is the inconstancy of the counterion concentration. Indeed, along with increase in c_surf, the counterion concentration in the bulk phase increases due to dissociation of the colloidal electrolyte (see eq. 8). This "negative adsorption" [17d] leads to screening of the interfacial charge and to corresponding alterations of $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$. Adding of an excess of supporting electrolyte eliminates the turning point [28a].

If the concentration of ionic surfactant is below its cmc value, interaction with oppositely charged dye species could result in formation of neutral water-insoluble dye-surfactant associates and mixed micelles [134]. The dye ions can be then regarded as large counterions with high S_i values [1m].

SOME OTHER LYOPHILIC OR LYOPHILIZED COLLOIDAL SYSTEMS

Along with surfactant micelles, a set of other nanosized self-assembled systems is of interest for both theoretical and practical reasons.

Usually, the droplets of surfactant-stabilized oil-in-water microemulsions contain also a cosurfactant, for example, an alcohol with limited solubility in water. Some data throwing light on the influence of microemulsions were already given in Tables 1, 3–5. In Fig. 6, the pK_a^{ac} values of sulfonephthalein, hydroxyxanthene, azo, and some other dyes are plotted against the pK_a^{ac} values of the same indicators in micelles of corresponding ionic surfactants [66]. Evidently, these two familiar kinds of colloidal systems display similar influence on acid–base equilibria:

$$pK_a^{ac}\text{ (in microemulsion)} = (0.47 \pm 0.18) + (0.91 \pm 0.06)\, pK_a^{ac}\text{ (in micelle)} \tag{43}$$

$n = 22$, $r = 0.988$, $s = 0.39$

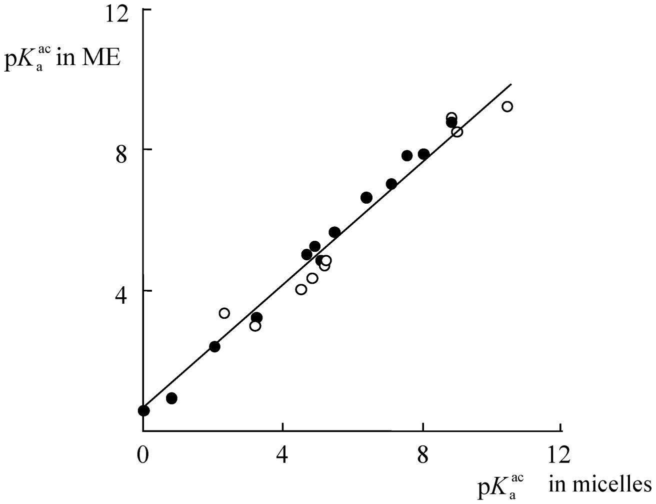

Fig. 6 Dependence of pK_a^{ac} in microemulsions ($\varphi = 1.3$ %, surfactant – pentanol-1 – benzene) on pK_a^{ac} in micelles: closed and open circles are systems based on CPC and SDS, respectively, $I = 0.05$ M, 25 °C (This has been reproduced from ref. [66] with permission of the author).

Indeed, microdroplets can be considered as "swollen" micelles. In the interfacial region, also called "membrane" [135], the surfactant head-groups are somewhat diluted with the cosurfactant. Probably, the indicators are situated just in this region, not in the hydrophobic interior, notwithstanding the fact that the size of the microdroplets is on average one order greater than that of surfactant micelles.

The pK_a^{a} values of manifold indicators in microemulsions are available in the literature [46m,66,73d,n,136], as well as the data on partition between bulk water and microdroplets [66,73k,n,137].

It is not without interest to ascertain to what degree the nature of the microemulsion components with the fixed surfactant influences the pK_a^{ac} value of an indicator. The pK_{a2}^{ac} values of bromothymol blue were determined to within ±0.02 in 13 microemulsions stabilized with Tween 80 and containing different hydrocarbons and co-surfactants, at $\varphi = 1.3$ %, $I = 0.05$ M, and 25 °C [73n,136a]. The registered scatter from 9.28 to 9.61 denotes the drawbacks, which can arise in attempts to compare the data obtained for different indicators in systems, which seem to be similar.

Phospholipid bilayers are reduced models of biomembranes. Unilamellar phosphatidylcholine + diphosphatidylglycerol (18:1, mol:mol) liposomes with average radius of ca. 50 nm exhibit more complicated influence on the indicator equilibria [48]. Some of the data are given in Tables 1, 3, and 4. The treatment of the systems examined in terms of the binding constants of various dye species allowed extrapolating experimentally determined $\mathrm{p}K_{\mathrm{a}}^{\mathrm{a}}$ to the values $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$. The results suggest that microenvironments of neutral red, acridine orange, and bromothymol blue in the lipid bilayer are intermediate between those of nonionic and anionic micelles. Below pH 3, the medium effects became similar to those for nonionic micelles, as it was observed for methyl yellow and some other dyes. This is in line with the fact of protonation of the lipid's phosphate groups.

Theoretical model of the dielectric properties of phosphatidylcholine/water interface suggests strong dielectric anisotropy [138]. Furthermore, as follows from the up-to-date models of membrane electrostatics, there exists a complex potential profile across the lipid bilayer [23a,b,139]. The protolytic behavior of indicators can be influenced by both the surface and dipole (C=O group) potentials [23b,132,139]. The existence of steep gradients of electrostatic potential and dielectric constant at the lipid/water interface may be important in determining the observed shifts of indicator protolytic equilibria in lipid systems and must be considered in interpreting the results of $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ studies. The indicator dyes are believed to experience first of all the properties of their local microenvironment [23b,29c,44a].

