

Review

Solvatochromic and Acid–Base Molecular Probes in Surfactant Micelles: Comparison of Molecular Dynamics Simulation with the Experiment

Nikolay O. Mchedlov-Petrosyan *, Vladimir S. Farafonov and Alexander V. Lebed

Department of Physical Chemistry, V. N. Karazin Kharkiv National University, 61022 Kharkiv, Ukraine; farafonov@karazin.ua (V.S.F.); alebed@karazin.ua (A.V.L.)

* Correspondence: nikolay.mchedlov@gmail.com

Abstract: This article summarizes a series of seventeen publications by the authors devoted to molecular dynamics modeling of various indicator dyes (molecular probes) enclosed in surfactant micelles. These dyes serve as generally recognized tools for studying various types of organized solutions, among which surfactant micelles in water are the simplest and most explored. The modeling procedure involves altogether 50 to 95 surfactant molecules, 16 to 28 thousand water molecules, and a single dye molecule. The presentation of the simulation results was preceded by a brief review of the state of experimental studies. This article consists of three parts. First, despite numerous literature data devoted to modeling the micelles itself, we decided to revisit this issue. The structure and hydration of the surface of micelles of surfactants, first of all of sodium *n*-dodecylsulfate, SDS, and cetyltrimethylammonium bromide, CTAB, were studied. The values of the electrical potential, Ψ , were estimated as functions of the ionic strength and distance from the surface. The decrease in the Ψ value with distance is gradual. Attempts to consider both DS^- and CTA^+ micelles in water without counterions result in a decay into two smaller aggregates. Obviously, the hydrophobic interaction (association) of the hydrocarbon tails balances the repulsion of the charged headgroups of these small “bare” micelles. The second part is devoted to the study of seven pyridinium *N*-phenolates, known as Reichardt’s dyes, in ionic micelles. These most powerful solvatochromic indicators are now used for examining various colloidal systems. The localization and orientation of both zwitterionic and (colorless) cationic forms are generally consistent with intuitive ideas about the hydrophobicity of substituents. Hydration has been quantitatively described for both the dye molecule as a whole and the oxygen atom. A number of markers, including the visible absorption spectra of Reichardt’s dyes, enable assuming a better hydration of the micellar surface of SDS than that of CTAB. However, our data show that it is more correct to speak about the more pronounced hydrogen-bonding ability of water molecules in anionic micelles than about better hydration of the SDS micelles as compared to CTAB ones. Finally, a set of acid–base indicators firmly fixed in the micellar pseudophase were studied by molecular dynamics. They are instruments for estimating electrostatic potentials of micelles and related aggregates as $\Psi = 2.303RTF^{-1} (pK_a^i - pK_a^{app})$, where pK_a^i and pK_a^{app} are indices of so-called intrinsic and apparent dissociation constants. In this case, in addition to the location, orientation, and hydration, the differences between values of pK_a^{app} and indices of the dissociation constants in water were estimated. Only a semi-quantitative agreement with the experimental data was obtained. However, the differences between pK_a^{app} of a given indicator in two micellar solutions do much better agree with the experimental data. Accordingly, the experimental Ψ values of ionic micelles, as determined using the pK_a^{app} in nonionic micelles as pK_a^i , are reproduced with reasonable accuracy for the corresponding indicator. However, following the experimental data, a scatter of the Ψ values obtained with different indicators for given micelles is observed. This problem may be the subject of further research.

Keywords: surfactant micelles; molecular dynamics modeling; solvatochromic Reichardt’s dyes; hydration; acid–base indicators; apparent dissociation constants; electrical surface potential



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1. Introduction

Organized solutions belong to the most explored liquid media for performing numerous chemical processes [1]. The origin of the term “organized solutions” can be found in [2,3]. Among these systems, surfactant micellar solutions are the oldest [4–6] and well-defined [7–12]. Among the most popular tools for studying the properties of surfactant micelles in water are indicator dyes of various types [10,13–23]. They are utilized as acid–base [10,13–20], solvatochromic [1,19,21], and fluorescent [22–26] molecular probes.

These compounds have long been used in sensor devices [27–31], for examining polyelectrolyte solutions [32,33], gelatin films [34], nanodiamond and fullerene dispersions [35,36], calixarene [37,38] and cucurbituril solutions [39], surfactant monolayers on water/air interfaces [40–42], monolayers on solid/liquid interfaces [43], multilayers of different types [44–46], and even water/air interfaces without introducing additional surfactants [47–49].

With the help of such tools, the electrical surface potential, polarity, hydration, effective permittivity, and viscosity of the micellar pseudophases and related systems can be examined. The problems associated with the molecular probes are a matter of detailed consideration and discussion, and the corresponding publications are huge in number. Some of them are regarded in the above-cited articles, reviews, and books.

In addition to this abundant, but often quite contradictory information, we decided to investigate the “micelle + molecular probe” systems, first “micelle + indicator dyes” using molecular dynamics (MD) simulations. Despite numerous studies devoted to MD modeling of surfactant micelles in water, the systems containing molecular probes were almost overlooked. Some works were devoted to dye molecules in phospholipid bilayers [50,51]. An example of such a study of micelles is the MD investigation of the location of a dye sulforhodamine B in the micellar pseudophase [52].

Within the course of our study, we used first sodium *n*-dodecylsulfate, SDS, and *n*-hexadecyl- (or cetyl-) trimethylammonium bromide, CTAB, micelles in water as the most well-defined surfactant systems. In addition, six other surfactants were occasionally used. In total, seventeen molecular probes were examined mainly in SDS and CTAB micellar solutions. The results of our research group have been reported in seventeen articles from 2016 to the present [53–69]. We thought it is expedient to summarize the data obtained and the regularities found. In particular, a comparison of the theoretically derived models with the experimental data is of a special interest.

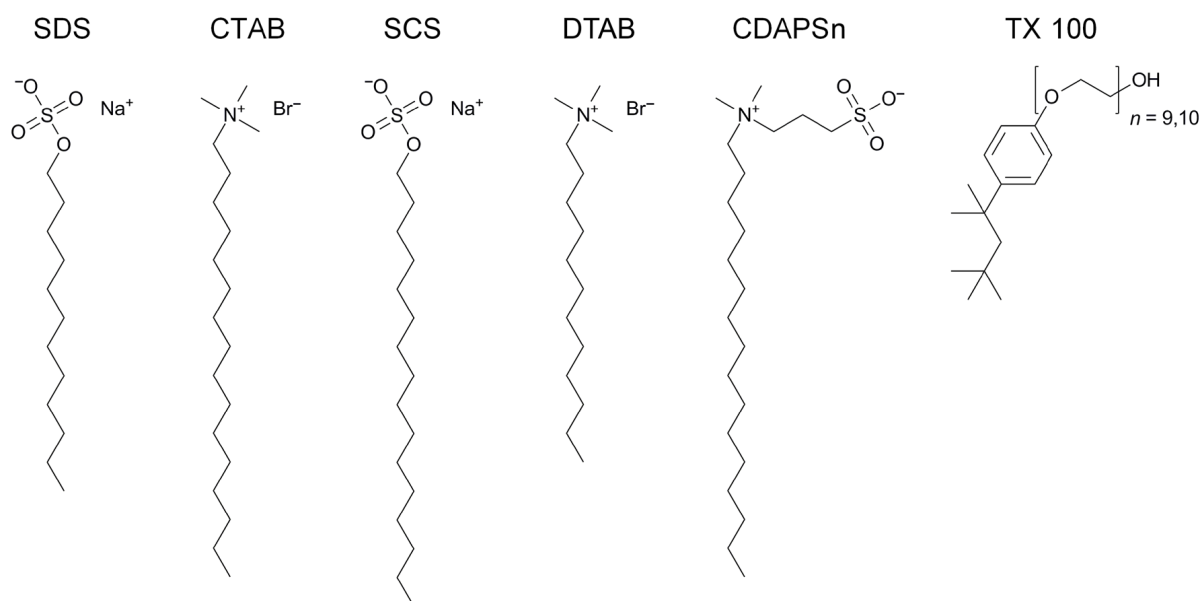
Since theoretical methods for studying solvation began to be considered as an integral part of the knowledge of solutions, it was important to apply modern MD modeling approaches not only to the structure of micelles, but also to the placement and hydration of molecular probes in the surfactant micelles.

Several theoretical models were proposed in order to qualitatively describe the structure of surfactant micelles. At the same time, molecular dynamics simulation may serve as the most physically grounded model to validate the other ones because it explicitly takes into account most of the interactions present in the solutions discussed. Such simulations go back several decades and revealed the features, which are hardly accessible otherwise.

The works devoted to MD simulations of surfactants and surfactant micelles are numerous. Here, we mention only some of them as an example [70–74], as well as a new review article [75], and a MD modeling of surfactant monolayers on the water/air interface [76]. There are some studies of surfactant micelles [77,78] or bilayers [79] based on other theoretical methods, including those analyzing the systems with incorporated lauric acid [77,79].

Within the course of our studies, the following ionic surfactants attracted our attention: sodium *n*-dodecylsulfate, SDS; sodium *n*-hexadecylsulfate (or cetylsulfate, SCS); cetyltrimethylammonium bromide, CTAB; *n*-dodecyltrimethylammonium bromide, DTAB; *N*-cetylpyridinium chloride, CPC. A zwitterionic surfactant, *N*-cetyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate, CDAPS_n, and a nonionic surfactant Triton X-100 (TX-100), were also examined (Scheme 1). In order to compare the results with literature data, *N*-

cetylpyridinium bromide, CPB, and cetylsulfonic acid with a triethanolammonium cation, TEACSn, were also studied (not shown in Scheme 1).



Scheme 1. Molecular structures of surfactants considered in our studies.

The leitmotif of this article is the MD simulation of “micelle + molecular probe” systems and comparison of the obtained results with experiment. We started with the study of solvatochromic dyes, whereas the idea of estimating the surface electric potential of micelles arose in the course of this research. As such, we performed a series of molecular dynamics simulations in order to elucidate the state of a set of dyes enclosed in surfactant micelles. The following characteristics were revealed: localization and spatial orientation of dye molecules with respect to the micelle surface and their degree of hydration. The collected data allowed us to identify the effect of various surfactant and dye parameters on these characteristics:

- Charge of the surfactant headgroup;
- Length of the surfactant hydrocarbon tail;
- Micellar size.
- Substituents in the dye molecule;
- Protonation state of the dye;

2. Simulation Setup

The potential models for all the dyes were manufactured in the framework of the widely used and well-validated OPLS-AA (Optimized Potentials for Liquids Simulation, All-Atom) force field, following the methodology recommended therein. The atomic charges were calculated anew in a two-stage process. Firstly, the geometry of the molecule was optimized in a quantum chemical calculation using Hartree–Fock method and 6–31G(d) basis set. The spatial distribution of the electrostatic potential around the molecule was produced at the same time. Secondly, the distribution was subjected to the RESP (Restrained Electrostatic Potential) algorithm. The RED server was used to carry out the stages [80].

For the surfactants, the OPLS-AA models developed by us were taken [55,56,58,62,65] to ensure the mutual compatibility of all species present in the system. Water was described with the SPC (Simple Point Charges) model.

All simulations were set up uniformly following the same protocol. At first, a surfactant micelle is taken containing the number of monomers corresponding to the range of typical aggregation numbers of the surfactant. It was 60 for SDS, 80 for CTAB and SCS, as well as 50 for DTAB. For CTAB, an aggregation number of 95 was also tried. The micelle is

placed in a water-filled cubic box allowing ~ 2 nm margins around, and the dye of interest in the examined protonation state is placed in the micelle. The resulting number of water molecules is about 16–28 thousands. Three initial configurations are prepared ready to start three production MD runs of the same system, allowing enough sampling to be achieved and the uncertainty of the calculated characteristics to be estimated.

The production runs were carried out at standard conditions (temperature of 298 K and pressure of 1 bar) for 50–130 ns depending on the system. The following parameters and algorithms were used: time step 2 fs for SDS and DTAB or 1.6 fs for longer-chain CTAB and SCS, three-dimensional periodic boundary conditions, Berendsen thermostat and barostat, PME (Particle Mesh Ewald) method for electrostatic interactions, cutoff of van der Waals interactions at 1 nm, LINCS (LINear Constraint Solvent) constraints for all covalent bonds. The beginning of the trajectories was discarded during the analysis as equilibration.

3. Ionic Surfactant Micelles

Although the formation of surfactant micelles in aqueous solutions was proved more than a hundred years ago [5,6], the exact nature of these particles is still a matter of debate.

The ideas about the structure of surfactant micelles found in the literature were generally established quite a long time ago and are periodically refined and improved. It is impossible to consider this issue in detail here. As typical examples of the traditional approach, the model developed by Stigter [81–83] and the article by Larsen and Magid [84] should be mentioned. These and similar works correspond rather to Hartley's model of spherical micelles. At the same time, Menger [85] leans more towards McBain's theory of a lamellar (bilayer, plate-like) surfactant micelle; see also Philippoff's articles [86,87].

Fromherz proposed a hybrid of the two main models, a surfactant-block model, which presumes the contact of water molecules with the hydrocarbon core to some extent ("The entire hydrocarbon chain of all molecules is wettable in time average. The average number of wetted methylenes per chain is given by the wetted alpha-carbon, by the smooth surface of saturating cube configuration—about two methylenes—and by roughness") [88].

The schematic structure of a globular surfactant micelle considered by Grieser and Drummond on the basis of a number of studies by other authors seems to be quite realistic [13]. In addition to the dynamic character of the micelle $\rightleftharpoons$ surfactant monomer equilibrium, their model includes two important features. These are as follows. First, "a large hydrocarbon/aqueous solution contact area, i.e., the headgroups do not completely cover the hydrocarbon core". This is in line with the scheme proposed by Israelachvili [89]. Second, "a fluid hydrocarbon core, containing *no* water, in which some chain bending can occur, thereby permitting some of the terminal CH_3 groups to be in contact with the interface." [13]. Today, both statements have been confirmed by MD simulations (see below).

In addition, Gilanyi [90] proposed a concept of fluctuating micelles, based on the small system thermodynamics. Rusanov proposed a detailed consideration of structural, mechanical, thermodynamic, and electrostatic aspects of cylindrical, lamellar, and (first) spherical surfactant micelles in water [91]. Us'yarov [92,93] also considers a spherical model of the SDS micelles even at surfactant concentrations up to 0.9 M.

A key characteristic of all micelles of ionic surfactants is their electrostatic potential, Ψ . A more detailed consideration allows to distinguish between the surface potential, Ψ_0 , the Stern layer potential, Ψ_δ , and the electrokinetic potential, ζ . The last is available for direct determination, but corresponds to the share surface (slip plane) located in the diffuse layer of the electrical double layer, EDL. For a charged spherical or cylindrical colloidal particle, the Ψ value can be calculated by an equation proposed by Ohshima, Healy, and White, based on the approximate analytical solution of Poisson–Boltzmann equation [94]. For surfactant spherical micelles, the method was adapted by Hartland et al. [95], to give Equation (1). The left-hand side in this equation is the surface charge density, $\alpha = 1 - \beta$, where β is the degree of counterion binding, s_1 is the molecular area of the headgroup.

$$\frac{\alpha}{s_i} = \frac{2\varepsilon\varepsilon_0 kRT}{F} \sinh(Y/2) \left(1 + \frac{2}{kr \cosh^2(Y/4)} + \frac{8 \ln[\cosh(Y/4)]}{(kr)^2 \sinh^2(Y/2)} \right)^{\frac{1}{2}} \quad (1)$$

Here, $Y = \Psi_\delta F/RT$, κ is the reciprocal Debye length, r is the micellar radius, $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$, and $\varepsilon = 78.5$ at $T = 298.15 \text{ K}$. It should be noted, that the calculations require the knowledge of r_i , s_i , and β and therefore are possible only for such well-defined surfactants as CTAB and SDS.

Though the present article is devoted to hydrophilic colloidal systems, an important work concerning the EDL at hydrophobic surfaces [96] should be mentioned, as well as a theoretical approach for the determination of ζ [97].

It is clear that for a better understanding of the nature of surfactant micelles, the α values are of critical importance. These values determine the micelle charge and electrostatic potential, and can be deduced from experimental data. As early as 1951, Philippoff presented α values for nine representative ionic surfactants, although even then there was much more such data; for SDS, $\alpha = 0.183$ [87]. An overview of the literature accumulated over many years [92,95,98] shows a significant spread of the α values for a given surfactant. For instance, let us consider the data for SDS and related anionic surfactants. Sasaki et al. [98] determined $\alpha = 0.27$ by activity measurements of Na^+ and DS^- and compared this value with those obtained in thirteen other works by seven different experimental methods: α varies from 0.14 to 0.54, 0.26 on average. Frahm et al. [99] used two methods and determined $\alpha = 0.36\text{--}0.49$, while Lebedeva et al. [100] compared values from four different publications, from 0.272 to 0.322, with 0.290 on average.

Still in practice different methods provide dissimilar values. This is because the position of the boundary between bound and free counterions is not an intrinsic characteristic of the micelle but depends on the method used. Hartland et al. [95] noted that micelle mobility methods give α values of approximately 0.3 to 0.4, which is higher than those determined from measurements of sodium ion activity, which give α values of approximately 0.20 to 0.25. Simultaneously, Gilanyi [101] proposed an interpretation of the experimental α values in terms of specific and nonspecific electrostatic interactions between the colloidal particles and small ions.

At the same time, utilization of one and the same method reveals the tendency of α decreasing along with lengthening of the hydrocarbon tails. This is not so pronounced when comparing $\text{C}_{10}\text{H}_{21}\text{OSO}_3\text{Na}$ and $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ with $\text{C}_{14}\text{H}_{29}\text{OSO}_3\text{Na}$, and $\text{C}_{16}\text{H}_{33}\text{OSO}_3\text{Na}$ [98], but for seven surfactants, $\text{C}_n\text{H}_{2n+1}\text{OSO}_3\text{Na}$, from $n = 8$ and 9 to 13 and 14, α decreases from 0.41–0.42 to 0.19–0.22 (average of values obtained by different methods) [99].

The increase in the concentrations of both surfactant and foreign electrolyte can lead to a decreasing α value. For example, Us'yarov performed a detailed theoretical study of the SDS solutions within a wide concentration range, without and with NaCl additions [92,93]. At SDS concentrations up to 0.9 M and a total Na^+ concentration in the bulk aqueous phase from 0.01 to $\approx 0.9 \text{ M}$, the $\alpha = 1 - \beta$ values vary from 0.19 to 0.025–0.04 [92,93].

4. New Molecular Dynamics Modeling Results for Surfactant Micelles

Now let us consider our results concerning the micellar structure. Particularly, the simulations show that water molecules do not penetrate deeply into the hydrocarbon core. In other words, the core is completely dry; see Figure 1A, which is in line with earlier proposed picture [13] and theoretical results [72]. Nevertheless, the continuous thermal motion of surfactant monomers and the character of their packing enable every CH_2/CH_3 bead of the tail to have occasionally contact to water. This occurs when the bead appears on the micelle surface for some time, which in turn depends on its position in the chain. However, if a micelle adopts a prolate or rod-like shape instead of being close to spherical, then the dry core appears rather thin, as was observed for DTAB micelles. Probably, the most appropriate term for the micellar structure is globular.

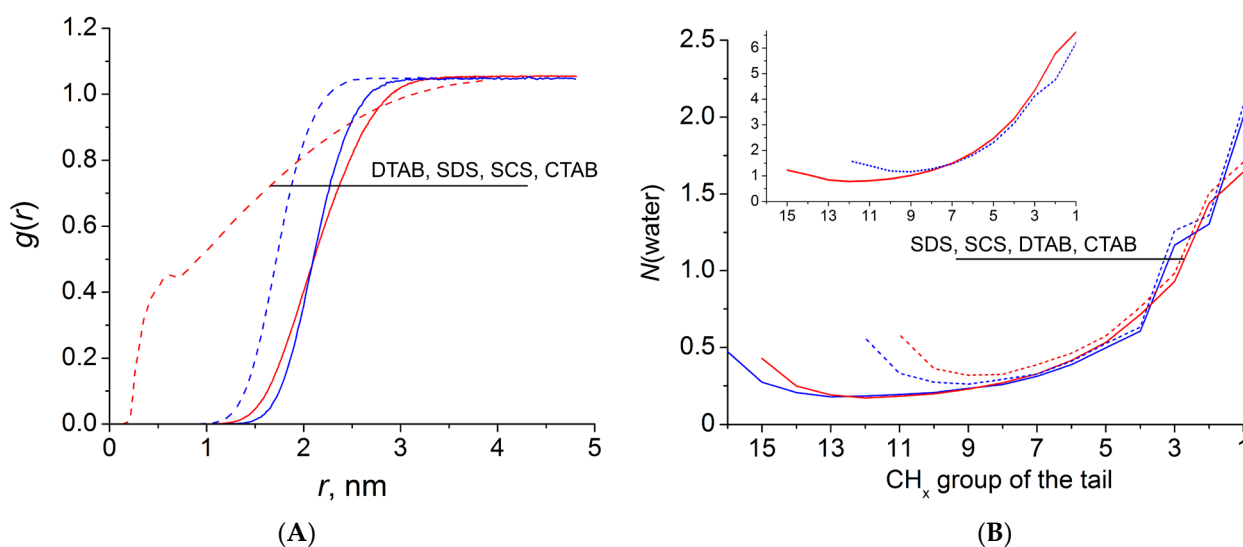


Figure 1. (A) Radial distribution functions of water with respect to the micelle center. (B) Average number of water molecules within 0.4 nm or 0.5 nm (inset) of the CH₂ (CH₃) groups of hydrocarbon tail in micelles [54,55]. Here, the red color corresponds to the cationic surfactants, solid lines correspond to the surfactants with a cetyl group.

MD simulation with explicit water allows directly counting the amount of water in micelles using various metrics. On one hand, we estimated the extent of hydration of each CH₂/CH₃ bead of hydrocarbon tails. Figure 1B shows the average number of water molecules staying within 0.4 nm of each bead in the micelles of SCS and CTAB having a *n*-C₁₆H₃₃ hydrocarbon tail, and SDS and DTAB with a *n*-C₁₂H₂₅ one. In alkylammonium surfactants, we attributed the first methylene group as belonging to the headgroup, basing on the charge distribution. While the hydration decreases quickly with moving away from the headgroups, it still never reaches zero, and even somewhat increases for the last two beads. The hydration of the first and third beads in the anionic surfactants is ca. 30% higher than in cationic ones, while it is ca. 9% lower for the second and fourth beads. On average, the hydration of the first four beads is somewhat higher in the anionic surfactants. However, this does not mean that the surface layer contains more water because the beads may share water molecules. Instead, if hydration is calculated using a radius of 0.5 nm then CTAB ions have some preference. Hence, we conclude the DS[−] and CTA⁺ ions in micelles are hydrated to a similar extent.