Taking into account the wide application of CTAB-modified silica/water interfaces [140], it was of interest to clarify to what degree the properties of CTAB bi- and multilayers formed on SiO_2 nanoparticles resemble those of common spherical micelles. With that end in view, we studied the protolytic equilibria of sulfonephthalein, hydroxyxanthene, azo, pyridinium-*N*-phenolate, and some other indicators in suspensions of 40 and 85 nm-sized silica particles coated with CTAB [141]. The increase in the ζ-potential value of nanoparticles from –(27–34) to +(37–54) mV on going from pure silica suspension to the CTAB-containing system points to the silica surface recharging and formation of surfactant bilayer (or multilayer) on the silica/water interface. The average surface area per 1 dye molecule (ion) varies from 3 to more than 50 nm^2, while in the case of common spherical CTAB micelles it is ≈ (70–150) nm^2. *The* $\mathrm{p}K_{\mathrm{a}}^{\mathrm{ac}}$ *values of sulfonephthalein dyes in* SiO_2*/CTAB system and in CTAB micellar solution at the fixed ionic strength practically coincide* (within ±0.1 logarithmic units). The agreement is somewhat poorer for more complicated indicators, such as fluorescein and 2,7-dichlorofluorescein. Whereas the band shifts of anionic species of the sulfonephthaleins in the two types of colloidal systems are similar, the difference became more evident in the case of tautomeric conversions of oxyxanthenes, solvatochromic and solvatofluoric behavior of dyes.

Water-soluble ionic calixarenes belong to very promising receptor molecules owing to their applications in biochemistry and other fields [142]. However, the state of such substances in aqueous media is still unclear. The behavior of dyes in aqueous solutions of calixarenes is usually explained in terms of "Host + Guest" interactions [143], analogous to dye-cyclodextrin systems [144]. We studied the influence of sixteen acid–base indicator dyes in water in the presence of a cationic calixarene, 5,11,17,23-tetra(*N*,*N*-dimethyl-*N*-hydroxyethylammonium)-methylene-25,26,27,28-tetrapropoxy-calix[4]arene tetrachloride, within a wide concentration range [145]. The deviations of the apparent ionization constants from the $K_{\mathrm{a}}^{\mathrm{w}}$ values and the shifts of the absorption bands of the dyes were compared with those in micellar solutions of cationic surfactants. These studies, as well as dynamic light scattering measurements, confirm the existence of *small positively charged aggregates, which are able to strongly modify protolytic properties of other dissolved substances, just like common cationic micelles. The cavity effects of the receptor are less expressed here.*

Dendrimers represent another kind of "Host" molecules [146]. The cationic dendrimers in solution can be considered as oligomers of cationic polyelectrolytes, or surfactant-like species, capable of forming micelles through self-association. Within the course of this research, aqueous solutions of four cationic poly(propylenimine) second-generation dendrimers of different architecture and hydrophobicity have been examined as media for acid–base reactions of indicator dyes [147]. Cationic dendrimers affect protolytic equilibria in aqueous solution by favoring the more negatively charged species, similar to effects registered in micellar solutions of cationic surfactants. This causes large negative values of ΔpK_a^{ac} for sulfonephthalein dyes, fluorescein, decylfluorescein, and methyl orange. The dendrimers markedly influence absorption/emission/excitation spectra, ionization constants, tautomerism, and fluorescence of the dyes. *In general, the effects are similar to those displayed by micelles of cationic surfactants*. However, the agreement is far from complete. In some cases, the poly(propylenimine) second-generation dendrimers or their probable aggregates act as oligomeric polycations without a micellar hydrophobic interior.

It turned out that one of the most indicative test tools, which allow us to distinguish between the common sphere-sized micelles of cationic surfactants and other micelle-like self-assemblies, is the velocity of the alkaline fading of bromophenol blue. The nucleophilic attack of the central carbon atom by the hydroxyl anion

$$R^{2-}\text{ (blue)} + OH^- \rightarrow ROH^{3-}\text{ (colorless)} \qquad (44)$$

occurs in water with an easily measurable rate. So, at pH = 12 (0.01 M NaOH + 0.02 M NaCl) the pseudo-first-order rate constant is $(1.0 \pm 0.4) \times 10^{-5}\ s^{-1}$. As early as 1959, Duynstee and Grunwald [148] reported the ability of cationic surfactant micelles to protect R^{2-} species from decolorization, despite condensation of OH^- ions in the Stern region; this result was numerously reproduced in our laboratory. The mechanism of protection is still not conclusively rationalized; it can be treated from the viewpoint of screening the bounded dye with surfactant head-groups, in terms of the Olson–Simonson rule.

Contrary to CTAB micelles, the CTAB-modified silica/water interfaces appeared to be unable to prevent the fading process; the rate constant was only ca. 40 % lower than that in water [141b]. In solutions of a second-generation cationic dendrimer, the dye fades just as in water. According to this criterion, the aggregates of aforementioned cationic four-membered calixarene appeared to be most micellar-like. Nevertheless, slow decolorization of the dye was also registered here. This test reaction is so sensitive that in tosylate-modified CTAB micelles or even in CTAB micelles with addition of 1 M KBr, the fading process is detectable.

Hence, the collective action of surfactants [149] demonstrates its specificity to more or less degree, depending on the kind of indicator reaction studied.

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