On the other hand, we estimated the complete amount of water within the surface layer of SDS, SCS, DTAB, and CTAB micelles. As such, we used a simplified geometric model where micelle and its hydrocarbon core were represented as concentric triaxial ellipsoids; see Figure 2. Axes of the latter ellipsoid were chosen to make its volume and moments of inertia equal the values computed by MD simulation. The axes of the former ellipsoid were $2 \times \delta$ nm longer to reflect the δ -thick surface layer around the core. Then, the water molecules within δ nm of the core were enumerated and a time-average number was computed using the MD trajectories. Having this input data, we found the hydration H of the complete micelle as volume fraction of water in the Stern layer via Equation (2).

$$H(\delta) = \frac{V_{\text{water}}}{V_{\text{Stern layer}}} = \frac{N_{\text{water}} \cdot V_{1\text{mol}}}{V_{\text{micelle}} - V_{\text{core}}} \quad (2)$$

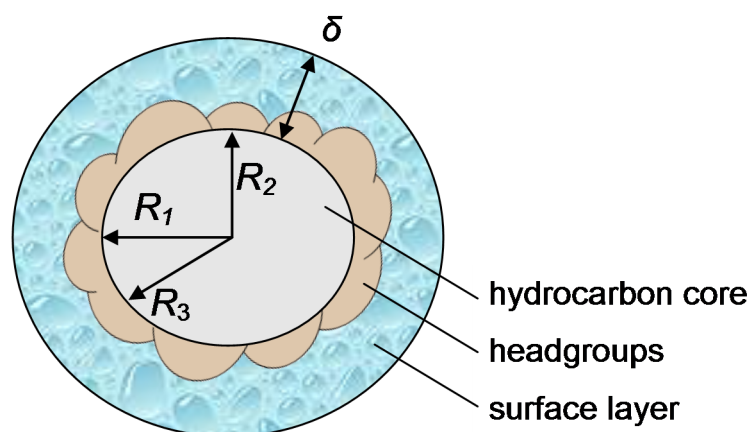


Figure 2. The geometric model used for estimating the hydration of micelles.

Here, δ is the Stern layer thickness; $V_{\text{Stern layer}}$, V_{water} , V_{micelle} , V_{core} are volumes of the surface layer, water, micelle ellipsoid, and the hydrocarbon-core ellipsoid, respectively; N_{water} is the number of water molecules in the surface layer; and V_{mol} is the volume of a single water molecule (0.030 nm^3).

The results indicate that, despite the difference in the headgroup charge and micelle size, the $H(\delta)$ parameter appears almost equal for all four surfactants considered (the spread is no more than 0.05 units). This agrees well with the previously shown similarity of hydration of individual CH_2 beads of the surfactant ions.

As mentioned before, the degree of counterions binding, β (and the related degree of dissociation, α), is an essential quantity determining the behavior of an ionic micelle in solution. MD simulation allows examining the complete distribution of counterions instead of a single-point value. The calculated β values for some of the inspected surfactants are collected in Table 1 for two values of the boundary position. The lower boundary is found from the distribution of counterions around headgroups, and corresponds to the first minimum in the radial distribution function of Na^+ (Br^-) with respect to S (N) atoms. The upper one is somewhat arbitrarily chosen as 0.9 nm. The comparison indicates that considering the most tightly bound counterions only (the lower boundary) leads to underestimation of β , so the boundary must be chosen farther from the micelle. According to our simulations of SDS, potential models that provide higher counterion binding within the lower boundary also lead to deformation of structure of large micelles [55]. The upper boundary provides β values, which fit in the experimental range, except of CTAB where small underestimation of ca. 0.05 remains.

Table 1. Computed and experimental degrees of counterions binding of micelles, β .

Surfactant	MD	Experiment
SDS	0.23–0.67	0.45–0.86
CPC	0.37–0.65	0.45–0.67
CTAB	0.59–0.69	0.74–0.84

Note. Experimental β values for SDS, CTAB, and CPC were taken from various publications [11,102,103] and [104–107], respectively.

In order to elucidate the role of counterions, we applied an unusual approach. By means of MD simulations one can easily study systems, which cannot be prepared in the laboratory. We performed simulations of “bare” micelles, composed of DS^- or CTA^+ ions only, without any other ions present in the aqueous solution. Usually, counterions are considered as a necessary factor for the formation of a micelle, which compensates the electrostatic repulsion between like-charged surfactant ions. In the simulations, the DS^- micelle of 60 monomers expelled a small aggregate and reduced to 43 monomers. The CTA^+ micelle of 80 monomers was split into two comparable micelles; see Figure 3. This

result indicates that the hydrophobic interaction itself is able to keep the aggregate together without additional stabilization up to some size.

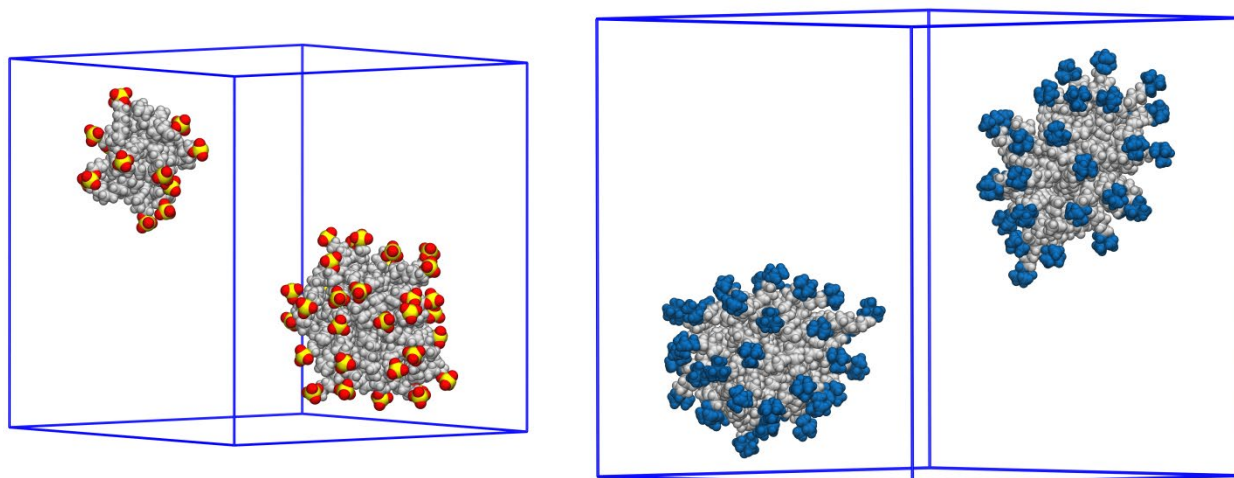


Figure 3. The results of 20 ns simulation of DS^- (left) and CTA^+ (right) micelles without counterions. The small micelles differ only in the aggregation number.

It is well proven and documented that in mixed nonionic + ionic surfactant micelles at low content of the second component, the fraction of the counterions is small or even zero [14,108–110]. In such cases, the hydrophilic portions of the nonionic component ensured micelle stabilization. In any case, the diffuse layer of counterions exists around the micelle. In the case of polyelectrolytes, according to Manning’s theory, there is a critical degree of counterions condensation [111]. It should be noted that some early theories do not assume an adsorption layer of counterions in the monolayers of ionic surfactants at the water/air and water/hydrocarbon interfaces [112].

The formation of pre-micellar, or sub-colloidal, species $(\text{DS}^-)_2$ occurs rather without than with the participation of the sodium ions [113,114], though at SDS and NaClO_4 concentrations of 10^{-4} M, the $(\text{DS}^-)_2\text{Na}^+$ particles were fixed by the electrospray spectrometry [115].

Though the hydration of ionic groups certainly takes place in the case of counterion-free dodecylsulfate aggregates, the MD prediction of formation of such aggregates can be considered as an illustration of the efficiency of the hydrophobic interaction.

A related issue is the profile of the electrostatic potential around the micelle. This problem was extensively studied previously, but simplified geometries (sphere, cylinder) were mostly used because they enable analytical solutions. We performed the calculation of $\Psi(r)$ considering micelles of natural shapes, which were produced by MD simulation. The suitable method of calculation was the numerical solution of the Poisson–Boltzmann equation. The discrete character of charge distribution and complex shape of micelle were taken into account, as well as the finite size of counterions. Solvent and micelle were treated as dielectric continuums, as is usually done in such calculations. The profiles $\Psi(r)$ predict the expected fade of Ψ with distance and ionic strength, Figures 4 and 5. They were then interpreted in terms of the commonly used characteristics: surface potential Ψ_0 and Stern layer potential, Ψ_δ . For SDS and CTAB micelles, the values $\Psi_0 = -100$ mV and $+(149\text{--}151)$ mV, $\Psi_\delta = -75$ mV and $+(70\text{--}78)$ mV were found (at $I = 0.05$ M), which stays in line with the estimations of other methods. The Stern layer boundary δ was chosen 0.32 nm for SDS and 0.45 nm for CTAB according to the distribution of counterions around the micelle surface, more details may be found in our previous work [66].

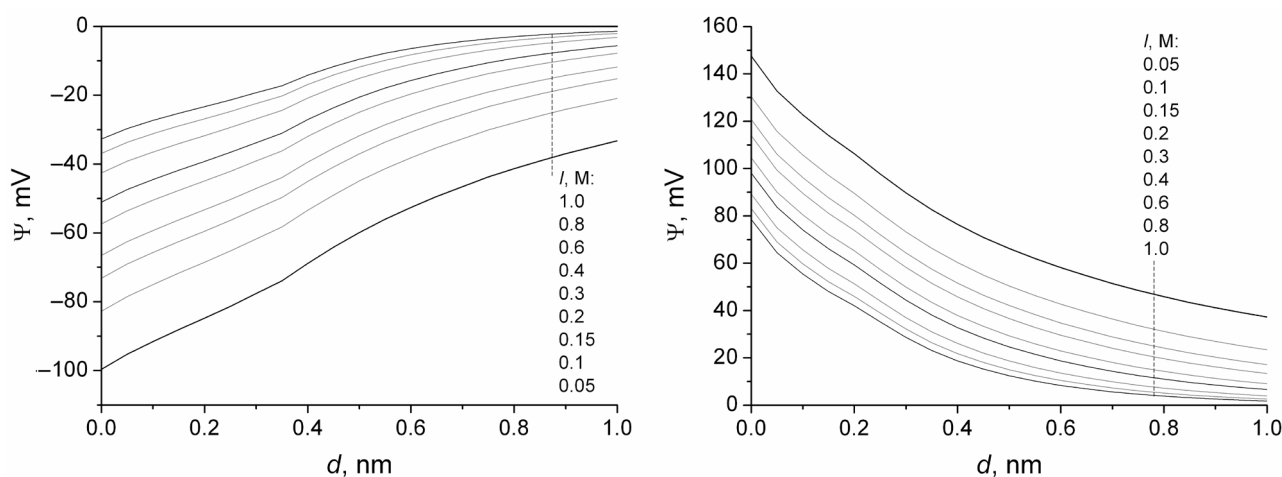


Figure 4. Profiles of electrostatic potential fade with distance for SDS (left) and CTAB (right) micelles at different ionic strengths. Reprinted from [66] with permission.

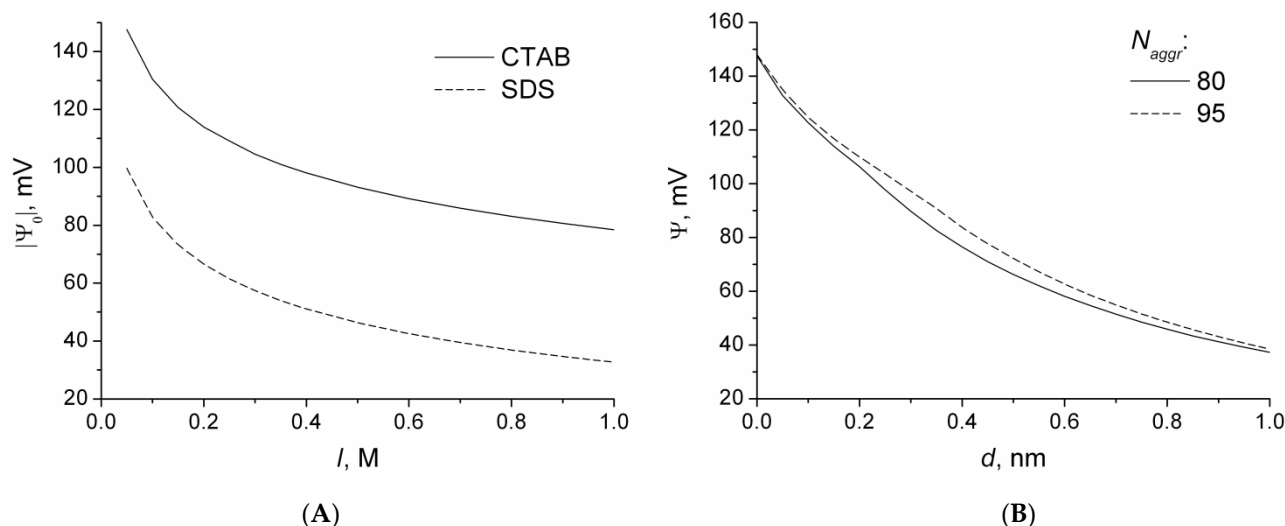


Figure 5. (A): Dependence of surface electrostatic potential on the ionic strength for SDS and CTAB micelles; (B): The profile of the electrostatic potential fade with distance for CTAB micelles of different size at $I = 0.05$ M. Reprinted from [66] with permission.

Note that Figures 4 and 5B do not show a sharp change in the potential near the surface.

The method chosen by us allows us to calculate the surface electrostatic potential of “bare” micelles without counterions. We used the micelles consisting of 41–43 monomers produced as a result of MD simulations presented before. The Ψ_0 values are -420 mV and $+380$ mV. Importantly, these numbers are of lesser magnitude than found for the original size micelles, where Ψ_0 is -535 mV and $+630$ mV. Evidently, a decrease in the aggregation number led to a reduction in the surface charge density and headgroup–headgroup repulsion up to the magnitudes, which can be compensated by hydrophobic interactions. On the other hand, calculations of the electrostatic potential of the dodecylsulfate micelle with “empty”, i.e., counterions-free Stern layer using Equation (1) lead to a value of $-(193\text{--}199)$ mV at $\alpha = 1$ [14,95]. The screening of the surface charge by the diffuse layer was accounted for in this case, contrary to the above mentioned MD simulations. Therefore, the influence of the diffuse layer corresponds to -340 mV.

From the computational perspective, we identified the importance of bonded parameters for potential models of surfactants. It was previously identified for higher hydrocarbons and lipids and led to derivation of improved potential models, but it was not applied for

common surfactants. Usually, the non-bonded parameters (point charges, Lennard–Jones potential σ and ϵ) are in focus during the parameterization. However, for SDS, the parameters of dihedral (torsion) angles governing the rotation around C–C bonds strongly affect the micelle properties, as well. Too rigid tails (i.e., with high potential barriers for the rotation) superfluously tend to adopt a parallel arrangement. In small micelles (<100 monomers), this affects only the degree of counterions binding because the headgroups become more grouped. However, large micelles may artificially adopt a bilayer-like shape instead of a rod-like one. Whether this occurs depends also on the non-bonded parameters. The problem was solved by making the tails more flexible, which was achieved by employing the dihedral parameters proposed for description of higher hydrocarbons and lipids.

A crucial feature of micelles is their ability to bind (adsorb) molecules and ions present in solutions. The properties of the molecule often undergo a change after adsorption, and experimental registration of this change is the basis of the method of investigating micelle properties by means of molecular probes. Still, this method heavily relies on the a priori information about the state of the molecular probe, which is needed to interpret the registered changes. This is a severe problem because the state itself cannot be observed directly and must be deduced from some other experiments. By using properly prepared and mutually consistent potential models it is possible to recapitulate the adsorption process in MD simulation and examine the state of the molecular probe including its localization, local environment, and diffusion coefficient. For example, we simulated the adsorption of $N(C_3H_7)_4^+$ ions in SDS micelle, and observed a significant reduction in its diffusion coefficient as result [53]. Still, even for these oppositely charged species adsorption may demand a quite long simulation time; therefore, we concluded it is more practically convenient to have the molecular probe initially located in the micelle at the start of MD. The final result (Figure 6) demonstrates the location of this cation; it is in line with the scheme proposed by Bales et al. [116], who considered the tetra-*n*-propylammonium and other tetraalkylammonium cations in the Stern layer of the micelles of tetraalkylammonium dodecylsulfates.

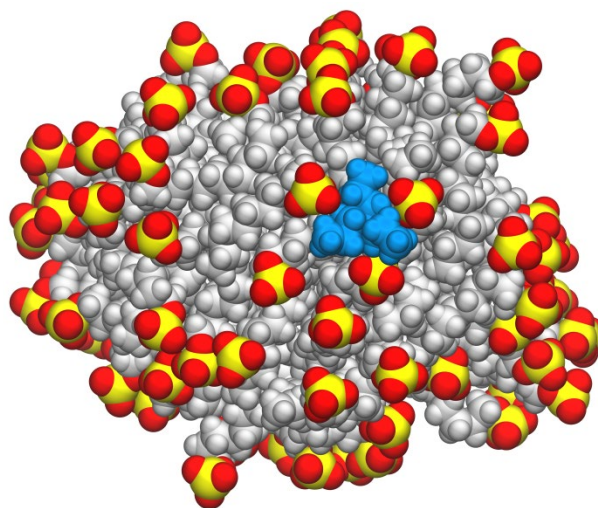


Figure 6. Location of the tetra-*n*-propylammonium cation (colored blue) in a SDS micelle; sodium ions are not shown.

We also paid attention to nonionic micelles with and without an adsorbed dye molecule, since they are used in the indicator method of estimating the surface electrostatic potential [10,13,14].

The micelles of TX-100 with an aggregation number of 110 adapted a curved rod shape in accordance with experimental observations. The diameter of the rods is ~5 nm and their length is ~12 nm (in unbend state), as determined by visual inspection in Visual Molecular Dynamics (VMD) software. The thickness of the hydrophilic shell was approximately 1 nm, while some polyoxyethylene chains extended for 1.5 nm out of it. The detailed structure of

the hydrophilic shell is quantified by means of the fraction of O atoms found at a given distance from the hydrocarbon core. The graph is shown in Figure 7; here, a mistake made in this graph in the original paper is corrected. Estimated in such a way, shell thickness equals 1.4 nm, from which the half of O atoms are located within 0.45 nm of the surface [64].

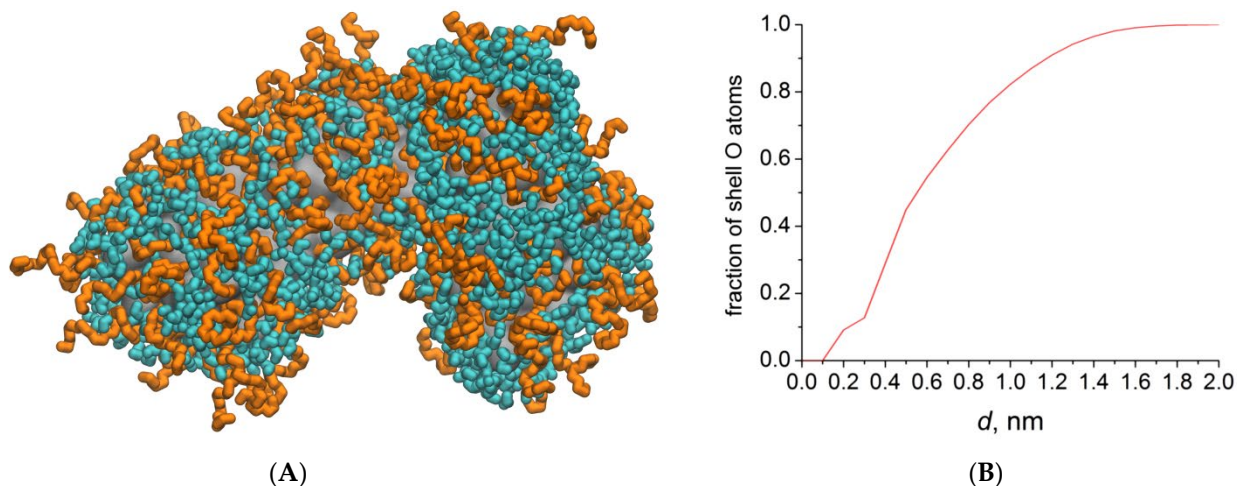


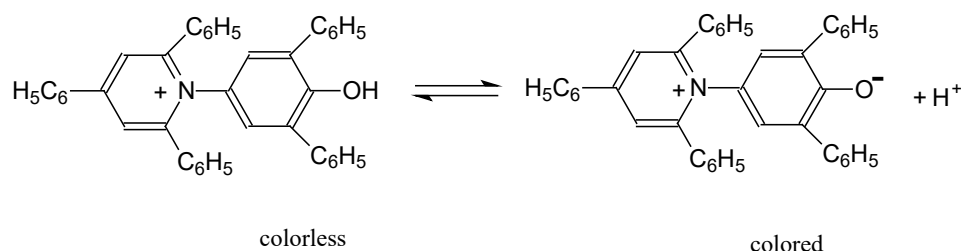
Figure 7. (A) Rod-like TX-100 micelle. Gray: hydrocarbon core, orange: polyoxyethylene chains, blue: water molecules within 0.7 nm from the core. (B) fraction of oxyethylene groups that are within distance d from the core surface.

5. Solvatochromic Indicators in Surfactant Micelles

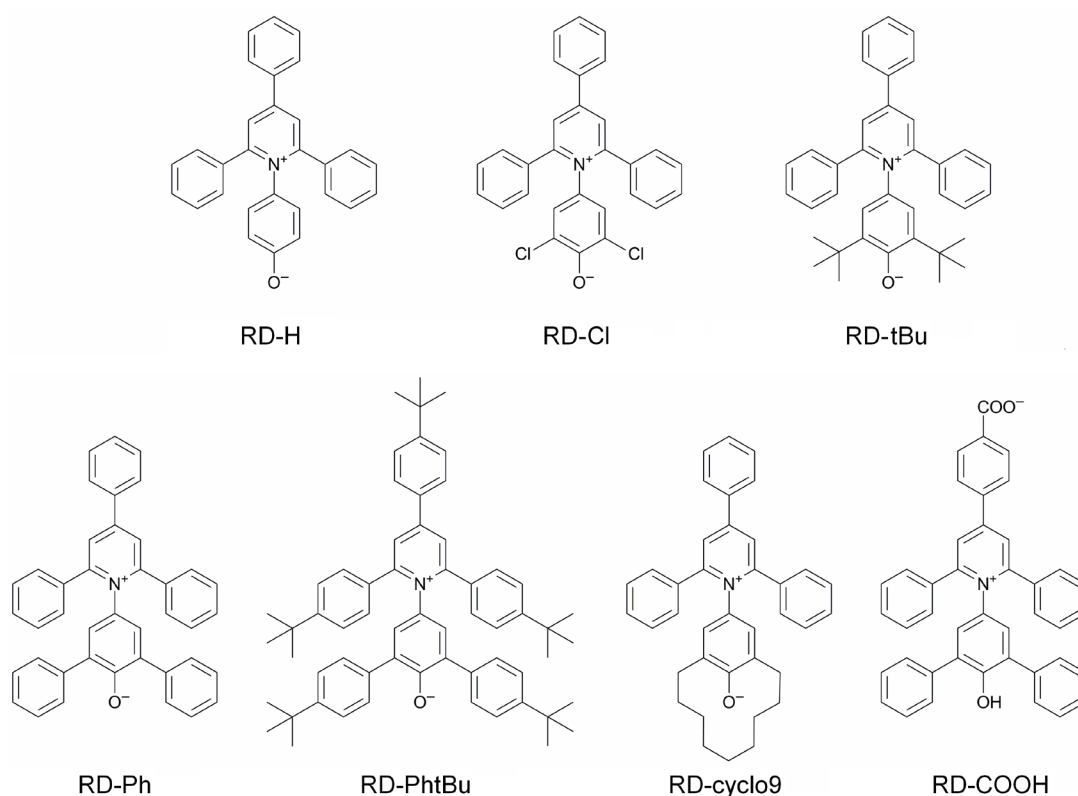
5.1. Choice of Pyridinium-*N*-Phenolate Dyes

Solvatochromic dyes have been widely used for studying colloidal systems since long ago [117], and such works are ongoing [1,118–121]. Among other solvatochromic indicators, the pyridinium *N*-phenolate betaine dyes belong to the most powerful ones [21]. These compounds were often used for studying surfactant micelles and similar nano-sized species [21,117,122,123].

Therefore, we started our research with these dyes in micellar surfactant solutions. The MD simulations were aimed to reveal the locus of the dyes and the solvation/hydration character in the micellar pseudophase. Another reason for this choice is the application of these dyes as acid–base indicators in micellar media. This was first demonstrated for standard Reichardt's dye, a solvatochromic pyridinium *N*-phenolate dye, i.e., 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate (Scheme 2) [19]. Accordingly, not only the colored solvatochromic neutral (zwitterionic) forms (Scheme 3), but also the colorless cations were examined here in micellar environments.



Scheme 2. Acid–base equilibrium of the solvatochromic pyridinium-*N*-phenolate dye, RD-Ph.



Scheme 3. Molecular formulae of betaine dyes examined in this study.

The main results of our modeling are presented below.

5.2. Localization of the Solvatochromic Betaine Dyes in Surfactant Micelles

Overall, molecules of most of the dyes are located on the surfaces of the micelles staying in contact with both the hydrocarbon core and the solution. Still, the dyes differ by the depth of immersion (penetration) into the micelles. It can be described as the distance between the micelle center and the dye molecule center. As dye center, it is convenient to consider the N atom of the pyridinium ring. The average distances are collected in Table 2 and schematically represented in Figures 8 and 9 as a diagram for convenient comparison. The distances below 1.35 nm (SDS) or 1.55 nm (CTAB) are highlighted gray to indicate the approximate extent of the hydrocarbon core. It is difficult to unambiguously set the border because of the ellipsoidal shape of micelles, so we conventionally defined it here as the distance where water fraction appears at least 5%.

Table 2. Average distance (nm) of the N atom of the betaine dyes to the center of the mass of micelles.

Dye	SDS		CTAB	
	⁺ D [−]	⁺ DH	⁺ D [−]	⁺ DH
RD-H	1.47	1.48	1.73	1.91
RD-Cl	1.52	1.45	1.73	1.94
RD-cyclo9	1.37	1.46	1.67	1.84
RD-tBu	1.31	1.40	1.57	1.89
RD-Ph	1.45	1.41	1.67	1.88
RD-PhtBu	0.96	1.10	1.11	1.39
RD-COOH	1.43	1.44	1.76	1.88
RD-COOH	^{D[−]} 1.51		^{D[−]} 1.81	

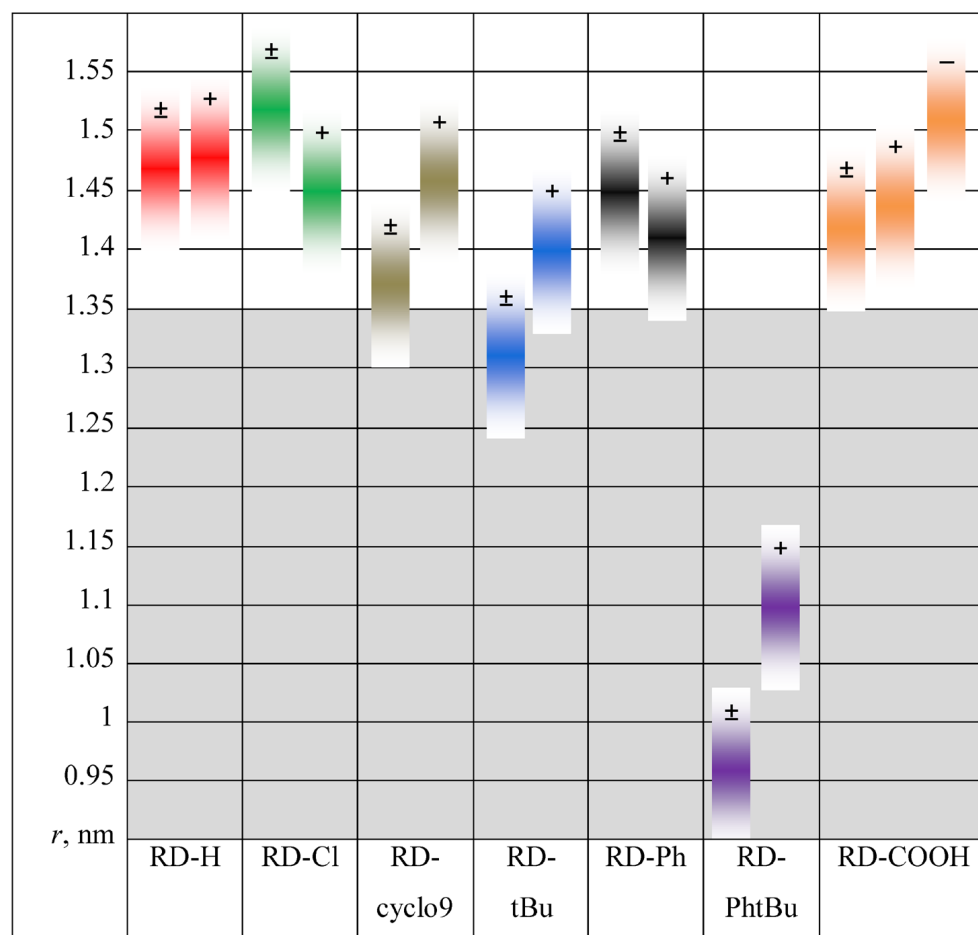


Figure 8. Average distance of the N atom of the betaine dyes to the center of mass of the SDS micelles. The band length corresponds to the range of typical distances.

Less convenient but a more informative characteristic is the distribution function of this distance, $p(r)$, which was computed over MD trajectories and served to find the time-average value. An example of such graphs is shown in Section 5.5 below.

Three observations stem immediately from the diagrams:

- In CTAB micelles, protonation pushes the dye molecule considerably towards the bulk solution by 0.2–0.3 nm, while in SDS micelles the effect is smaller and depends on the dye;
- For zwitterionic forms, the immersion correlates with the steric demands of the substituents. Compact dyes RD-H and RD-Cl are in average located closer to the bulk solution than bulky dyes RD-cyclo9, RD-tBu, RD-Ph, and RD-COOH, with rare exceptions. This becomes most evident in the extreme case of RD-PhtBu, which is deeply buried in the hydrocarbon cores of both micelles.
- In SDS micelles, the dye RD-PhtBu is located ca. 0.35–0.4 nm deeper in the micelle as compared with other dyes. In CTAB micelles, this difference is ca. 0.5–0.55 nm, which is somewhat larger.

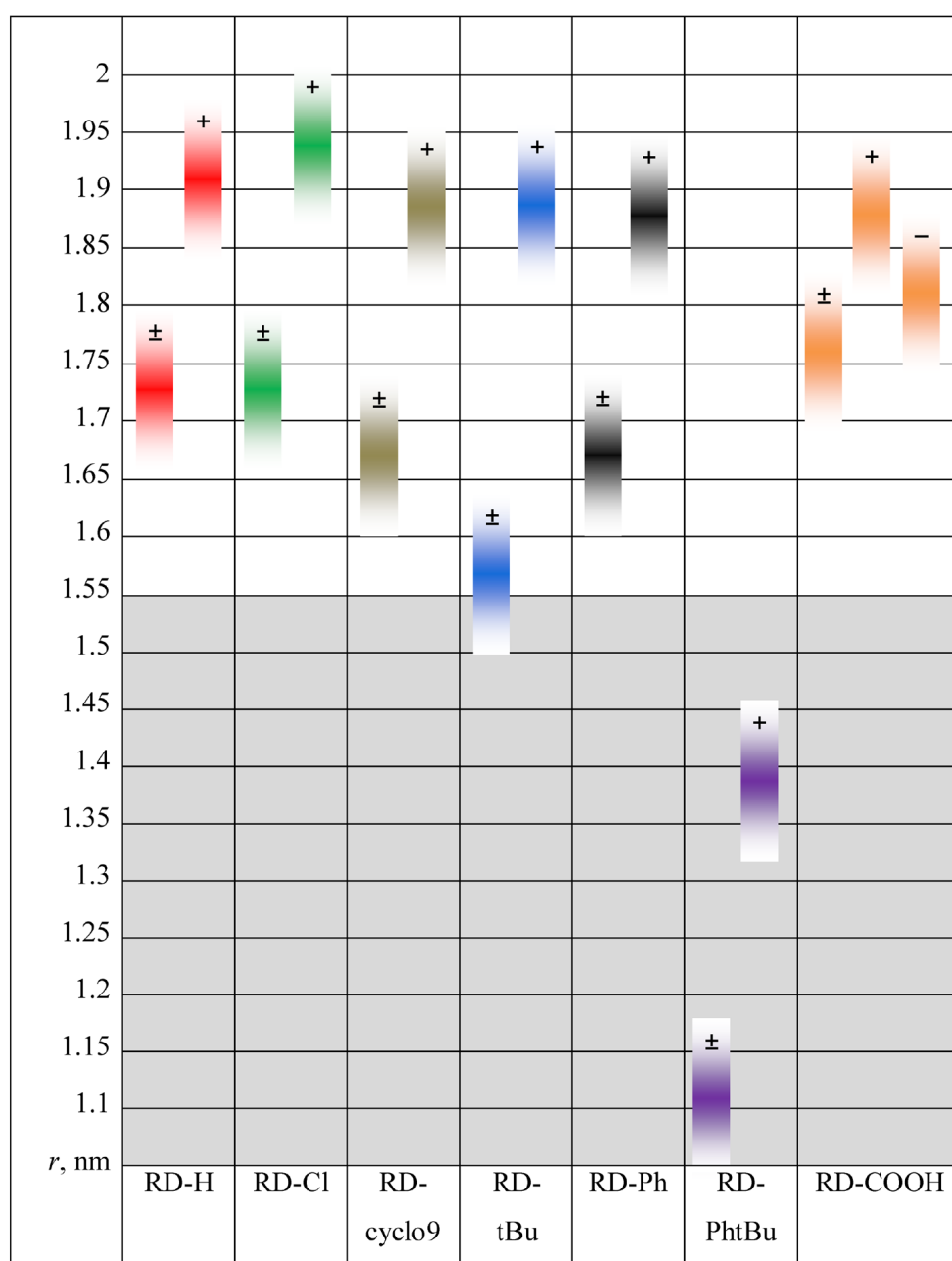


Figure 9. Average distance of the N atom of the betaine dyes to the center of mass of the CTAB micelles. The band length corresponds to the range of typical distances.

5.3. Orientation of the Solvatochromic Betaine Dyes in Surfactant Micelles

An important aspect of the dye localization is the orientation, or placement, of the dye molecule with respect to the micelle surface. Typically, the molecule is placed either roughly parallel to the surface or perpendicular to it (Figure 10). Sometimes both orientations are sampled by turns. The particular placement depends mainly on the substituents, while other factors show a smaller effect. The results of our observations are collected in Table 3.

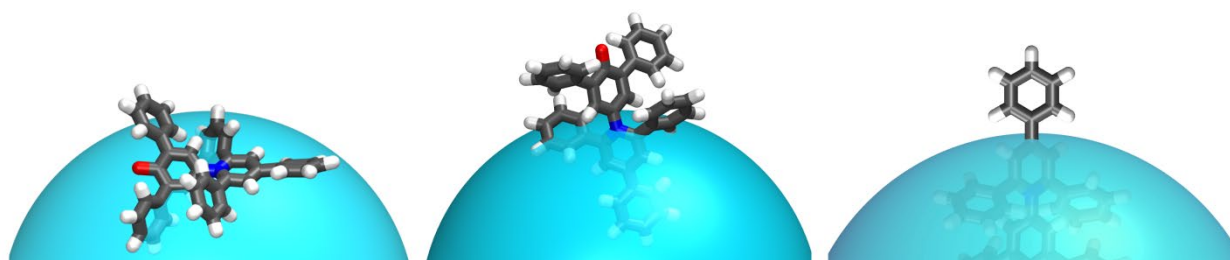


Figure 10. Typical placements of Reichardt's betaine dyes in micelles, shown for the example of the standard dye, RD-Ph. **(Left)** "horizontal" orientation, **(middle)** "vertical" orientation, **(right)** "inverted vertical" orientation.

Table 3. Dominant orientation of Reichardt's dyes molecules in micelles. "H" means horizontal orientation, "V" means the vertical one, "I" means the inverted vertical one. "Sometimes" means a probability of 10–30%; "often" means a probability of >30%.

Dye	SDS		CTAB	
	⁺ D [−]	⁺ DH	⁺ D [−]	⁺ DH
RD-H	H, often V	H	H, sometimes V	H
RD-Cl	H, sometimes V	H	H	H
RD-cyclo9	H, sometimes V	H	H	H
RD-tBu	H, sometimes V	H	H	H
RD-Ph	H, sometimes V	H, sometimes I	H	H, sometimes I
RD-PhtBu	V, often H	I, sometimes H	V, often H	I, sometimes H
RD-COOH	I, sometimes H	H	H, sometimes I	H
RD-COOH		D [−] H	D [−] H	

In more precise terms, we defined the inclination angle of the molecule as $\angle(\text{micelle COM, dye N atom, dye O atom})$ and calculated it for each MD frame. The molecule was said to be in the vertical orientation when θ was less than 40° . The inverted vertical one corresponded to $\theta \leq 130^\circ$, and the horizontal one to $40^\circ < \theta < 130^\circ$. Fraction of time, which the molecule spent in a given orientation, indicates probability of the latter. Still, it was important to perform additional visual examination to check the correct identification of the major orientation: simple geometric criteria were insufficient for characterizing such soft and nonspherical particles as micelle + dye aggregates. It was especially important in the case of RD-PhtBu having very deep immersion into micelles. More elaborate analysis was made using distribution functions of θ , $p(\theta)$, the example of such functions is shown below in Section 5.5.

The horizontal orientation is observed as the most often. The dyes RD-Cl, RD-cyclo9, and RD-tBu behave quite similarly, while each of the other dyes has some unique features. The inverted vertical orientation is sometimes adopted by protonated standard dye RD-Ph and is dominant for protonated RD-PhtBu. The neutral RD-PhtBu mostly stays vertical, and neutral RD-COOH in SDS stays in inverted vertical orientation.

We see that the same dye in the same state shows rather similar behavior in both anionic and cationic micelles, which indicates a minor influence of the headgroup charge on this characteristic. This is a quite unexpected result due to the opposite signs of the charge–charge interactions with the micelles.

The substituents also affect the orientation weakly: the zwitterions of RD-Cl, RD-cyclo9, RD-tBu, and RD-Ph behave similarly. Only the extreme cases of the absence of R^3 substituents (RD-H) or with very bulky substituents $R^1 = R^2 = R^3$ ones (RD-PhtBu) express some deviations. The dye RD-COOH is also an individual case because in the zwitterionic form the negative charge is located on the COO^- group instead of O^- .

The most influential factor appears to be the protonation state of the betaine dyes, which determines the overall charge of the molecule. The protonated forms of all betaine dyes (except of the bulkiest RD-PhtBu) are coherent in having a horizontal orientation in micelles of both surfactants.

To be more precise, for zwitterionic forms, the horizontal orientation is usually skewed towards having the phenolate part somewhat pushed towards the bulk solution. Oppositely, for cationic forms, this orientation implies the molecule being accurately parallel to the surface, or sometimes having the pyridinium part advanced towards the solution.

It is important to compare our data with the information on the locus of the colored zwitterionic form of these dyes in micelles obtained by ^1H NMR spectroscopy. Zachariasse et al. [122] studied the dye RD-Ph in CTAB micelles, with a surfactant: dye ratio of 20:1. It was demonstrated that the dye exerts the largest influence on the methyl groups of $\text{N}(\text{CH}_3)_3^+$ and the hydrogen atoms of the α and β methylene groups. Hence, the dye is located in the micellar surface region. Tada et al. [124] have found that the dichloro derivative RD-Cl is rather deeply penetrated into the cationic micelles, though our MD simulations enable concluding that the locus of the RD-Ph dye is deeper (Figure 9).

For the dye RD-H in cationic micelles, Plieninger and Baumgärtel [125] deduced from the ^1H NMR data the location of the anionic center of the molecule among the $\text{N}(\text{CH}_3)_3^+$ groups, and exposition of the cationic pyridinium part to water. A reverse picture was proposed for the same dye in the SDS micelles. Here, the pyridinium center of the molecule is situated in the plane of the $\text{O}-\text{SO}_3^-$ groups, whereas the phenolate moiety is “immersed in water layers” [125]. Our MD simulations did not confirm such a pronounced penetration of this betaine dye towards the aqueous phase. Additionally, the change in the direction of the zwitterion was observed only for three dyes: RD-Ph (protonated form), RD-PhtBu, and RD-COOH. This is the above-mentioned inverted vertical state.

In Figures 11 and 12, the most probable states of Reichardt’s dyes in zwitterionic and cationic forms in SDS and CTAB micelles, elicited from the observation of the MD data, are presented. The orientation of the dyes with the phenolic part placed inside the micelle occurs due to either their extremely pronounced hydrophobicity (RD-PhtBu) or the good solvation of the COOH and COO^- groups (RD-COOH).

The special case of the acid–base equilibria of the last dye is presented in Scheme 4.

In this case, the colored solvatochromic species is the anion, because of the much stronger basic properties of the phenolate as compared with the carboxylate.

All the above information concerning the location and orientation of different dye species in SDS and CTAB micelles should be understood as an average picture of a huge number of snapshots. It reflects the most probable states of the dyes.

5.4. Hydration of the Solvatochromic Betaine Dyes in Surfactant Micelles

Another essential question that we examined is the local environment, or microenvironment, of the dye molecules. In the surface layer of ionic surfactant micelles, water, hydrocarbon, and electrolyte contact the dye simultaneously, and their proportion affects its visible absorption spectrum. We employed the following approach to elucidate this point. At each time point, the atoms located within 0.4 nm from the dye molecule were enumerated and then divided into three categories: belonging to the micelle hydrocarbon core, belonging to the surfactant headgroups, or belonging to the water molecules. The time-average number of atoms of each category was then computed and converted to the molar fraction of the corresponding component (hydrocarbon, headgroups, or water) in the dye microenvironment. The values for the discussed dyes are presented in Figure 13. The protonated forms of all the dyes (except RD-PhtBu) have a similar hydration in both SDS and CTAB micelles, regardless of the substituent and surface charge. Only RD-PhtBu is considerably less hydrated, which is natural for its deep localization in the micelles.

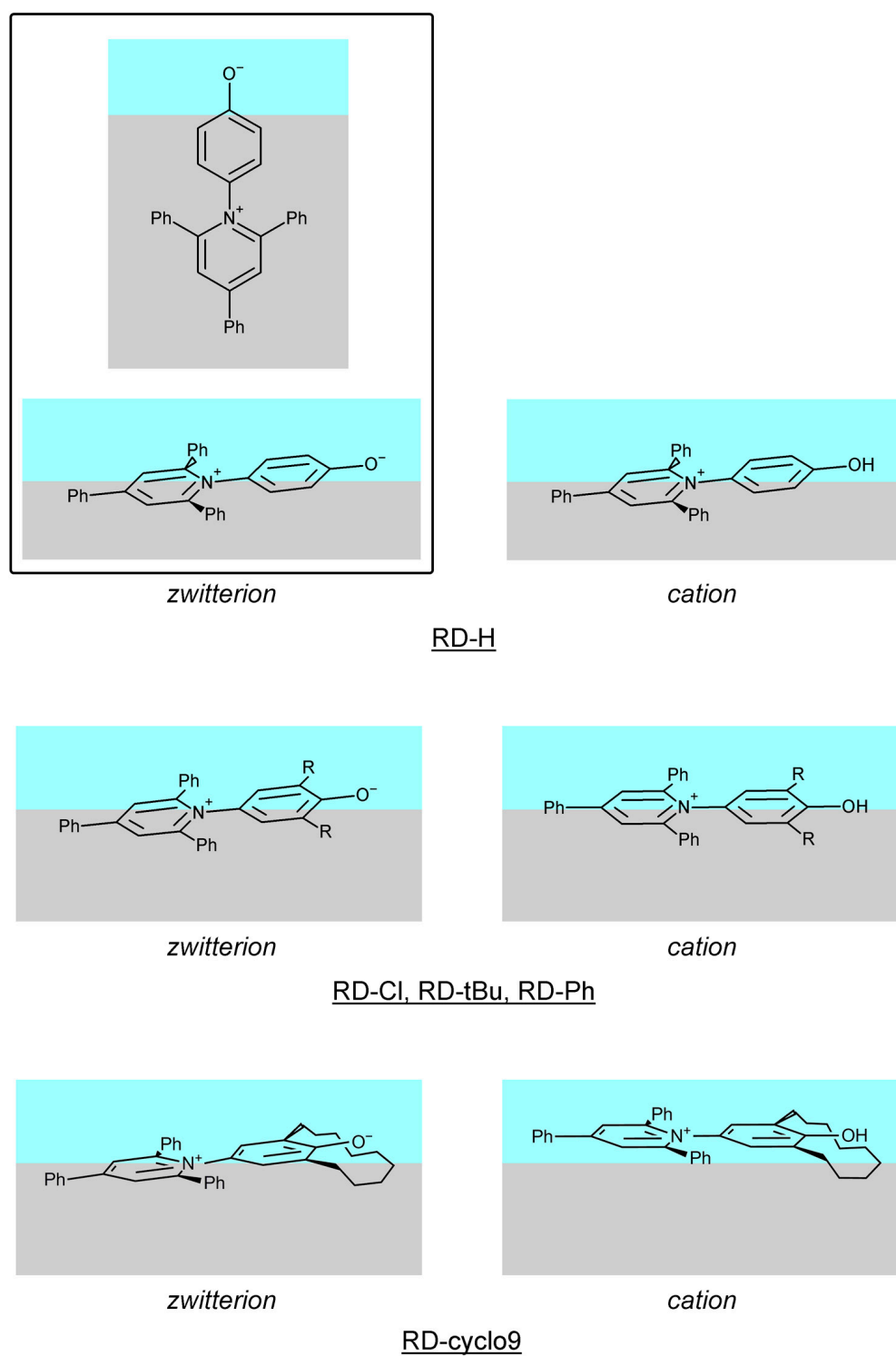


Figure 11. Most probable orientations of the dyes RD-H, RD-Cl, RD-tBu, RD-Ph, RD-cyclo9 in ionic surfactant micelles as deduced from MD simulations.

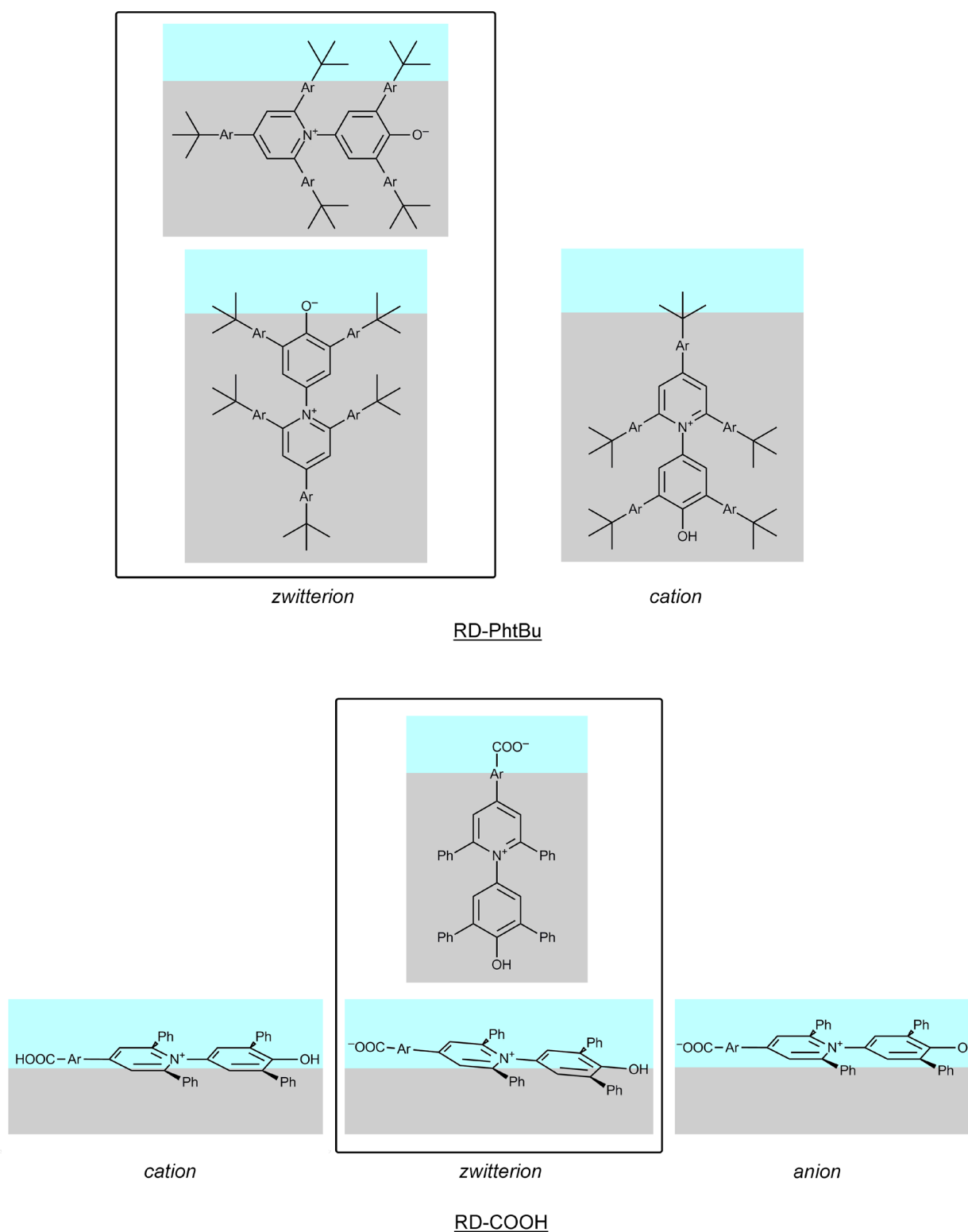
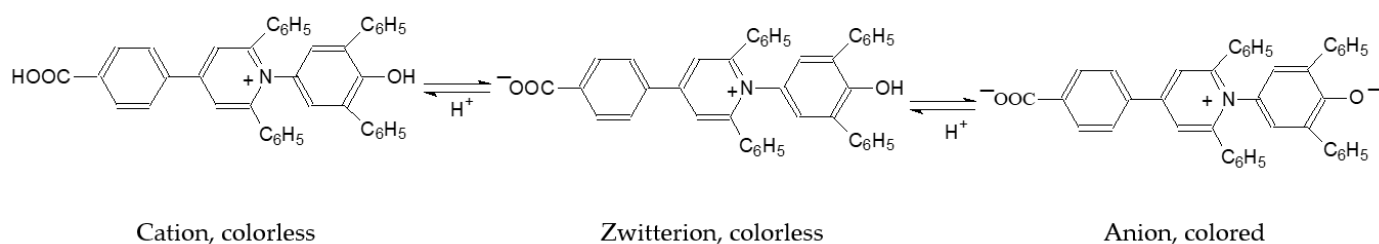


Figure 12. Most probable orientations of the dyes RD-PhtBu and RD-COOH in ionic surfactant micelles as deduced from MD simulations. Adapted from [61].



Scheme 4. Protolytic equilibria of the carboxyl-containing dye RD-COOH. For this dye, only the anion is colored and hence solvatochromic.

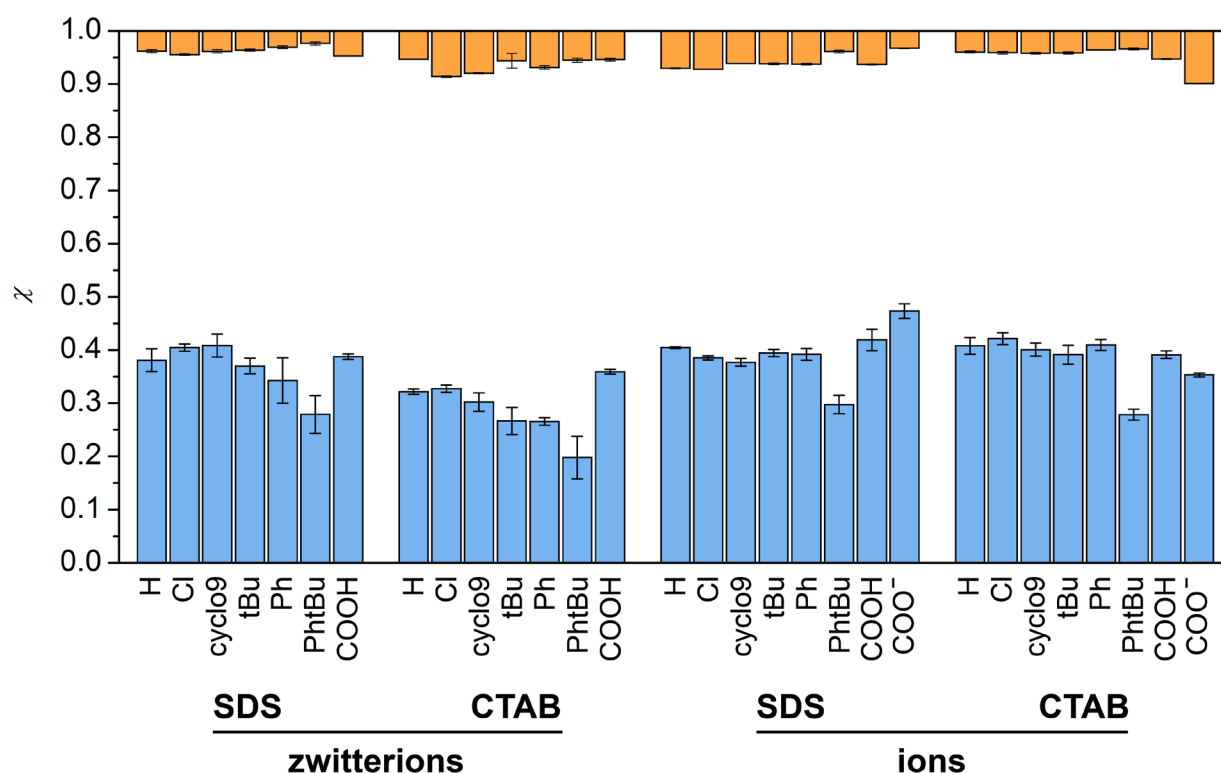


Figure 13. Molar fraction of water atoms (blue columns below) and headgroup atoms (orange columns above) around molecules of different dyes in various conditions. For the dye RD-COOH, zwitterion is colorless and contains OH and COO[−] groups. In the ions section, COOH denotes RD-COOH cation and COO[−] denotes its anion.

- For zwitterions, the influence of substituents is somewhat stronger.
- Zwitterions in CTAB micelles are ~20% less hydrated than in SDS ones (the average difference of $\chi(\text{water})$ is ~0.08 out of ~0.38).
- The molar fraction of headgroups around the dye molecules is short (<0.1). Zwitterions in CTAB and cations in SDS have ca. 2-fold more headgroups around than in the other cases.

Overall, if RD-PhtBu is not considered, the degree of hydration varies in a rather narrow interval. This can be explained by the large size of the betaine dye molecules, which facilitates contact with water, and their quite similar localization.

To get additional insight, similar calculations were performed for the individual phenolic O atom, Figure 14. As will be discussed below, its microenvironment is of a particular importance.

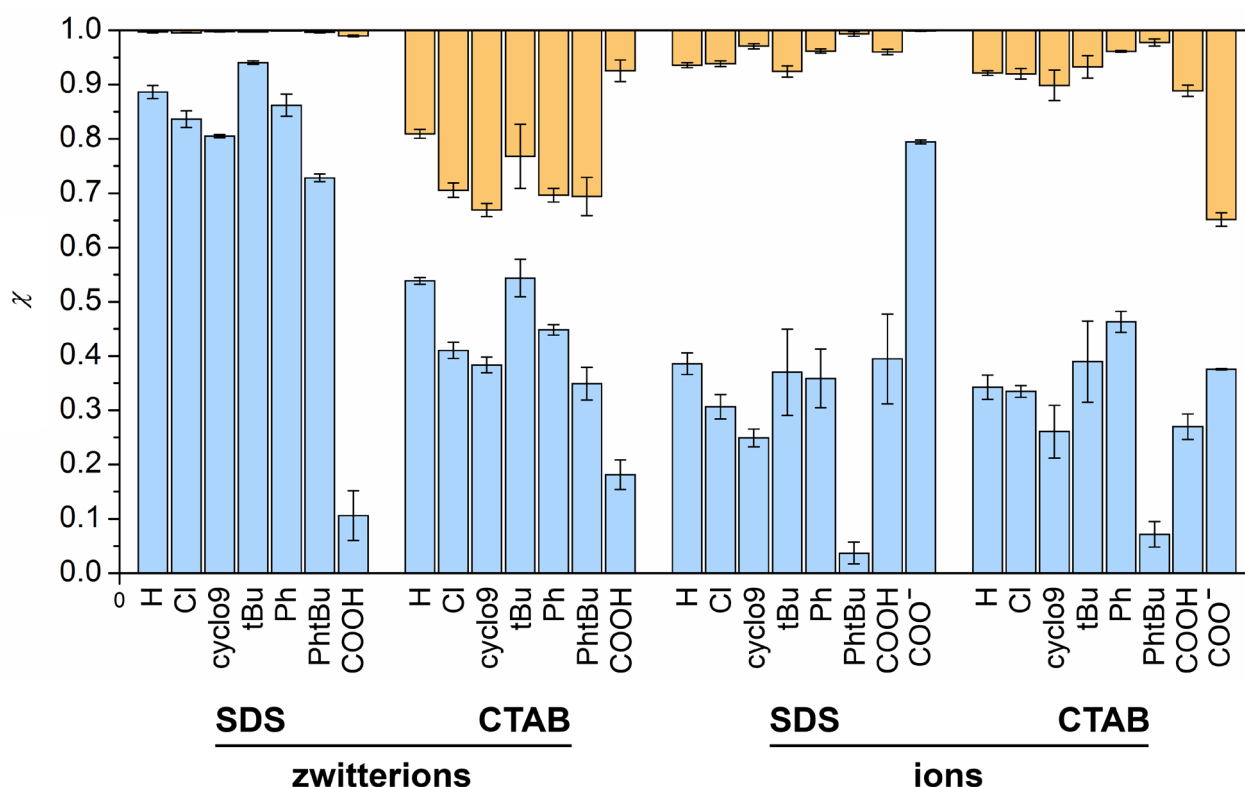


Figure 14. Molar fraction of water atoms (blue columns below) and headgroup atoms (orange columns above) around phenolic O atom of different dyes in various conditions. For the dye RD-COOH, zwitterion is colorless and contains OH and COO[−] groups. In the ions section, COOH denotes RD-COOH cation and COO[−] denotes its anion.

Here, the substituents pronouncedly affect $\chi(\text{water})$ in micelles of both kinds. This is natural because of their proximity to the phenolic O atom.

- The hydration of the OH group in protonated forms depends only weakly on the surface charge, as it was observed for the whole molecule.
- Oppositely, the O[−] atom of zwitterions is much better hydrated in SDS than in CTAB micelles: the $\chi(\text{water})$ difference is ca. 0.4.
- While PhtBu shows the weakest hydration of the OH group among the cations (it is almost isolated from water), RD-COOH is at this place among zwitterions. This occurs due to the competition for water with the COO[−] group in the latter case: the molecule is oriented in such a way that COO[−] is hydrated well, while OH is mostly immersed into the micellar hydrocarbon core.
- Surprisingly, the effect of substituents does not correlate with their steric demand. Under the same conditions, RD-tBu and RD-Ph have the highest $\chi(\text{water})$ together with RD-H despite of the bulky R³ groups. Instead, RD-Cl and RD-cyclo9 have lower $\chi(\text{water})$, succeeded by RD-PhtBu.
- The O[−] atom of zwitterions strongly attracts cationic headgroups and repulse anionic ones. Instead, the OH group of cations interacts similarly with both kinds of headgroups.
- The hydration efficiency of O[−] atom of the zwitterions ⁺D[−] in SDS micelles decreases in the following sequence: RD-tBu > RD-H > RD-Ph > RD-Cl >, etc. In turn, in CTAB micelles, an interaction of the negative oxygen with the positively charged alkylammonium groups takes place. The difference between the hydration of cations ⁺DH in SDS and CTAB micelles is not significant. The special cases of the RD-PhtBu and the anion COOH (RD-COO[−]) in CTAB micelles are quite understandable.

5.5. Influence of Other Factors on the Aforementioned Characteristics

The influence of the length of the hydrocarbon chain of a surfactant on the state of the dye molecule in the micelles was studied separately. For this purpose, simulations of the RD-Ph zwitterion in DTAB and SCS micelles were carried out. In the latter case, the temperature was 50 °C, since at room temperature SCS does not form micelles. To ensure the possibility of a correct comparison with SCS, the simulation of RD-Ph in SDS micelles was repeated at this temperature. It was found that the indicator dye is localized deeper in DTAB micelles than in SDS micelles with the same hydrocarbon chain.

Compared with CTAB micelles, in DTAB micelles the pyridinium part of the indicator molecule is immersed deeper due to the fact that the probability of the orientation shown in Figure 10b (Figure 15B) is higher. On the contrary, in the micelles of SCS and SDS (at 50 °C), the molecule is localized and oriented almost similarly.

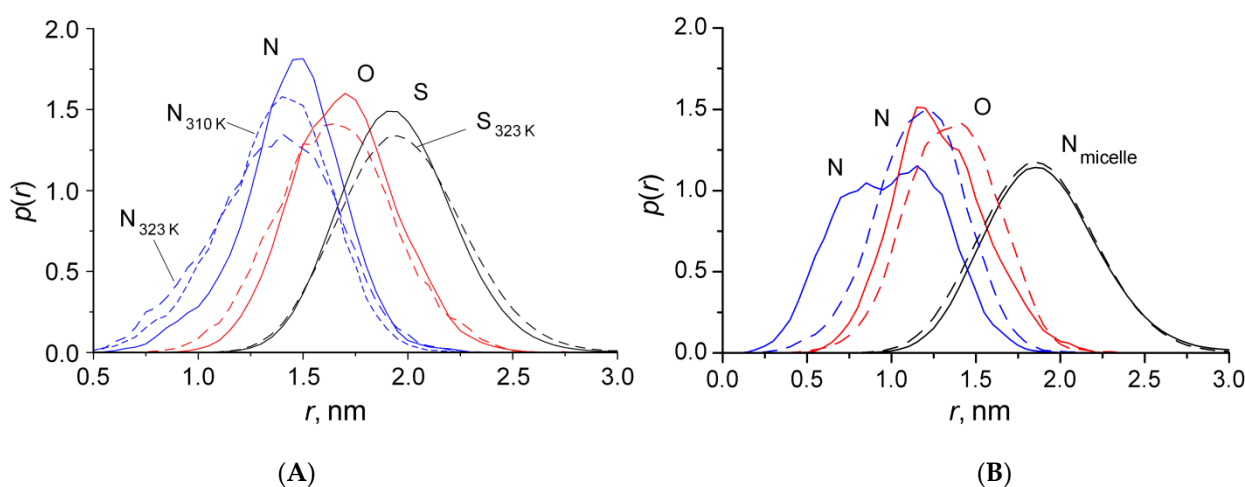


Figure 15. Distance distribution functions between micelle COM and N, O atoms of RD-Ph and N (S) atoms of surfactants. (A) SDS at 298 K (solid), 310 K (short dash), 323 K (long dash). (B) DTAB and CTAB. The curves for CTAB are dashed and shifted left by 0.5 nm.

Thus, the position of the molecule of standard Reichardt's dye in surfactant micelles during the transition from a hydrocarbon chain of one length to another may change differently, depending on the character of the headgroups.

With regard to the microenvironment, in surfactant micelles with a longer hydrocarbon chain, the hydration of both the molecule as a whole and its O atom somewhat decreases, while the fraction of hydrocarbon around it increases [57].

In addition to anionic and cationic surfactants, RD-Ph was studied in micelles of the zwitterionic surfactant CDAPS_n. It was found that the location and microenvironment of the dye in these micelles are generally similar to those in the micelles of CTAB. The dye molecule is located 0.1–0.2 nm (zwitterionic form) or 0.3–0.4 nm (cationic form) closer to the surface than in CTAB micelles. It is important to note that the molecule is almost not in contact with the negatively charged SO_3^- fragment, i.e., it is actually surrounded by positively charged $[\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2]^+$ fragments. This makes its microenvironment in this zwitterionic surfactant close to that in the cationic surfactant CTAB.

Finally, using the example of SDS micelles, the effect of temperature on the state of the solubilized dye in the zwitterionic form was studied. It can be seen that, as the temperature increases from 298 K to 310 K and 323 K, the dye gradually immerses into the micelle, although the difference is small (~ 0.1 nm) and is observed primarily for the pyridinium fragment of the molecule (Figure 15A). The orientation of the dye remains generally unchanged (Figure 16).

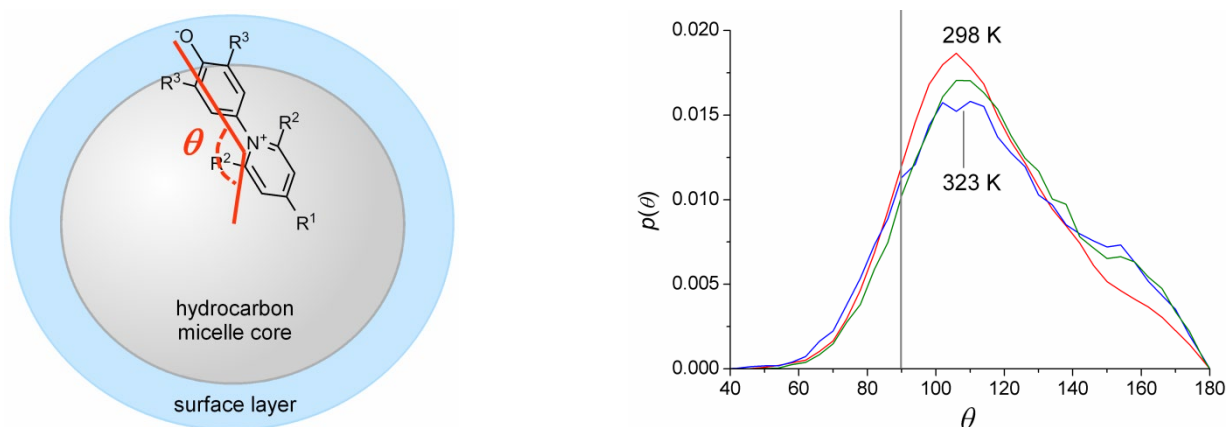


Figure 16. Definition of inclination angle θ (left) and its distribution functions $p(\theta)$ (right) for RD-Ph in SDS micelles at 298 K, 313 K, 323 K. Adapted from [57,61].

The effect of temperature on the microenvironment of the molecule is also insignificant, but in the microenvironment of the O atom the water content gradually decreases from 10.30 ± 0.04 at 298 K to 10.28 ± 0.14 and 9.97 ± 0.09 atoms at 310 K and 323 K, respectively. This can be caused by the thermal expansion of water, because the microenvironment of a constant volume accommodates fewer molecules [57].

5.6. Hydrogen Bonding of the Solvatochromic Betaine Dyes in Surfactant Micelles

Formation of hydrogen bonds through the phenolic O atom was shown to affect the spectrum of Reichardt's dyes. MD simulation allows calculating the average number of hydrogen bonds formed between the chosen species, n_{hb} ; therefore, we examined this point in more detail for standard Reichardt's dye RD-Ph. We used the following criteria to identify an H-bond: (a) donor–acceptor distance no longer than 0.35 nm, and (b) angle $\angle$ (H atom; donor; acceptor) no more than 30° . As the acceptor, the phenolic O atom was chosen, the donors were water molecules. The results for micellar solutions, as well as for pure water solutions, are listed in Table 4 (data for selected entire organic molecular solvents and an ionic liquid $\text{bmim}^+\text{PF}_6^-$ are given for comparison). The values of E_T^N parameter of these solutions are shown alongside for the Discussion below.

This parameter is defined as follows:

$$E_T^N = \frac{E_T(30) - 30.7}{32.4} \quad (3)$$

The numbers 30.7 and 32.4 are chosen so that the E_T^N values for water and tetramethylsilane are 1.00 and 0.00, respectively. Reichardt's $E_T(30)$ parameter is:

$$E_T(30) = hc\tilde{\nu}N_A = 28591 \times \frac{1}{\lambda} (\text{kcal/mol}) \quad (4)$$

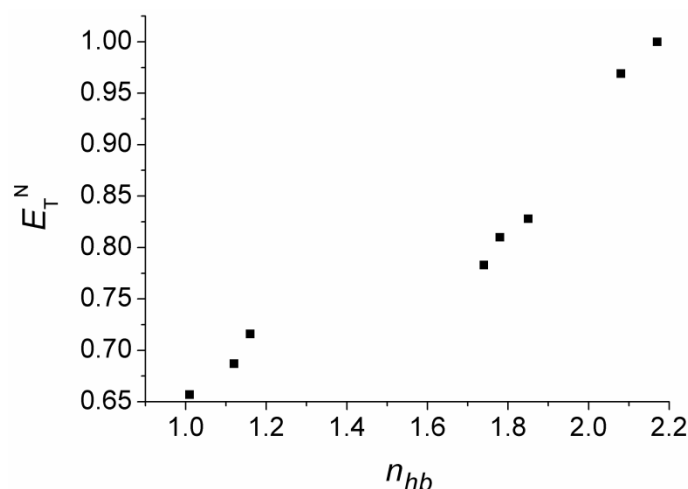
Here, h is the Planck constant, c is the speed of light, $\tilde{\nu}$ is the wavenumber, cm^{-1} , N_A is the Avogadro number, and λ is the wavelength, nm, of the charge-transfer absorption band of the dye. The indicator dye denoted here as RD-Ph was numbered “30” in the original paper, which described a series of similar compounds [126]. This dye is now known as standard Reichardt's solvatochromic dye.

Table 4. Calculated number of hydrogen bonds formed by the O atom of the standard dye RD-Ph with water and the experimentally measured E_T^N parameter of micelles and organic solutions (*in italic*).

Surfactant	$t, ^\circ\text{C}$	n_{hb}	E_T^N ^a
No (pure water)	25	2.17	1.000
No (pure water)	50	2.08	0.969 ^b
SDS	25	1.85	0.828
SDS	50	1.78	0.810
SCS	50	1.74	0.783
<i>Methanol</i>	25	—	0.762
DTAB	25	1.16	0.716 ^c
CTAB	25	1.12	0.687 ^{d,e}
<i>bmim⁺PF₆[−]</i>	25	—	0.667
CDAPSn	25	1.01	0.657 ^d
<i>Ethanol</i>	25	—	0.654
<i>Acetonitrile</i>	25	—	0.460
<i>Dimethyl sulfoxide</i>	25	—	0.444

Note. ^a [14], $c(\text{surfactant}) = 0.01$ M; ^b [127]; ^c [128]; or 0.724 [19]; ^d $c(\text{surfactant}) = 0.001$ M, [14]; ^e 0.705 [19].

An interesting observation follows from Table 4: the $E_T^N(n_{hb})$ dependence is monotonic (Figure 17). The formation of extra hydrogen bonds with surrounding water proportionally increases the measured polarity parameter. The points in Figure 16 form three separate groups: alkylammonium surfactants (left), alkylsulfate surfactants (middle), and water (right). Within each group, the dependence is close to linear with almost the same slope: 0.39 for the first two groups and 0.34 for the third one.

**Figure 17.** E_T^N parameter of a solution vs. the number of hydrogen bonds between the RD-Ph O atom and water.

This observation has a clear theoretical justification: in the total excitation energy of a Reichardt's dye molecule a term can be distinguished that corresponds to the difference in the hydrogen-bonding energy between the electronic ground and excited states. It is natural to assume that the number of H-bonds in both states is the same, because according to the Franck–Condon principle, the system has no time to rearrange during the excitation–relaxation act. Therefore, this term is proportional to the number of H-bonds in the ground state (Equation (5)). This explains the linearity of the dependence E_T^N vs. n_{hb} of micellar solutions.

$$E_T(30) = E_1 - E_0 = \Delta E_{hb} + \Delta E_{non-hb} = (e_{hb\ 1} - e_{hb\ 0}) n_{hb} + \Delta E_{non-hb} \quad (5)$$

where E_0 and E_1 are the ground and excited state energies of the RD-Ph molecule, ΔE_{hb} and ΔE_{non-hb} are contributions of hydrogen bonding and of other interactions to $E_T(30)$,

$e_{hb\ 0}$ and $e_{hb\ 1}$ are the average energies of a single RD-Ph—water H-bond in the ground and excited states.

Beginning from the publication by Zachariasse et al. [122], there is a number of papers that give evidence for higher values of the E_T^N parameter of SDS and other anionic surfactants as compared with that of cationic ones [14,19]. For example, in our laboratory, the values for 16 different anionic surfactant systems, at different concentrations, ionic strength, and temperature, including microemulsions, are determined to be within the range of 0.779–0.835 [14]. For nine different cationic surfactant systems, E_T^N was 0.623 to 0.708, whereas for seven nonionic surfactants, it was 0.645–0.702 [14]. On the first glance, this allows concluding that the surface of the anionic surfactants is better hydrated than that of the cationic ones.

Moreover, it would not be an exaggeration to say that at least a dozen of publications give evidence for a more hydrated or more polar state of different molecular probes in SDS micelles as compared with those in the case of CTAB. Such information is provided by visible spectra of nitroxides [129], fluorescence of 3,3-dimethyl-2-phenyl-1-3H-indole [130], fluorescence of rose Bengal B [131], absorption and pK_a of this dye [132], and position of the visible absorption maximum of the anion of 4-*n*-heptadecyl-7-hydroxy coumarin [133]. The formation of the nonpolar lactone of 5-(*N*-octadecanoyl)aminofluorescein is less expressed in the SDS micellar aqueous solution as compared with cationic and nonionic surfactants micellar systems [134].

MD simulations demonstrate similar hydration of surfactant ions in anionic and cationic micelles if the tail length is the same (Figure 1). In contrast, it should be noted that the Krafft temperature for SCS is approximately 30 °C higher than that of CTAB. This allows assuming that the Stern layer of the SCS is less hydrated than in the case of CTAB. At the same time, the E_T^N value for SCS, 0.783, even after taking into account the temperature influence (see Table 4), can be estimated at 25 °C as 0.801 and is substantially higher than the value $E_T^N = 0.687$ for CTAB. Additionally, the E_T^N value for SDS, 0.828, is substantially higher than that for DTAB, 0.716–0.724. The corresponding values for CTAC and CPC are close to that for CTAB, and the same is true for DTAB and DTAC [14,19]. At the same time, Figure 1 shows similar hydration of the Stern layers of DTAB and SDS.

Therefore, the different behavior of numerous molecular probes in SDS and CTAB is caused by a more pronounced hydration of foreign molecules involved in the Stern layer of SDS, despite comparable water content on the surfaces of the two micelles. Hence, a hypothesis about the more pronounced hydrogen bond ability of water molecules in anionic micelles can be deduced. In any case, the resulting effect manifests itself in the form of an (apparently) more polar surface of SDS micelles.

Here, it is appropriate to recall a new paper, that allows to shed additional light upon the origin of the λ_{max} and, accordingly, E_T^N values [135]. The authors consider the problem of one of the most common solvatochromic indicators, the aforementioned Reichardt's dye, in terms of micro- and macrosolvation. In this work, based on the study of IR spectra in an argon matrix with water additives, it was shown that the direct formation of a hydrogen bond between a water molecule and the oxygen atom of the indicator dye does not itself introduce fundamental changes in the dye, but enhances the effect of the entire solvent continuum. So, even if the true polarity of the micellar surface of CTAB and SDS is similar, more numerous hydrogen bonds in the last case cause an E_T^N increase.

In some cases, the location character of the solvatochromic or solvatofluoric dyes is more specific. For example, Pal et al. report that some fluorescent 3H-indoles are able to recognize two different sites in SDS micelles, while only one type of locus is observed in the case of CTAB micelles [136]. Another very popular fluorescent molecular probe is pyrene [137]. Thiosemicarbazide and thiosemicarbazide pyrene derivatives are also used for examining CTAB and SDS micelles [137]. The location of pyrene in surfactant micelles will be considered in Section 9.

6. Acid–Base Indicators as Useful Tools for Studying Micelles

6.1. Acid–Base Dissociation in Surfactant Micelles

The application of acid–base indicators began from the papers by Hartley [138] and Hartley and Roe [139]. In reviews by El Seoud [140] and Jana and Pal [141], data for a large number of molecular probes, mainly indicators, in surfactant micelles and related systems were accumulated. The key characteristic is the so-called apparent dissociation constant, K_a^{app} :

$$\text{p}K_a^{\text{app}} = \text{pH} + \log \frac{[\text{HB}]}{[\text{B}]} \quad (6)$$

Here, pH refers to the aqueous phase, the values in brackets are equilibrium concentrations of the acidic and basic forms of the molecular probe; charges are omitted for simplicity. They may or may not be fully bonded by the micellar pseudophase, with the former being preferred. The articles by Mukerjee and Banerjee [142], Fromherz [143,144], and Funasaki [145–147] enabled substantiating the relation between the electrical surface potential of micelles, Ψ , and the $\text{p}K_a^{\text{app}}$ value of an indicator (or other molecular probe) completely bound by the micellar pseudophase. This equation therefore may be named as the Hartley–Mukerjee–Fromhertz–Funasaki, or HMFF, equation:

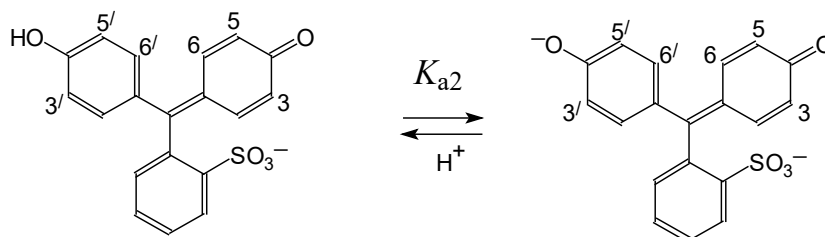
$$\text{p}K_a^{\text{app}} = \text{p}K_a^{\text{w}} + \log \frac{\gamma_{\text{B}}}{\gamma_{\text{HB}}} - \frac{\Psi F}{RT \ln 10} = \text{p}K_a^{\text{i}} - \frac{\Psi F}{RT \ln 10} \quad (7)$$

Here, K_a^{w} is the dissociation constant in water, γ is the activity coefficient of transfer from water to the micellar pseudophase, and K_a^{i} is the so-called intrinsic dissociation constant. Hence, the Ψ value can be determined as given below:

$$\Psi = \frac{RT \ln 10}{F} (\text{p}K_a^{\text{i}} - \text{p}K_a^{\text{app}}) \quad (8)$$

From these positions, one may consider data for a variety of compounds: nitrophenols [148], hydroxyanthraquinones [149], substituted diarylamines [150], fluorescein dyes [17,18,132,134], rhodamines [31,151–155], azo dyes [156]; acridines [157], and many other indicators [13,19,97,133,140–147,158–166].

Sulfonephthaleins (Scheme 5) belong to the most popular acid–base indicators, and it is not surprising that they were widely used in examining surfactant micelles [142,145–147,164,166–176].

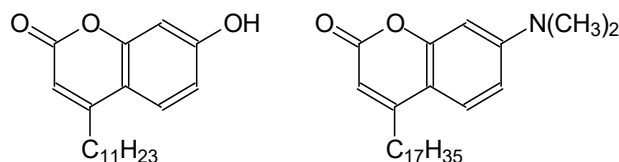


Scheme 5. Dissociation of sulfonephthalein dyes (phenol red: no substituents; bromophenol blue: 3,3',5,5'-tetrabromo phenolsulfonephthalein; bromocresol green: 2,2'-dimethyl-3,3',5,5'-tetrabromo-; bromocresol purple: 3,3'-dimethyl-5,5'-dibromo-; bromothymol blue: 2,2'-dimethyl-5,5'-di-*iso*-propyl-3,3'-dibromo-; *o*-cresol red: 3,3'-dimethyl-; *m*-cresol purple: 2,2'-dimethyl-; thymol blue: 2,2'-dimethyl-5,5'-di-*iso*-propyl phenolsulfonephthalein).

Some $\text{p}K_a^{\text{app}}$ values of these dyes, which were used for the Ψ determination, will be analyzed below.

Coumarin dyes are of particular interest due to their frequent use in determining the electrical potential of interfaces. The indicator properties of the relatively hydrophilic mother compound were demonstrated as early as 1970–1973 [177,178]. In order to ensure the fixation of the reporter molecule to lipid and surfactant assemblies, long hydrophobic

hydrocarbon chains were tailored to the coumarin dye [25,95,97,143,144,179–184]. The hydrophobic coumarins (Scheme 6) were basic compounds for developing the quantitative interpretation of the pK_a^{app} values in micelles [95,97,133,144,160,161,184].

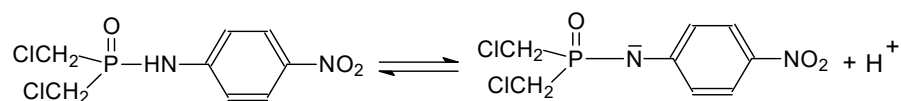


Scheme 6. Molecular structures of two hydrophobic coumarins.

Petrov and Möbius used the hydrophobic coumarin for studying mono- and multilayers [40,41,43–45], and Yamaguchi et al. applied it to pH spectrometry both in surfactant monolayers on water [42] and on pure water interface [48,49].

As mentioned above, the standard solvatochromic Reichardt's dye was applied as an acid–base indicator for micelles [19]. The large size of the dye raises questions about the credibility of the information about the micelle itself, because the obtained data rather reflect the properties of the dye [185]. Nevertheless, the Ψ values obtained via Equation (8) [13,14,20] did not differ significantly from those determined using other indicators. The pK_a^{app} values of different Reichardt's dyes were determined also in surfactant micelles [186] and microemulsions [187]. These and other results are referred to in a review paper by Machado et al. [21].

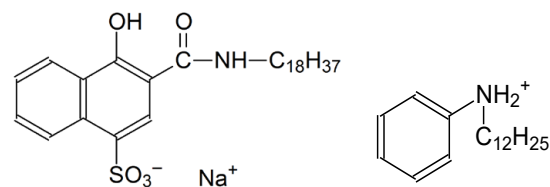
Several rarely used molecular probes should also be mentioned. For example, Zakharaova et al. [188] determined the pK_a^{app} values of a NH-acid, 4-nitroanilide of *bis*(chloromethyl) phosphinic acid (Scheme 7), in CTAB and SDS micellar solutions:



Scheme 7. Dissociation of the 4-nitroanilide of the *bis*(chloromethyl) phosphinic acid.

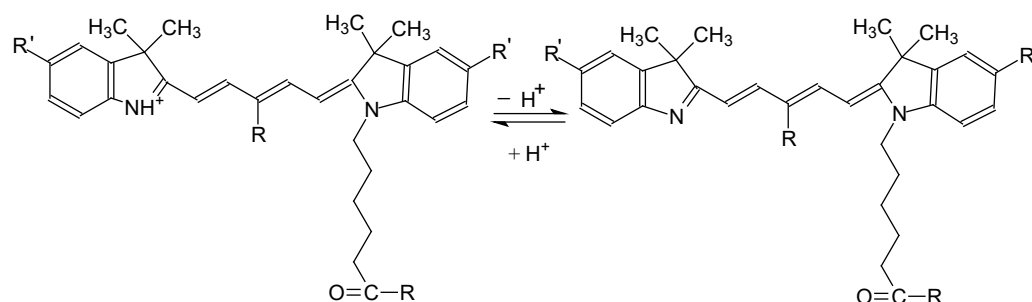
Even earlier, a set of derivatives of phosphonic acid were examined in CTAB, CTAC, and SDS solutions [189]. In both studies, the dependence of the pK_a^{app} values on the surfactant concentrations was obtained in order to estimate the pK_a^{app} s under conditions of complete binding to micelles, which is difficult to reach experimentally.

Khaula et al. [162] used the following two indicators (Scheme 8): in solutions of CTAB, SDS, and a nonionic surfactant Tween 80.



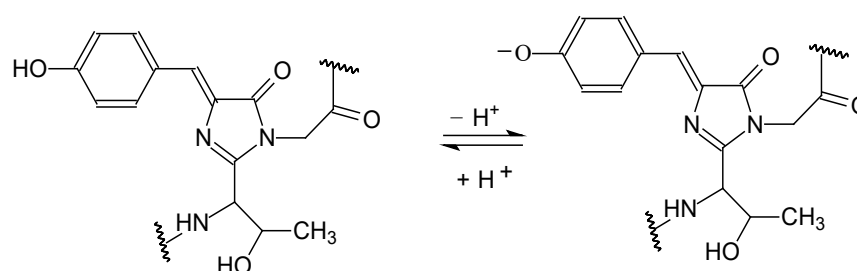
Scheme 8. Hydrophobic indicators used for studying micellar solutions [162].

In addition to such small molecules, large-sized ones are also used in studying colloidal and biocolloidal systems. For instance, relatively recently, Clear et al. [190] applied polymethine dyes (Scheme 9) as optical liposome pH sensors:



Scheme 9. Acid–base equilibrium of polymethine dyes proposed for pH sensing [190].

Of special interest is the experimental and theoretical study of the acidic dissociation of the so-called GFP (or green fluorescent protein) fluorophore (Scheme 10) [191,192]:



Scheme 10. Acid–base equilibrium of Green fluorescent protein fluorophore (GFP) [191,192].

In addition to spectrophotometric and fluorimetric methods, potentiometric determination of the pK_a^{app} values of molecular probes, including carboxylic and phosphororganic acids, in surfactants were described in detail [193–201].

Maeda performed a detailed thermodynamic analysis of potentiometric acid–base titrations in micellar systems [202,203]. Popović-Nikolić et al. [204,205] used the potentiometric method in studying some biologically active compounds in water in the presence of surfactants.

The dependence of the ^{13}C NMR shifts on pH was used for determination of the pK_a^{app} value of tetradecanoic acid in micelles of a sugar-derived surfactant [206]. ESR probes were also used as acid–base indicators in different colloidal systems [207–212].

6.2. Binding of Indicators by Surfactant Micelles

In any case, the problem of the completeness of binding by micelles is of key significance. A potentiometric study of eleven carboxylic acids with concentrations of 5×10^{-4} M in 0.01 M Triton X-100 solutions allowed Chirico et al. [196] to conclude that, judging by their pK_a^{app} s, acids from acetic to valeric were not bound by the micelles. Even pelargonic and undecanoic acids are included into the micelles almost completely only on increase in the TX-100 concentration. The results obtained by Boichenko et al. with propanoic, butanoic, pentanoic, and hexanoic acids in Brij 35 and SDS solutions [199] and by Eltsov and Barsova with undecanoic, tetradecanoic, and hexadecanoic acids in solutions of CTAB, SDS, Brij 35, and CDAPS [197] confirm these observations.

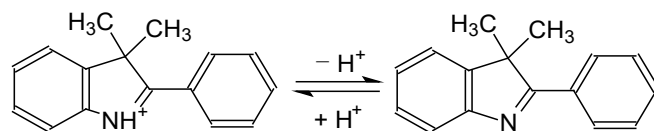
The binding of indicator dyes can be described by so-called binding constants, K_b ; see Equation (9).

$$K_b = \frac{[i_m]}{[i_w](c_{surf} - \text{cmc})} \quad (9)$$

Here, the equilibrium concentrations of the dye ion or molecule, i , fixed at micelles (m) or located in the bulk phase (w) are expressed in moles per liter of the whole solution; $c_{surf} - \text{cmc}$ corresponds to the micellized surfactant; cmc is the critical micelle concentration. These constants can be determined using the dependence of pK_a^{app} on c_{surf} [188,189]. For the above shown *p*-nitroanilide of the bis(chloromethyl) phosphinic acid, the binding

constants were determined using the dependence of pK_a^{app} on the CTAB concentration [188]. For the anion and molecule in CTAB solutions, $K_b = (4.0\text{--}4.8) \times 10^4 \text{ M}^{-1}$ and $(300\text{--}540) \text{ M}^{-1}$, respectively, depending on the buffer nature. In SDS solvents, the values were much lower, 1 and 64, respectively. These values of binding constants enable estimating the pK_a^{app} values at complete binding [188].

Sarpal et al. [130] estimated the binding constant of the equilibrium forms of 3,3-dimethyl-2-phenyl-3H-indole (Scheme 11), a fluorescence polarity probe, using fluorescence measurements.



Scheme 11. Acid–base equilibrium of 3,3-dimethyl-2-phenyl-3H-indole.

In SDS micellar solutions, the values $K_b = 1.01 \times 10^3 \text{ M}$ and $12.9 \times 10^3 \text{ M}$ for the B and HB^+ forms were determined at pH 9.5 and 1.0, respectively. Therefore, the ionic strength is relatively high in the second case. This is in line with the cmc values of SDS determined by the authors in these two cases, $(7.0\text{--}7.4) \times 10^{-3} \text{ M}$ and $(1.4\text{--}1.8) \times 10^{-3} \text{ M}$, respectively. Whereas the value in water, pK_a^w , equals to 3.25, the pK_a^{app} value in 0.06 M SDS solution is 4.75. As it follows from the $K_{b,B}$ value, under these conditions the $[B_m]/[B_w]$ ratio is 61, and hence the experimental pK_a^{app} should be considered as a value at complete binding by micelles.

In Table 5, the binding constants obtained using the dependencies of pK_a^{app} vs. c_{surf} , as a rule at 25 °C; the values of the ionic strength, I , are indicated. Here, some typos in the previous paper [14] are corrected.

Table 5. Binding constants, K_b , of indicators and the pK_a^{app} values [$\pm(0.03\text{--}0.06)$], obtained by extrapolation to complete binding of both equilibrium forms [154,174,213].

Indicator System	Surfactant	I , M	$K_{b,HB}$, M^{-1}	$K_{b,B}$, M^{-1}	pK_a^{app}
Methyl yellow, HB^+/B	Brij 35	0.05	65	5.8×10^3	1.12
Rhodamine B, $HB^+/B^\pm$	Brij 35	0.05	4.0×10^3	5.9×10^2	4.08
Bromophenol blue, HB^-/B^{2-}	Brij 35	0.01	1.2×10^4	1.25×10^3	5.10
Bromophenol blue, HB^-/B^{2-}	Triton X-100	0.01	1.1×10^4	1.7×10^3	5.00
Bromophenol blue, HB^-/B^{2-}	Triton X-305	0.01	2.4×10^3	1.3×10^2	4.88
Bromophenol blue, HB^-/B^{2-}	Nonylphenol 12	0.05	2.0×10^4	2.7×10^3	4.80
Bromophenol blue, HB^-/B^{2-}	Tween 80	0.05	1.3×10^4	9.0×10^2	5.09
Phenol red, HB^-/B^{2-}	Brij 35	0.01	2.85×10^2	32	8.73
Phenol red, HB^-/B^{2-}	CTAB	0.02 (KBr)	3.75×10^4	9.06×10^4	7.45
Phenol red, HB^-/B^{2-}	CTAB	0.05 (KBr)	1.64×10^4	1.55×10^4	7.71
Phenol red, HB^-/B^{2-}	CTAB	0.4 (KBr)	2.5×10^3	2.6×10^2	8.72
Bromothymol blue, HB^-/B^{2-}	SDS	0.2 (NaCl)	1.3×10^4	16	9.90

Corresponding values were also determined for indicator dyes in microemulsions [172,173] and phospholipid liposomes [171].

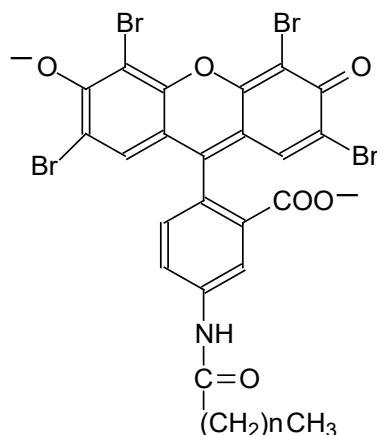
The most popular method for ensuring complete binding of acid–base indicators to micelles is attaching long hydrocarbon chains to them [25,40,41,43–45,95,99,133,134,143,144,152,153,155,160,162,179–184,190]. Otherwise, the opposite charge of the ionic forms of indicators and inclusion of halogen atoms and nitro groups favors the binding by micelles. Therefore, another issue is the depth of penetration of such modified molecular probes into the pseudophase. This will be considered in the present paper using MD simulations.

Application of the NMR spectroscopy method allows expecting the location of the acid–base indicators as a rule in the Stern layer region [99,122,124,125,160,181,182].

Finally, it is important to know to what extent the pK_a^w values of long-tailed indicators coincide with those of the unmodified compounds [133,134].

The same refers to the pK_a^{app} values, which is easy to check experimentally, contrary to the case of aqueous solutions, where the long-tailed dyes are poorly soluble and can form their own micelles.

Additionally, despite firm fixation to micelles, similar dyes with hydrocarbon tails of unequal length sometimes exhibit different properties. For example, the quenching of fluorescence by *N,N*-dimethylaniline in CTAB micelles occurs dissimilarly for two eosin derivatives with hydrocarbon length, $n = 11$ and 15 , respectively (Scheme 12) [214].



Scheme 12. Molecular structure of hydrophobic derivatives of eosin (the dianionic form).

As the pK_a^w values for long-tailed dyes are difficult to determine in water, the comparison was made in aqueous 1-butanol (Table 6).

Table 6. Indices of the dissociation constants of esters of fluorescein dyes in aqueous 1-butanol and CTAC micelles.

Dye	<i>n</i> -Butanol—Water, 82: 18 by Mass [215]		CTAC Micelles, 4.0 M KCl [18]	
	pK_{a0}	pK_{a1}	pK_{a0}^{app}	pK_{a1}^{app}
Ethylfluorescein	2.68 ± 0.02	8.44 ± 0.07	1.86 ± 0.02	6.59 ± 0.03
<i>n</i> -Decylfluorescein	2.53 ± 0.02	8.56 ± 0.03	2.13 ± 0.01	6.61 ± 0.07
<i>n</i> -Hexadecylfluorescein	—	—	1.58 ± 0.04	7.06 ± 0.03
Ethyleosin	—	3.71 ± 0.05	—	1.11 ± 0.03
<i>n</i> -Decyleosin	—	3.86 ± 0.04	—	1.18 ± 0.05

Additionally, the data in CTAC micelles at high ionic strength of the bulk phase shed some light upon the role of the length of the hydrophobic radical on the acid–base properties of the firmly bound indicator.

Bissell et al. created earlier a very interesting complicated construction [216]. These authors synthesized a number of fluorescent photoinduced electron-transfer sensors with targeting/anchoring modules called by the authors as “molecular versions of submarine periscopes” for mapping membrane-bounded protons. The pK_a^{app} s in micellar solutions of CTAC, SDS, and Triton X-100 were determined; the complete binding is observed at proper hydrophobicity of the anchoring tail group [216].

On the other hand, an approach was developed for estimating the Ψ values in the diffuse layer beyond the micellar surface with the help of indicators—derivatives of the benzoic acid [15,16].

In addition to examining surfactant micelles, the pK_a^{app} values of indicator dyes were determined in phospholipid liposomes [19,25,133,143,171,178–183,190,207], polyelectrolyte solutions [32,33], gelatin films [34], solid surfaces [35,36,217], mono- and multilayers of

surfactants [40–45] and polymers [46,152], and on pure water surface [47,48,218–223], including air bubbles in water [49].

7. Experimental Determination of the Surface Electrical Potential of Micelles Using Acid–Base Indicators

Now it is important to consider different methods used for the Ψ determination (Equation (7)), first, for evaluation of the pK_a^i in ionic micelles. This question has been systematized by Grieser and Drummond [13] and afterwards discussed in several articles from this group [10,14,224].

The first approach is based on equating the pK_a^i to pK_a^w [139,145]. However, it was revealed that as a rule, the pK_a^{app} value in nonionic surfactant micelles substantially differs from the value in water [142,146,225]. The above assumption is reasonable only if the surface is well hydrated, and there are some other reasons for using such an approach [35,36].

The second approach consists in screening the surface charge of micelles by high concentrations of an electrolyte in the bulk (aqueous) phase [18,169,170,226]. This allows consider the pK_a^{app} value in the same ionic micelles at high ionic strength as the pK_a^i . However, there is some evidence for incomplete charge screening even at several moles per liter of electrolytes, and too high concentrations also strongly influence the viscosity and other properties of the aqueous phase [10,14,18,156,157,163,164]. Contrary to the micellar solutions of CTAB and nonionic surfactants, in the case of SDS the precipitation at high NaCl concentrations may occur [149]. High ionic strength often leads to polymorphic transformations of the micelles. Additionally, the interpretation of the pH measurements using glass electrodes in cells with liquid junction in such salt solutions becomes less obvious.

The third approach uses the pK_a value of an indicator in water–organic solvents for estimating the pK_a^i value. In this case, two steps are to be made: (i) the composition of a water–organic solvent “s” should be selected, and (ii) the pK_a^i value should be equated to the difference ($pK_a - \log {}^w\gamma_{H^+}^s$) [19,133,134,144,147,156,157,163,164,227,228]. The choice of the appropriate composition of the binary solvent is made using the absorption maximum of the dye. This value must coincide with that in the micelles, and the relative permittivity of the mixed solvent is equated to that of the micellar pseudophase. However, it should be remembered that both λ_{max} values and pK_a s in isodielectric solvents sometimes differ substantially. Additionally, the ${}^w\gamma_{H^+}^s$ values used in the cited papers differ from those estimated by the commonly accepted tetraphenylborate assumption [10,14,224].

The fourth approach proposes to use the pK_a^{app} value in micelles of nonionic surfactants as the pK_a^i in ionic micelles [10,13,14,62,95,144,146,149,229]. This method is probably the most often used. The idea of equating the pK_a^i to the pK_a^{app} of the same indicator located at a noncharged surface was also implemented at studying mono- and multilayers [40,41,43–45].

The fifth approach presumes utilization of two indicators, which are cationic and nonionic acids, HB^+ and HA , respectively [99,144,162,183]. The main idea consists in the assumption ${}^w\gamma_{HB^+}^s = {}^w\gamma_{A^-}^s$ for the two indicators. This is based on comparing the dependence of the pK_a s of a cationic and neutral hydrophobic coumarins [144]. Our experiments with the *n*-decylfluorescein that is a dual cationic and neutral acid two-step indicator demonstrated that the ${}^w\gamma_{H_2R^+}^s = {}^w\gamma_{R^-}^s$ assumption is not universal [14].

However, the determination of Ψ values both by different approaches and by different indicators, as a rule, leads to different results for the same ionic micelle.

In Tables 7–11, some examples of the Ψ scatter are presented. Here, the pK_a^{app} values in micelles of nonionic surfactants were used as the pK_a^i in ionic micelles, Equation (8). The data refer to the complete binding by all kinds of micelles under consideration, as a rule, at 25 °C or room temperature. The ionic strength is indicated if the exact value is available in the cited papers. At low ionic strength, its variation has a particularly noticeable effect on the Ψ value.

Table 7. Value of Ψ of the CPC micelles at an ionic strength of 0.05 M [14].

Indicator	$\Delta pK_a^{app} = pK_a^{app} - pK_a^w$		Ψ , mV
	In CPC Micelles, 0.05 M Cl^-	In Nonionic Micelles	
Bromophenol blue, $-/=$	−2.16	0.61	+164
Bromocresol green, $-/=$	−1.68	1.03	+160
Bromocresol purple, $-/=$	−1.32	0.91	+132
Bromothymol blue, $-/=$	−0.94	1.64	+152
<i>n</i> -Decyleosin, 0/−	−1.9	0.71	+154
<i>n</i> -Decylfluorescein, 0/−	−1.39	0.69	+123
<i>n</i> -Decylfluorescein, +/0	−2.15	−0.80	+80
Reichardt's dye, +/±	−1.55	0.46	+118
<i>N,N'</i> -di- <i>n</i> -octadecylrhodamine, +/±	−0.76	0.97	+102

Table 8. Value of Ψ of the CTAB micelles at low ionic strengths [10,148,160,197].

Indicator	pK_a^{app}		Ψ , mV	Ionic Strength, M
	In CTAB Micelles	In Brij-35 Micelles		
Bromophenol blue, $-/=$	2.26	5.10	+168	0.011
Bromothymol blue, $-/=$	6.59	9.19	+153	0.011
2-Nitro-4- <i>n</i> -nonylphenol, 0/−	5.86	8.52	+157	<0.01
4-Octadecylnaphthoic acid, 0/−	4.20	6.60	+142	0.014
<i>N,N'</i> -di- <i>n</i> -octadecylrhodamine, +/±	2.24	4.12	+111	0.019
Tetradecanoic acid, 0/−	5.34	6.36	+60	<0.01

Table 9. Value of Ψ of the SDS micelles at an ionic strength of 0.05 M [10,14,62].

Indicator	ΔpK_a^{app}		Ψ , mV
	In SDS Micelles, 0.05 M Na^+	In Nonionic Micelles	
2,6-Dinitro-4- <i>n</i> -dodecylphenol, 0/−	1.51	−0.09	−95
<i>n</i> -Decyleosin, 0/−	2.63	0.71	−113
<i>n</i> -Decylfluorescein, 0/−	2.65	0.69	−116
<i>n</i> -Decylfluorescein, +/0	2.23	−0.80	−179
Reichardt's dye, +/±	2.06	0.46	−94
<i>N,N'</i> -di- <i>n</i> -octadecylrhodamine, +/±	1.97	0.97	−59
Rhodamine B, +/±	2.10	1.0	−65
Hexamethoxy red, +/0	2.14	−0.90	−179
Neutral red, +/0	≈2.3	≈−0.8	−183
Methyl yellow, +/0	1.56	−2.13	−218

Table 10. Value of Ψ of the SDS micelles at low ionic strengths [10,148,156,160,197].

Indicator	pK_a^{app}		Ψ , mV	Ionic Strength, M
	In SDS Micelles	In Brij-35 Micelles		
2-Nitro-4- <i>n</i> -nonylphenol, 0/−	10.05	8.52	−90	
4-Octadecylnaphthoic acid, 0/−	8.10	6.60	−88	
Tetradecanoic acid, 0/−	8.45	6.36	−123	
<i>N,N'</i> -di- <i>n</i> -octadecylrhodamine, +/±	5.52	4.12	−83	0.02

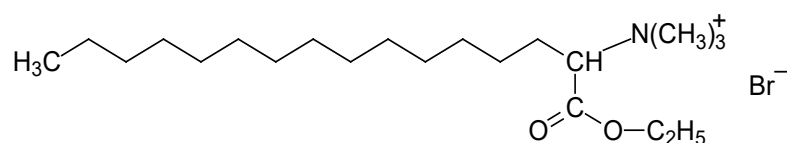
Table 10. Cont.

Indicator	pK_a^{app}		Ψ , mV	Ionic Strength, M
	In SDS Micelles	In Brij-35 Micelles		
Rhodamine B, +/±	5.70	4.08	−96	0.015
Hexamethoxy red, +/0	5.89	2.10	−224	0.01
Neutral red, +/0	9.17	5.64	−208	
Methyl yellow, +/0	5.28	1.12	−245	0.01
Acridinium, +/0	7.01	3.69	−196	

Table 11. Value of Ψ of surfactant—1-pentanol—benzene microemulsions; 1.3 vol.% pseudophase; ionic strength 0.05 M [14,173,187].

Indicator	Ψ , mV	
	CPC-Based	SDS-Based
Bromophenol blue, −/=	+179	—
Bromocresol green, −/=	+200	—
Bromocresol purple, −/=	+165	—
Bromothymol blue, −/=	+152	—
<i>n</i> -Decylfluorescein, +/0	+71	−150
<i>n</i> -Decylfluorescein, 0/−	+101	−90
Reichardt's dye, +/±	+65	−86
<i>N,N'</i> -di- <i>n</i> -octadecylrhodamine, +/±	+98	−47

The ΔpK_a^{app} values of sulfonephthaleins in cationic micelles gradually increase from bromophenol blue to thymol blue [167,168,175]. For example, Politi and Fendler [167] reported the values $\Delta pK_a^{app} = -1.25$ (bromocresol green); -1.05 (bromophenol red); -0.9 (bromothymol blue); and -0.2 (thymol blue) for a 0.008 M CTAB solution, ionic strength 0.01 M NaCl. Kulichenko et al. [175] reported the values $\Delta pK_a^{app} = -1.89$ (bromophenol blue); -1.51 (bromocresol green); -1.21 (bromocresol purple); -0.70 (bromothymol blue); -0.85 (phenol red); -0.54 (*m*-cresol purple); -0.74 (cresol red); and -0.20 (thymol blue) for a 0.06 M tridecylpyridinium bromide solution. Rosendorfová and Čermáková studied three sulfonephthaleins in micellar solutions of a cationic surfactant Septones, 1-(ethoxycarbonyl)-pentadecyl-trimethylammonium bromide (Scheme 13) [168]:



Scheme 13. Molecular structure of the cationic surfactant Septones.

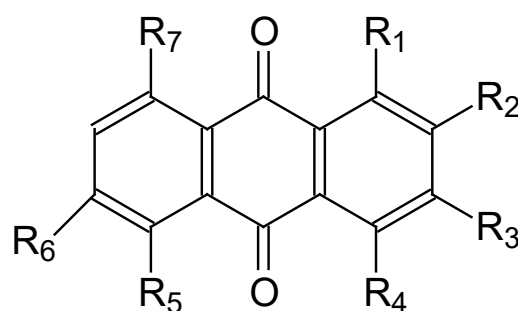
At ionic strength 0.2 M, the values $\Delta pK_a^{app} = -0.80$ (bromophenol blue); -0.45 (bromocresol green); and $+0.12$ (phenol red) were determined [168]. Our study for eight sulfonephthaleins in CPC micelles at ionic strength 0.05 M demonstrated the increase in ΔpK_a^{app} from -2.16 for bromophenol blue to -0.37 for thymol blue [230]. In CTAB at KBr + HBr or KBr + buffer concentrations of 0.005 M, the ΔpK_a^{app} s of four sulfonephthaleins change from -2.11 to -0.43 for bromophenol blue to thymol blue, respectively [231]. Importantly, the same sequence of the ΔpK_a s of the standard series of sulfonephthaleins is observed in binary water–acetone solvents [232] and in other mixtures of non-hydrogen bond donor solvents (acetonitrile, dimethyl sulfoxide) [213]. In the last named systems, the ΔpK_a values are substantially positive. It should be recalled here that, while studying acid–base reactions in CTAB micelles, Minch et al. [233] noted that “intramolecular water has a lower tendency to hydrogen bond with organic molecules than “ordinary” water”. Though the ΔpK_a^{app} s in cationic micelles are negative owing to the positive Ψ values, the differentiating

influence of this kind of the organized solutions is the same as in the above solvents. The more pronounced the delocalization of the negative charge in the R^{2-} anion is, the lower is the ΔpK_a value. However, the ΔpK_a^{app} values in nonionic micelles obey other regularities. Here, the total hydrophobicity of the compounds is of key significance. Obviously, the use of the pK_a^{app} values of these indicators in nonionic micelles will lead to different Ψ values for the same ionic micelles as calculated according to Equation (8).

The scatter of the Ψ values in Tables 7 and 8 reaches 100 mV.

Even more substantial it is in Tables 9 and 10.

The data gathered in Tables 7–11 may be supplemented by the results reported by Pal and Yana, who determined the pK_a^{app} s of seven hydroxyanthraquinones (Scheme 14) in micelles of cationic, anionic, and nonionic surfactants at an ionic strength of 0.3 M, 25 °C [149].



Scheme 14. Molecular structure of hydroxyanthraquinones used as acid–base indicators in micellar solutions. I: $R_1 = OH$; II: $R_1 = R_2 = OH$; III: $R_1 = R_4 = OH$; IV: $R_1 = R_7$; V: $R_1 = R_2 = R_7$; VI: $R_1 = R_2 = R_5 = R_7$; VII: $R_1 = R_2 = OH$, $R_3 = SO_3Na$ (the nonspecified substituents: $R = H$).

The authors compare the electronic absorption spectra and fluorescence in water, organic solvents, and micellar media, and demonstrate the increase and decrease in pK_a^{app} values along with increasing concentration of NaCl in CTAB and SDS micellar solutions, respectively. This study presents an abundant material demonstrating the role of the dye location in the interfacial region. The Ψ values, as determined by Equation (8) using the pK_a^{app} values in Triton X-100 micelles as pK_a^i of ionic micelles, vary in a wide range, and in some cases are positive even in SDS micelles [149].

Fernandez and Fromherz [144] used the long-tailed indicators 4-undecyl-7-hydroxycoumarin and 4-heptadecyl-7-(dimethylamino)coumarin. At CTAB and SDS concentrations of 0.024 M, the Ψ values at low bulk ionic strength were determined as +148 and −137 mV, respectively. The pK_a^i values of the indicators, 8.85 and 1.25, were determined in nonionic micelles of Triton X-100 [144]. The indicator 4-heptadecyl-7-hydroxycoumarin was used by Hartland et al. [95] for determination of the Ψ value of the SDS micelles at different NaCl concentrations; the $pK_a^i = 9.10$ of the indicator in $C_{12}E_8$ micelles was used for calculations. At 0.02 M SDS, the Ψ values are −141; −125; −110 mV at 0.007; 0.02; and 0.065 M NaCl, respectively [95]. Simultaneously, the Ψ values for micelles of series surfactants were determined with this indicator [133].

Concluding, the Ψ value of the interfacial region of a given micelle at a fixed ionic strength can vary within a wide range, as obtained with different acid–base indicators.

8. Theoretical Determination of the Surface Electrical Potential of Micelles

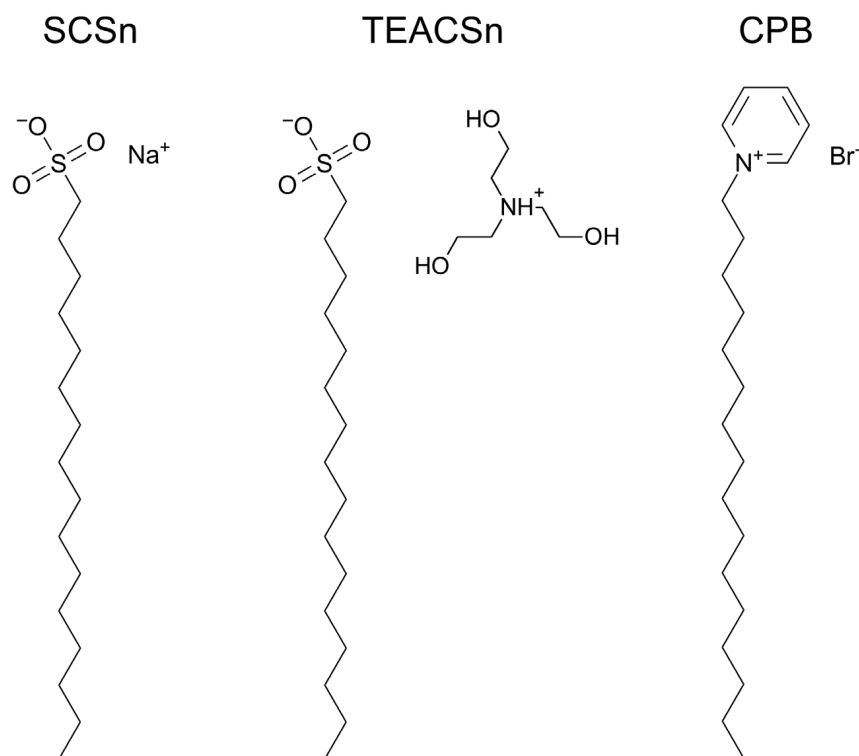
8.1. Formulation of the Problem

For well-defined micellar systems, different methods were used for theoretical calculation of the Ψ values. As an example, Equation (1) in Section 3 can be mentioned. Lukanov and Firoozabadi [78] developed more detailed approaches in this direction. For the SDS micelles, the calculated electrostatic potential values at 0.1 nm from the charged surface [78] agree quite well with the experimental Ψ values, determined with acid–base indicators at various NaCl concentrations [95,114,229]. Us'yarov calculated the whole set of parameters,

including α and Ψ [92,93], within a wide range of SDS and NaCl concentrations [92,93]. Some other papers were devoted to the theoretical estimations of the pK_a^{app} values in micelles and different biocolloidal systems [77,79,192]. However, the most popular method so far is the experiment with acid–base indicators.

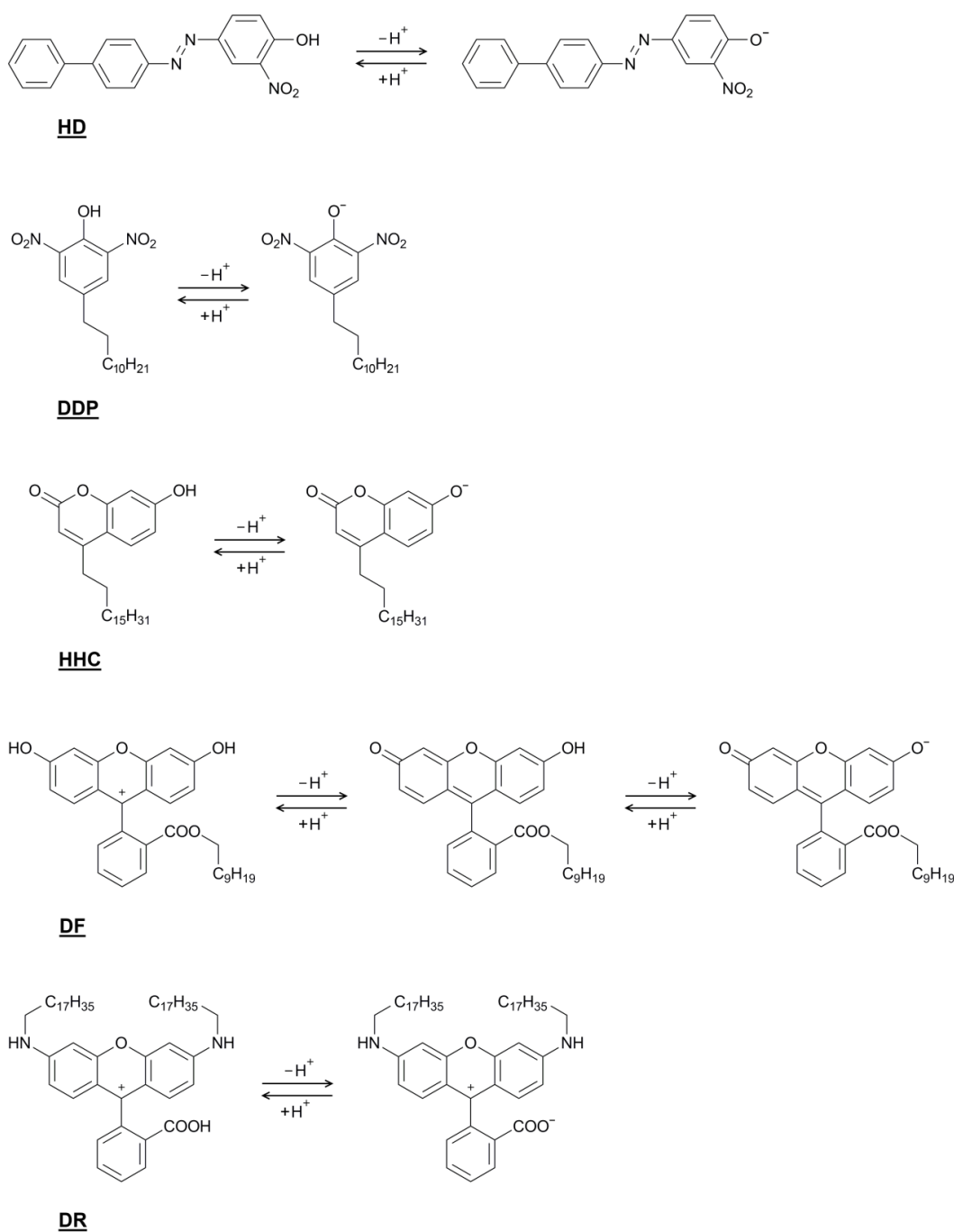
Below we present the main results obtained by our group. Our approach was based on the utilization of the acid–base indicators. Namely, the MD simulations were used for evaluation of the ΔpK_a^{app} of indicators, and the difference between the ΔpK_a^{app} s in nonionic and ionic micelles allows the estimation of the Ψ values of the latter. This study was accompanied by consideration of the localization, orientation, and hydration of the equilibrium forms of the acid–base indicators following the methodology described above for the betaine solvatochromic dyes.

The first step in this direction was devoted to the indicator 4-[(E)-([1,1'-biphenyl]-4-yl)diazenyl]-2-nitrophenol, which was first used for this purpose in a study published by Hartley and Roe as early as 1940 [139]. In this case, triethanolammonium cetylsulfonate, TEACSn, and *N*-cetylpyridinium bromide, CPB, (Scheme 15) were used in the modeling [59] because the same surfactants were used by the cited authors [139]. Sodium cetylsulfonate, SCSn, was also involved in our simulations.



Scheme 15. Molecular structure of the surfactants used in modeling with the Hartley indicator.

The acid–base dissociation of this and other indicators selected for modeling is presented in Scheme 16. In addition to the Hartley indicator, the 4-*n*-heptadecyl-7-hydroxycoumarin used by many authors for the Ψ determination (see above), was also involved in our theoretical study. Other three indicators were used in our experimental determinations of the electrostatic potential. They are as follows: 2,6-dinitro-4-*n*-dodecylphenol [62], *n*-decylfluorescein [14,173,213], and *N,N'*-di-*n*-octadecylrhodamine [14,152,153]. The results are published in a set of publications [59,62,64,65,67–69].



Scheme 16. Dissociation of the acid–base indicators used in molecular dynamics modeling. HD: Hartley indicator; DDP: 2,6-dinitro-4-*n*-dodecylphenol; HHC: 4-*n*-heptadecyl-7-hydroxycoumarin; DF: *n*-decylfluorescein; DR: *N,N'*-di-*n*-octadecylrhodamine.

8.2. Location of Acid–Base Indicators in Micelles

These phenomena were considered in detail for the dyes HD [59], DDP [62,64], and coumarin and xanthenes dyes [67].

The chromophoric moieties of the molecules are located either on the surface of the micelles between the hydrocarbon core and solution, or within the hydrocarbon core having only hydroxyl groups and adjacent atoms contacting with water. Both locations may be typical for the same molecule and alternate. Consequently, the dyes differ by the depth of immersion into micelles. Following the betaine dyes, we quantified it as the distance between the micelle center and a chosen atom of the dye molecule (the N atom bound

to the nitrophenol moiety of HD, the C atom of the α -CH₂ group of the hydrocarbon tail of DDP and HHC, and the C atom carrying the positive charge in carbocations of DF and DR). The average distances are collected in Table 12 and schematically represented in Figures 18 and 19. As before, the distances below 1.35 nm (SDS) or 1.55 nm (CTAB, CPB) are highlighted gray to indicate the approximate extent of the hydrocarbon core, conventionally defined as the distance where the water fraction appears to be at least 5%. The data were obtained from the distribution function of the distance $p(r)$, computed over MD trajectories.

Table 12. Average distance (nm) of acid–base indicator molecules to the center of mass of micelles.

Dye	SDS		CTAB	
	Acidic Form	Basic Form	Acidic Form	Basic Form
HD	1.62 ^a	1.93 ^a	1.37 ^b	1.56 ^b
DDP	1.23	1.16	1.48	1.30
HHC	1.29	1.42	1.48	1.50
DR	1.37	1.47	1.64	1.60
DF	1.47	1.35	1.90	1.65
DF	anion 1.44		anion 1.61	

^a Data for SCSn at 323 K; ^b data for CPB at 308 K.

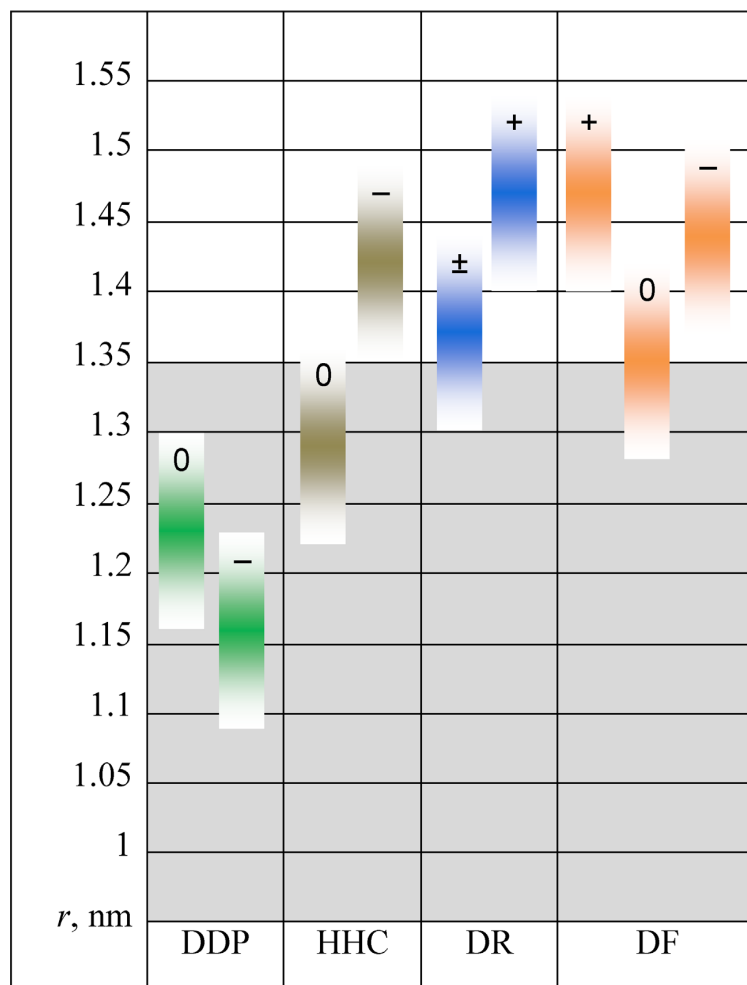


Figure 18. Average distance of the acid–base indicator molecules to the center of mass of SDS micelle. The band length corresponds to the range of typical distances.

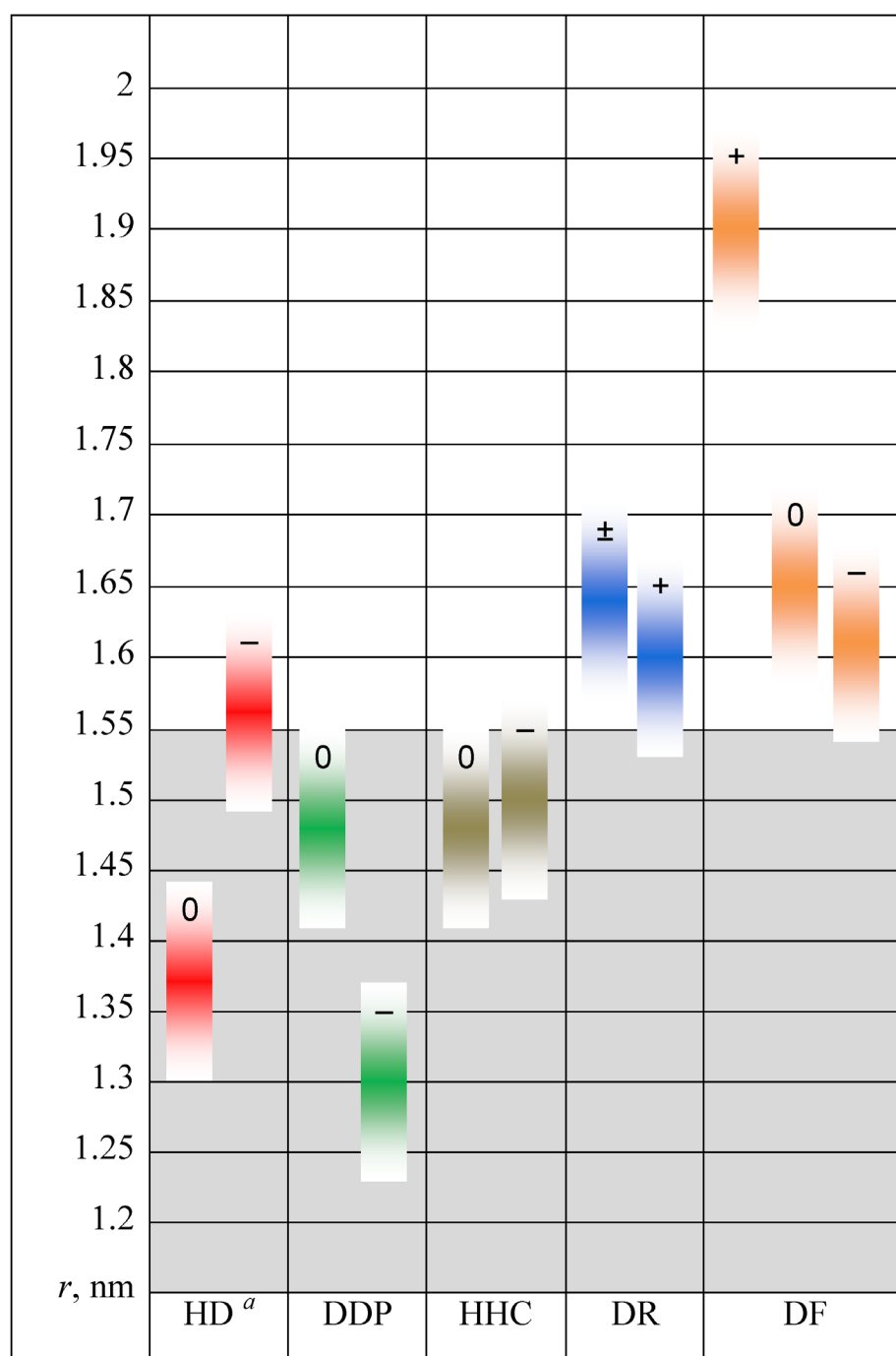


Figure 19. Average distance of the acid–base indicator molecules to the center of mass of CTAB micelles. The band length corresponds to the range of typical distances. ^a For HD, data for CPB are given.

Hence, the distance for the acidic forms in SDS micelles is 1.27–1.47 nm, while for the basic forms it is 1.16–1.47 nm. In CTAB micelles, the distances are 1.48–1.90 and 1.30–1.65 nm, respectively.

In SDS micelles, introducing charge to the molecule (by protonation or deprotonation) considerably pushes it towards the bulk solution, the only exception being DDP. In the cationic ones, the effect depends on the dye: for HD, DF cation, and HHC (a little) the trend is the same, while for the DR cation and the anions of DDP and DF acquiring charge immerses the molecule in average deeper into micelles. The exceptional advancement

of the DF cation in CTAB micelles is accompanied with reorientation of the molecule, as shown below. Similar exceptionally far location is observed for HD anion in anionic SCS (not shown in Figure 18) that is explained by electrostatic repulsion and absence of a long hydrocarbon radical that would hold the molecule in micelle.

8.3. Orientation of Acid–Base Indicator Dyes in Surfactant Micelles

Despite structural differences from Reichardt's betaine dyes (in particular, the presence of a long hydrocarbon tail), molecules of the considered acid–base indicators show similar placements: they are either roughly parallel or perpendicular to the micelle surface (Figure 20). Often both orientations are sampled by turns. The summary of our observations from MD trajectories is collected in Table 13. For analysis, the approach used for RD was employed (see Section 5.3 for details). The inclination angle of the molecule θ was defined for each dye. The fraction of time a molecule had $\theta < 40^\circ$ was assumed to be the probability of “vertical” orientation, and the rest of the time corresponded to the “horizontal” one. The inverted vertical orientation was not observed for these dyes, in contrast to Reichardt's betaines. For HD, the results of calculations were corrected according to visual examination of the MD trajectories.



Figure 20. Typical placements of acid–base indicator dyes in micelles shown using DDP as an example. Left: vertical orientation, right: horizontal orientation.

Table 13. Dominant orientations of acid–base indicator molecules in micelles. “V” means the vertical orientation, “H” means the horizontal one. “Sometimes” means a probability of 10–30%, “often” means a probability of >30%, “and” means a probability of approximately 50%.

Dye	SDS		CTAB	
	Acidic Form	Basic Form	Acidic Form	Basic Form
HD ^a	V and H	H, sometimes V	V, sometimes H	V
DDP	V and H	V	H, often V	V
HHC	V	V	V	V
DR	V and H	H	V	H, sometimes V
DF	H	V	H	V
DF		anion V		anion V

^a For HD, the data are for SCSn and CPB instead of SDS and CTAB, respectively.

In Figures 21 and 22, the most frequently observed state of the indicators in SDS and CTAB micelles is shown in accordance with the MD data. It summarizes the information of Table 13.

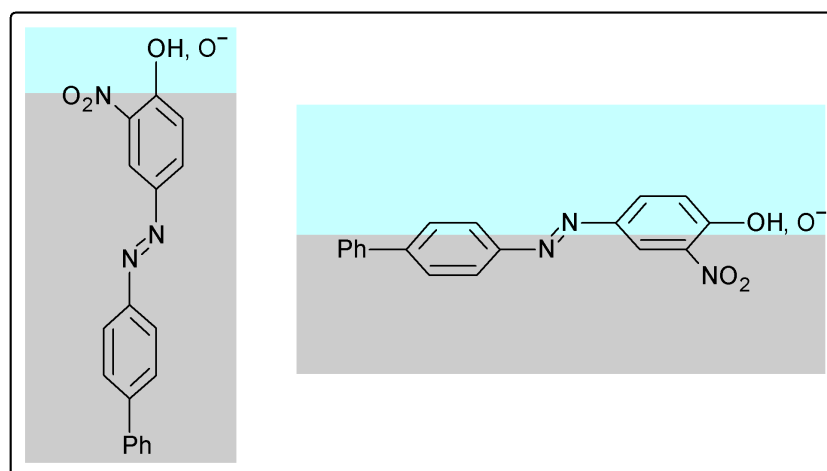
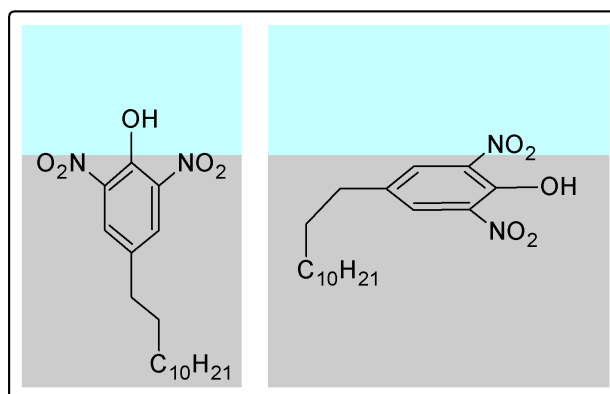
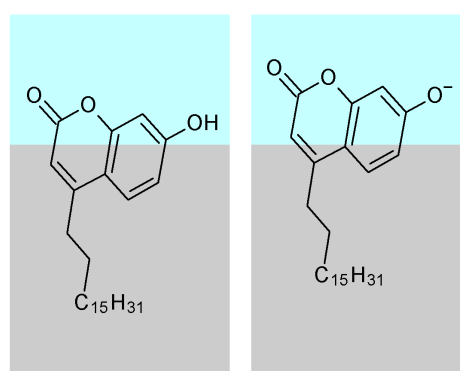
*neutral and anion*HD*neutral**anion*DDP*neutral**anion*HHC

Figure 21. Most probable orientations of the dyes HD, DDP, and HHC in ionic surfactant micelles as deduced from the MD simulations.

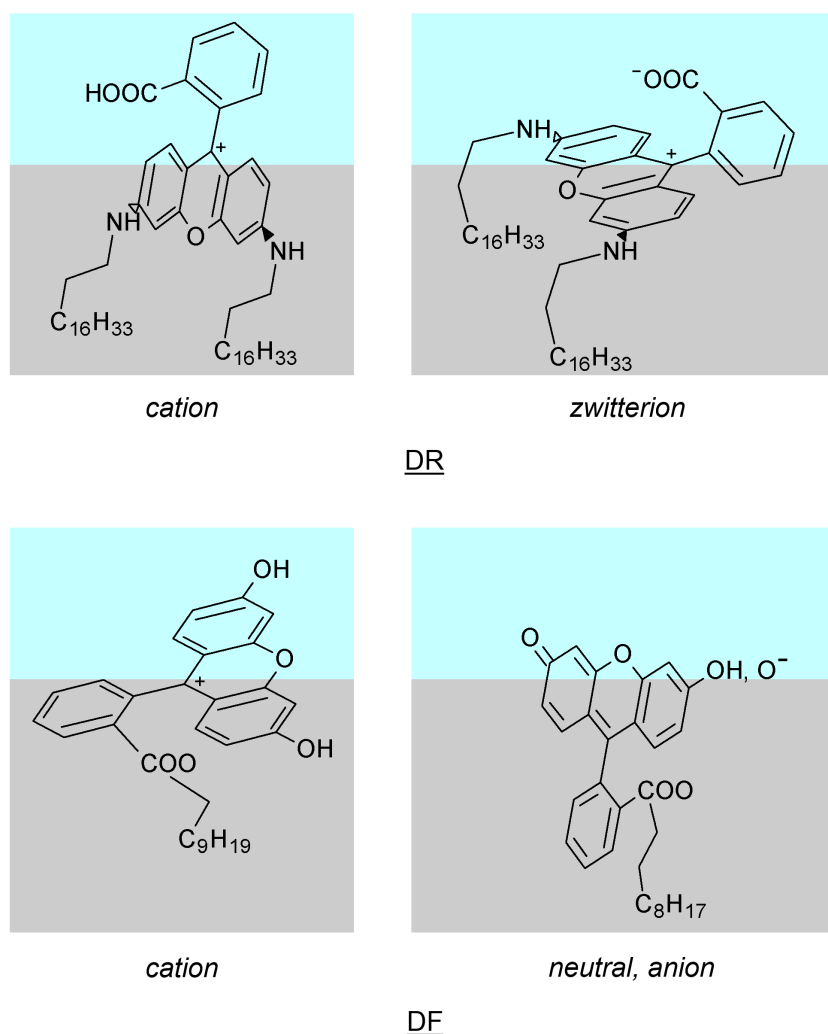


Figure 22. Most probable orientations of the dyes DR and DF in ionic surfactant micelles as deduced from the MD simulations. Adapted from [67].

The presence of a long hydrocarbon tail in a molecule (or even two of them in the case of DR) does not fix the position of its chromophoric moiety and does not prevent its rotation within a micelle. The particular placement of the molecule is difficult to predict on the basis of its molecular structure. Still, the common point is that the ionizing group (both protonated or deprotonated) continuously preserves contact with water molecules in the bulk solution.

8.4. Hydration of Acid–Base Indicator Dyes in Surfactant Micelles

Following the procedure used above for describing the local environment of betaine dyes (see Section 5.4), we examined it for acid–base indicators. The molar fractions of water and headgroups are depicted in Figure 23 for entire molecules and in Figure 24 for O atoms of ionizing groups.

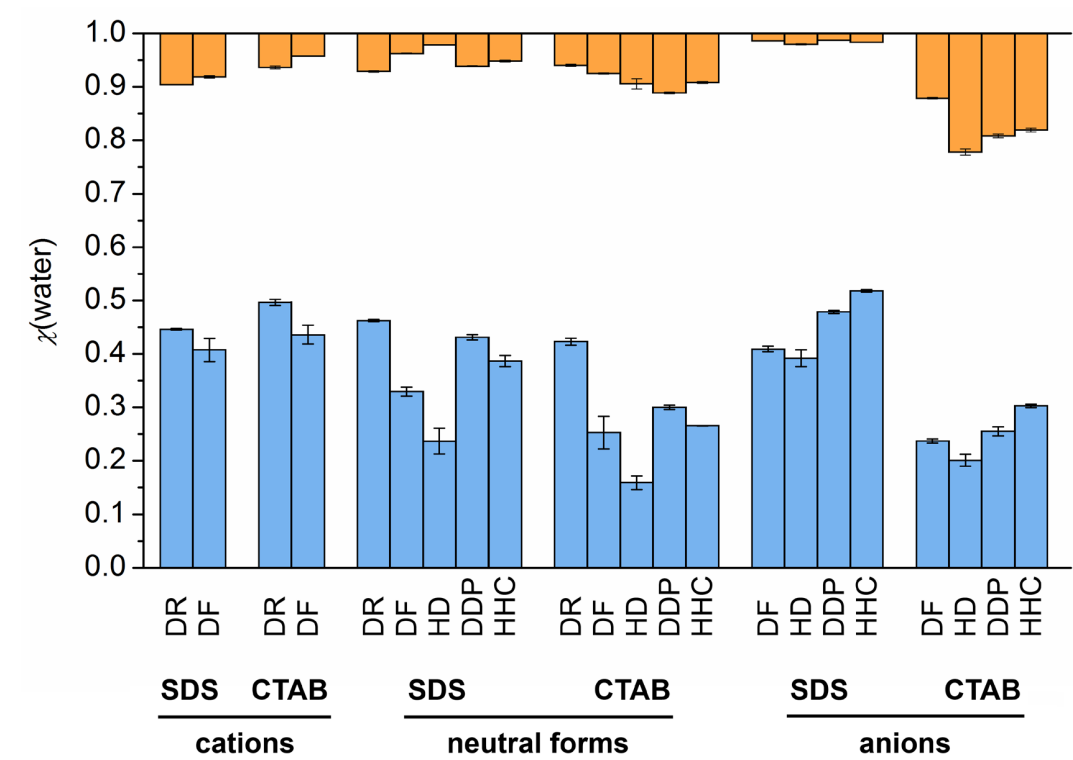


Figure 23. Molar fraction of water atoms (blue columns below) and headgroup atoms (orange columns above) around molecules of different acid-base dyes. For HD, the data for SCSn and CPB are given.

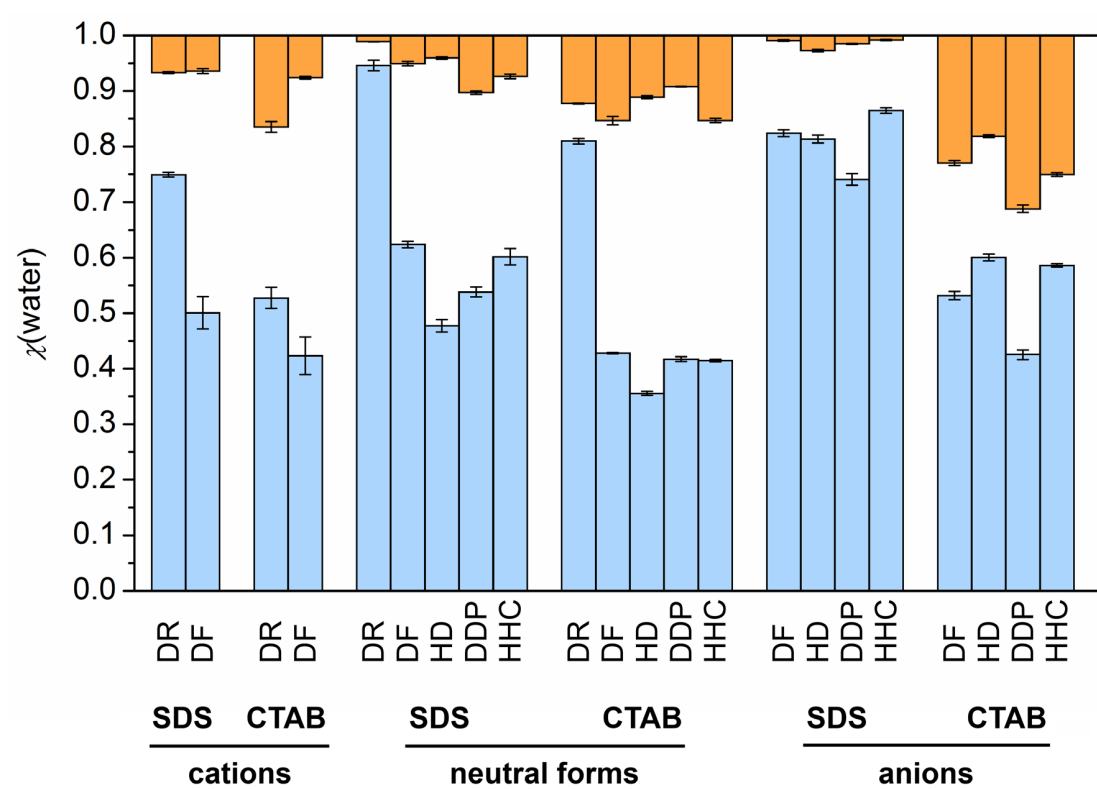


Figure 24. Molar fraction of water atoms (blue columns below) and headgroup atoms (orange columns above) around O atom(s) of the ionizing group of different acid-base dyes. For HD, the data for SCSn and CPB are given.

The most evident trend is higher hydration of anionic forms of the dyes in SDS as compared with CTAB, the difference approaches 0.2. The same is true for neutral forms, too, albeit to a smaller extent. The main reason for the effect is the close contact of anions with cationic headgroups of CTAB and their repulsion from the anionic ones of SDS.

The microenvironment of the ionizing groups quantitatively differs from that of the whole molecules. Still, the trend stated above is true, as well: transferring neutral and anionic forms from SDS to CTAB reduces the amount of water molecules around the groups. In all cases, deprotonation improves hydration of the group or, in few cases, keeps it constant.

8.5. Effect of Other Factors on the above Considered Characteristics

Following the original experiment, we investigated the Hartley's dye in two kinds of anionic micelles, which differ in counterions, namely, SCSn and TEACSn [59]. Both the localization and orientation of the molecule were found to be almost equal; however, hydration of the dye in the latter micelles was 1.4-fold less. The reason was that TEA⁺ ions considerably screened the dye and its hydroxyl group from water. An important consequence of this observation is that the two characteristics (placement and hydration) are not directly and unambiguously connected.

With the example of DDP we studied the role of the length of the hydrocarbon chain, of substituents, and of surfactant head groups on the molecule location. Firstly, an analogue of DDP with a shorter hydrocarbon tail, namely, 4-*n*-pentyl-2,6-dinitrophenol, was examined in SDS [59]. Both forms are situated 0.1–0.2 nm closer to the water phase than DDP, which proves that the effect is present albeit it is rather small.

Secondly, the impact of substituents was studied with the example of 2-nitro-4-*n*-nonylphenol in CTAB. The molecule has a single nitro group and a one bead shorter tail than DDP. Interestingly, this change affected neutral and anionic forms differently: while the former shifted deeper by ca. 0.15 nm, the latter advanced towards water by ca. 0.07 nm. As a result, the molecular form is hydrated 15% weaker than that of DDP, while the anionic form has 30% more water around than DDP anion.

Lastly, DDP was simulated in zwitterionic micelles of CDAPSn [62]. The neutral form was found to be immersed 0.1–0.2 nm deeper into the hydrocarbon core than in CTAB, while location of the anionic form was very similar. Orientation was similar, as well. Still, the bulkier headgroups of CDAPSn made the dye 10–15% less hydrated because of expulsion of water from Stern layer. Importantly, despite the zwitterionic headgroup having both positively and negatively charged moieties, [CH₂N(CH₃)₂CH₂]⁺ and SO₃[−], the indicator contacted almost exclusively with the former ones. This observation explained the highly positive value of Ψ determined for CDAPSn micelles with DDP.

8.6. Estimation of the ΔpK_a^{app} and Ψ Values

The opportunities provided by the MD simulation extend much beyond revealing geometric characteristics of “micelle + indicator” aggregates. One of the features of the method is evaluation of free energy changes that accompany both physical and chemical processes. We utilized this feature to computationally reproduce the described above experimental method of determination of Ψ .

The *in silico* method is based on computing the free energy change in deprotonation of an indicator molecules, ΔG_{deprot} , in water and in micelles. A well-suitable technique for this task is so-called alchemical transformation [65]. The difference of these ΔG_{deprot} values is proportional to the pK_a shift of the indicator on transfer from water to micelles, as is illustrated by Figure 25 and Equation (10).

$$pK_a^w = \frac{\Delta G_a^w}{RT \ln 10}; pK_a^{app} = \frac{\Delta G_a^{app}}{RT \ln 10}; \Delta pK_a^{app} = \frac{\Delta G_a^{app} - \Delta G_a^w}{RT \ln 10}$$

$$\Delta G_a^{app} - \Delta G_a^w = \Delta G_{deprot}^{app} - \Delta G_{deprot}^w \quad (10)$$

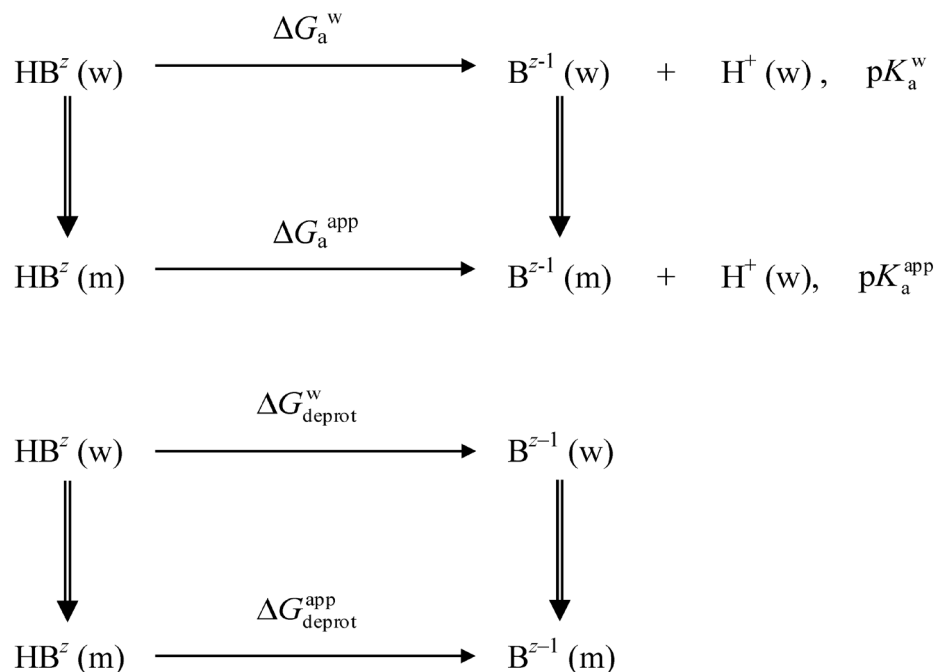


Figure 25. Thermodynamic cycle for computing pK_a shifts. Double arrows denote transfer between media. ΔG_a is the free energy change corresponding to HB^z dissociation. Adapted with permission from [65]. Copyright 2020 American Chemical Society.

This equation is possible because both pK_a^w and pK_a^{app} contain proton activity in bulk solution.

Estimated in this way ΔpK_a^{app} values appeared considerably more negative than expected (in average, by 1 unit in SDS and 3 units in CTAB), but overall a pronounced linear proportionality was found for each individual indicator. Furthermore, it was similar for different indicators (Figure 26A), and the order of increase in ΔpK_a^{app} values was mostly reproduced. We attributed the distortion to inaccurate reproducing indicator–water interactions by the used potential models [65]. In SDS micelles, the indicators are well-hydrated; hence transfer to water causes limited dehydration. Its contribution to $\Delta pK_{a\text{ calc}}^{app}$ is limited, as well. Conversely, when an indicator is transferred from water to CTAB micelles, it loses a large fraction of interacting water molecules around, and the energy effect of dehydration is high. If the energy effect is reproduced inaccurately, the distortion is bigger in the case of CTAB where the effect itself is higher. Other sources of errors in computed ΔG_{deprot} values were also discussed, but their role was identified as minor.

From the computational perspective we pointed out the importance of incorporating corrections to so-called finite-size effects, which appear when ΔG between states of different charge is computed in an MD cell of a finite size. In our simulation setup, their magnitude was found to be 0.2–0.7 units (if converted to $\Delta pK_{a\text{ calc}}^{app}$) for SDS and CTAB, and even ≥ 1 units for CDAPSn and TX-100 [234].

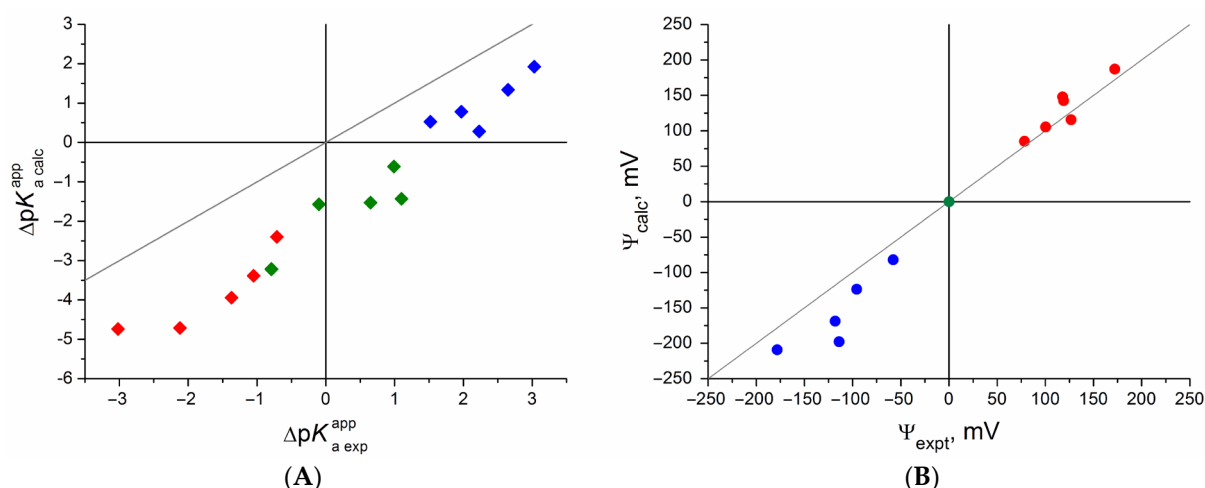


Figure 26. Calculated vs. experimental values of pK_a shifts (A) and Ψ (B). Blue, red, and green points are values for SDS, CTAB, TX-100 micelles, respectively; gray line is $y = x$.

Following the experimental method of estimating Ψ , the calculations of pK_a shifts were done in ionic (SDS, CTAB) and nonionic (TX-100) micelles, and their difference gives Ψ :

$$\Psi_{\text{calc}} = \frac{RT \ln 10}{F} \left(\Delta pK_{a \text{ calc}}^{\text{app}}(\text{nonionic}) - \Delta pK_{a \text{ calc}}^{\text{app}}(\text{ionic}) \right) \quad (11)$$

It also may be found directly from ΔG_{deprot} values, if the water phase is replaced with nonionic micelles in the thermodynamic cycle shown in Figure 25 [68].

$$\Psi_{\text{calc}} = \frac{1}{F} \left(\Delta G_{\text{deprot}}(\text{nonionic}) - \Delta G_{\text{deprot}}(\text{ionic}) \right) \quad (12)$$

Surprisingly, despite the large distortion of the input $\Delta pK_{a \text{ calc}}^{\text{app}}$ values, the obtained Ψ_{calc} values were in fine agreement with experimental results [68,69] (Table 14 and Figure 26B). For CTAB, the distortion was often of the order of magnitude of the experimental uncertainty (± 5 mV), while for SDS the coincidence was reasonable (± 30 mV), except for two cases where only the order of magnitude was preserved. We think this stems naturally from our explanation of $\Delta pK_{a \text{ calc}}^{\text{app}}$ distortion: there, the hydration energy error was high upon transfer from water to CTAB (and TX-100) where the indicator is poorly hydrated; while it was small upon transfer to SDS. Here, the transfer is done from TX-100 to CTAB having a similarly low hydration of the indicator; and between TX-100 and SDS where it differs strongly. This matches fine accuracy of Ψ_{calc} values determined in the former case and some distortion in the latter case.

Table 14. Experimental and calculated values of surface electrostatic potential of micelles. The values correspond to the ionic strength of 0.05 M. Adapted with permission from [68]. Copyright 2023 American Chemical Society.

Indicator	SDS		CTAB	
	$\Psi_{\text{calc}}, \text{ mV}$	$\Psi_{\text{exp}}, \text{ mV}$	$\Psi_{\text{calc}}, \text{ mV}$	$\Psi_{\text{exp}}, \text{ mV}$
DDP	−123	−96	189	172
HHC	−198	−114	115	127
DR	−82	−58	105	100
DF (cation)	−209	−178	85	79
DF (neutral)	−169	−118	142	119

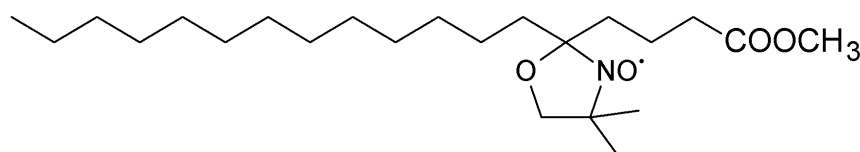
The results of this *in silico* computation of surface electrostatic potential by means of indicator dyes may be compared with those presented above computed for entire micelles.

While the two methods differ by the basic principle, treatment of water, usage of probe, they still share atomic models of surfactant micelles. Importantly, the obtained values lie in the same interval (70–200 mV by magnitude). Ψ_{calc} estimated with probes are close to Ψ_0 from Figure 4: average $\Psi_{\text{calc}}(\text{SDS}) = -156$ mV, $\Psi_{\text{calc}}(\text{CTAB}) = +127$, while Ψ_0 was found -100 mV and $+(149\text{--}151)$ mV, respectively. Taking into account the ca. 35% overestimation of $\Psi_{\text{calc}}(\text{SDS})$ with respect to experimental values, the correspondence is notable, which proves the consistency of our calculations. Furthermore, this shows that the indicator method provides rather surface potential Ψ_0 than Stern layer potential Ψ_δ , albeit probe molecules are proven to be located in the latter layer.

An essential point is that the computations reproduce the experimental variation in Ψ values of the same micelles as determined by different indicators. On one hand, this confirms the validity of the computations, on the other hand, this indicates that the spread is an intrinsic problem of the discussed method of estimating Ψ . Using the MD trajectories we investigated the problem deeper and deduced two origins of the spread. At first, pK_a^{app} in nonionic micelles of TX-100 is predicted to often mismatch the pK_a^i in ionic micelles because of different hydration of a dye molecule in these micelles. Second, each micelle + indicator aggregate has an individual structure, which also should affect the average value of electrostatic potential sensed by the indicator. Still, for the studied set of indicators, we did not find a correlation between these characteristics and reported Ψ values [69].

9. Some Other Reporter Molecules

Apart from indicator dyes, another instrument used to provide information about hydration of micelles are spin probes. We investigated a single probe, namely, methyl-5-doxylstearate (Scheme 17) that was previously examined in SDS and DTAB micelles [235,236].



Scheme 17. Molecular structure of methyl-5-doxylstearate.

The EPR measurements were originally interpreted as the molar fraction of water in the Stern layer, which was found to be 0.68 in the anionic micelles and 0.44 in the cationic ones. This stays in line with the information from previously discussed dyes, which in general shows higher hydration of the former micelles. We hypothesized that the values are relevant rather to the microenvironment of the spin label alone than for the entire Stern layer. Our simulations of these systems showed that hydration of the O atom carrying the unpaired electron in these micelles is 0.64 and 0.39 if compared with pure water solution, and number of O—water hydrogen bonds reduces in a similar proportion. At the same time, hydration of the whole molecule is almost the same in both micelles [63].

Fluorescent dyes are another important group of molecular probes [22–31,130,131,134,149,237–241]. An example of a fluorescent molecular probe that is not a dye in the traditional sense is the above mentioned pyrene [137]. Its solubility in aqueous micellar solutions is almost five orders of magnitude higher than in water [242]. The specific features of pyrene emission were used to determine the cmc values of surfactants, micellar polarity, and to investigate the extent of water penetration in micellar systems [243,244], to study the partition of *n*-pentanol [95], *n*-hexanol, and *n*-heptanol [245] between bulk water and the SDS micelles. MD simulations of the state of pyrene in SDS and CTAB micelles were studied in [246,247], respectively. The study revealed that the pyrene molecule is located in the last-named micelles in a more polar region than in SDS micelles [137,246]. The reason is the interaction of the electron-rich pyrene ring with the quaternary ammonium groups [137,247]. As a result, the pyrene molecule is located not only in the interior cavity,

but also in the palisade layer of the CTAB micelles [247]. By contrast, in the SDS micelles, the pyrene molecule is located in the hydrophobic core region only [246].

The acid–base indicators considered in the present paper also belong to fluorophores, e.g., coumarins [23,25], rhodamines [24,31,51,52,151–155], and fluorescein and its derivatives [24,29,30,131,134,240]. Additionally, fluorescence is used also for determination of the pK_a^{app} and Ψ values not only for coumarins (see Section 6.1), but also for fluorescein dyes [248]. Therefore, the results of MD modeling of these compounds in micellar media presented above can be useful for a better understanding of the systems where they are used as fluorescent molecular probes, too.

At last, a recent application of our approach for understanding the behavior of substrates in calixarene-based catalytic systems should be mentioned [249].

10. Conclusions

10.1. Molecular Dynamics Modeling of Micelles

Molecular dynamics modeling of SDS, CTAB, and some other surfactant micelles in water makes it possible to reveal their structure, hydration, and counterion binding. The electrical potential, Ψ , as a function of the distance from the micellar surface and bulk ionic strength may be computed and interpreted in terms of the surface potential Ψ_0 and the Stern layer potential Ψ_δ . Numerical methods of solving the Poisson–Boltzmann equation enable using atomic models of micelles instead of idealized spherical and cylindrical models.

Consideration of the surfactant ions DS^- and CTA^+ in water without counterions results in appearance of two small micelles in both cases. Hence, the hydrophobic association of the hydrocarbon tails balances the repulsion of the charged headgroups of these small “bare” micelles. The experimental verification is impossible in this case.

10.2. Location, Orientation, and Hydration of Seven Reichardt’s Solvatochromic Dyes in Micelles

In CTAB micelles, the dye zwitterions, $^+D^-$, penetrate deeper than the cations. This is not the case in SDS micelles. The dye RD-PhtBu in both forms is situated in the hydrocarbon region. The same is found but much less pronounced for the zwitterions of RD-tBu and RD-cyclo9 in SDS micelles and that of RD-tBu in CTAB.

For the zwitterions, $^+D^-$, of the dyes RD-H, RD-Cl, RD-cyclo9, and RD-tBu, the horizontal orientation is most probable, and the vertical one is sometimes found in SDS micelles. For the ^+DH cations, the horizontal orientation predominates in both kinds of micelles. The inverted orientation, with the phenol part directed to the micellar center, is probable for the cation of the most hydrophobic dye, RD-PhtBu, and for the RD-COOH dye in both forms bearing the OH group.

For the standard solvatochromic dye, 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate, RD-Ph, the horizontal orientation is more typical. The orientation, intermediate between inverted and horizontal, can be sometimes expected only for the colorless cation.

The obtained data do not contradict intuitive expectations based on the concepts of hydrophobicity and hydrophilicity of molecules, ions, and their individual fragments. For example, the dye RD-PhtBu, bearing five additional $C(CH_3)_3$ groups, is always most deeply immersed into the micelles of both types and hence less hydrated, though some contacts with water molecules nevertheless take place owing to the dynamic character of the surfactant micelles.

This is not the case for solvation of the oxygen atom of the O^- and OH groups. Indeed, the hydration of the phenolate oxygen of the $^+D^-$ forms is much more pronounced in SDS than in CTAB micelles. This is more than a convincing confirmation of the higher value of the E_T^N value in SDS micelles than in the CTAB ones.

10.3. Hydration of Surfactant Micellar Surfaces: SDS vs. CTAB

MD modeling does not demonstrate a serious difference in the hydration of micellar surfaces of anionic surfactants compared to cationic ones at the same tail length. The consideration of the Krafft temperature allows expecting even a better hydration in the case

of CTAB micelles. Therefore, the pronounced exceeding of the E_T^N values for SDS and other anionic surfactant micelles as compared with those for CTAB is caused by better hydration of the betaine dye. The same can be said about the data obtained with other molecular probes. Hence, it is more correct to speak about the more pronounced hydrogen-binding ability of water molecules in anionic micelles than about better hydration of the anionic micelles themselves.

10.4. Acid–Base Indicators in Surfactant Micelles: Molecular Dynamics Modeling

Location, orientation, and hydration of several popular acid–base indicators, used in experiments of Ψ determination, were studied using molecular dynamics simulation. They are 4-[(E)-([1,1'-biphenyl]-4-yl)diazenyl]-2-nitrophenol, a dye proposed in the pioneering work by Hartley and Roe as early as 1940 [139], 4-*n*-heptadecyl-7-hydroxycoumarin, a standard indicator used for this purpose, and three other dyes.

The simulation results generally consistent with the intuitive assumption about the location of acid–base indicators. The dyes are located in such a way that the ionizing groups remain in contact with water and on the surface, while the chromophore part can either lie at the interface between the hydrocarbon core and water, or be immersed in the core. Two positions can be observed for the same molecule as alternating. The immersion depth nontrivially depends on the state of protonation.

The vertical orientation is typical for both forms of 2,6-dinitro-4-*n*-dodecylphenol and 4-*n*-heptadecyl-7-hydroxycoumarin, neutral and anionic forms of *n*-decylfluorescein, cationic form of *N,N'*-di-*n*-octadecylrhodamine, and for neutral form of the Hartley dye; this is true for micelles of both charges. The horizontal orientation is typical for anionic forms of the Hartley dye and *n*-decylfluorescein, for the neutral form of *N,N'*-di-*n*-octadecylrhodamine; and it is also observed for some other cases.

Regarding the hydration of acid–base dyes, the important factor is the protolytic form and micelle charge. The neutral (including zwitterionic) forms are slightly more hydrated in anionic micelles, while the anionic forms are much more hydrated. This is observed both for entire dye molecule and for its ionizing group; however, the particular values are dissimilar.

10.5. Determination of the Electrical Surface Potential of Micelles Using Acid–Base Indicators

Utilization of techniques for computing free energy changes allows finding ΔpK_a^{app} values for transferring a dye molecule from water to micelles. The results appear strongly distorted. However, the correlation between experimental and computed values is pronounced and linear. The distortion is explained by the poor reproduction of the hydration energy by used potential models.

Nevertheless, if ΔpK_a^{app} is computed for both ionic and nonionic micelles, then Ψ can be found from the difference between the values in nonionic and ionic micelles. It may be called *in silico* implementation of the “wet” method. The calculated values agree well with the experiment: there is almost a quantitative match for CTAB and 35% (in average) overestimation for SDS. The reason is the partial cancellation of error of input ΔpK_a^{app} values.

The *in silico* calculation of Ψ is accurate enough to reproduce the variation in Ψ values of the same micelles as determined by different indicators. Hence, this variation is an intrinsic problem of the indicator method of estimating Ψ . We did not find a correlation between reported Ψ values and such characteristics of micelle + indicator aggregates as depth of immersion of the indicator in micelle and its hydration.

Still, the set of dyes currently under consideration is limited, and only TX-100 was studied as nonionic surfactant and used in the assumption that pK_a^i (in ionic micelles) = pK_a^{app} (in nonionic micelles). Therefore, there is room for further developing this issue.

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