



Examining surfactant micelles via acid-base indicators: Revisiting the pioneering Hartley–Roe 1940 study by molecular dynamics modeling

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ABSTRACT

Examining micellar pseudophases and related systems by using acid-base indicators is presently a very popular method. Normally, the acid-base couple of an appropriate indicator was expected to be located in a definite place, i.e., the microenvironment of both acidic and basic dye species is equal. This assumption allowed modeling the solvation properties of the pseudophase by water–organic mixed solvents or by some other media. This vision of the indicator locus should be checked using some independent approaches. In the present paper, the molecular dynamics modeling was used for such purpose. As indicator, an azo dye was used, which was first utilized for estimating electrical potential of micelles by Hartley and Roe in their pioneering study (1940). The modeling was processed in micelles of the same surfactants which were used by Hartley and Roe, namely cetylpyridinium bromide and cetyl sulfonate salt. The results support the idea of indicator location within the interfacial region (Stern layer). However, the orientation of the dye molecule and the hydration of the ionizing group, $\text{OH} \rightarrow \text{O}^-$, are quite different for the acidic (HA) and basic (A^-) forms in both cationic and anionic micelles. This is a precaution against the simple concept of uniform location of the equilibrium forms of indicators. Hence, further molecular dynamics study of other indicators, often used nowadays for examining micelles and other molecular assemblies, seems to be pertinent and timely.

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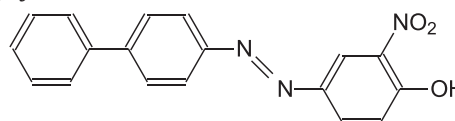
1. Introduction

Presently, surfactant micellar solutions belong to the most used media for conducting a number of chemical and physico-chemical processes. They are used in kinetic and equilibria studies, in organic synthesis, and in many technological processes including preparation of nanoparticles. The literature devoted to surfactant micelles is huge [1]. Probably, the first reports, which provided the adequate notion on micellar structure, were published in 1913 [2–4].

Surfactant micelles in water are nanosized disordered highly hydrated clusters, which are in dynamic equilibrium with monomers in the bulk phase [5–9]. The micellar solutions of surfactants are lyophilic, i.e., by definition reversible thermodynamically stable systems. Besides versatile physical and physico-chemical methods, used for examining the micellar structure, small molecular probes, either intensively colored or fluorescent organic dyes, were utilized [10–13].

The pioneering studies by Hartley initiated monitoring of interfacial electrical potential of ionic surfactant micelles via acid-base indicators. As early as 1940, Hartley and Roe [10] used for such purpose a

hydrophobic enough indicator in order to ensure the completeness of its binding by micelles:



The pK_a value of the indicator on the micellar surface, nowadays named “apparent”, pK_a^{app} , and determined photometrically, Hartley and Roe have designated as $(P_k)_s$. This index of the constant is connected with that of the same indicator in water, P_k , or pK_a^{w} in modern designation, via Eq. (1).

$$(P_k)_s = P_k - \zeta/60 \quad (1)$$

Here, ζ/mV is the electrokinetic potential, or zeta potential, whereas $pK_a^{w} = 6.35$. The authors expected that “the ionizable group must be situated in the interface rather than in the interior of the micelle.” Accordingly, the authors derived an equation for pH on the micellar surface, $(pH)_b$, at 30 °C, Eq. (2).

$$(pH)_s = (pH)_b - \zeta/61 \quad (2)$$

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Here, $(\text{pH})_b$ is the bulk pH. Even earlier, Hartley [11] put forward qualitative rules predicting the influence of ionic surfactant micelles on the acid-base indicator equilibria. In fact, Eq. (1) was the quantitative expression of these rules, afterwards named as “Hartley rules” [14]. Later Hartley generalized his concepts [12]. In turn, Davies and Rideal [15] noted that it is the surface electrical potential, Ψ , that rather should be used in such formulae instead of ς .

Since then, an impressing number of papers have been published in this field. The studies by Mukerjee [16], Fromherz [17–19], and Funasaki [20–22] resulted in the relationship which is justly named as HMFF (Hartley–Mukerjee–Fromherz–Funasaki) equation [23].

As a rule, the apparent $\text{p}K_a^{\text{app}}$ value of an indicator acid, HA, is obtained using the spectrophotometric procedure, whereas the bulk pH value is determined potentiometrically with a glass electrode in a cell with liquid junction, Eq. (3).

$$\text{p}K_a^{\text{app}} = \text{pH}_b + \frac{[\text{HA}]}{[\text{A}^-]} \quad (3)$$

Here, the brackets denote equilibrium concentrations of the corresponding forms of the indicator. The latter is completely fixed to the micellar pseudophase. Nowadays, such fixation is usually ensured by covalent attaching hydrophobic hydrocarbon chains to the indicator molecule [17–19].

More precise equation for the surface pH, or pH_s , contains besides the electrical potential also the Gibbs energy of transfer of the hydrogen ion from the bulk water to the micellar surface. This $\Delta G_{tr}(\text{H}^+)$ value reflects the so-called “non-electrostatic” contribution to the solvation, Eq. (4).

$$\text{pH}_s = \text{pH}_b + \frac{\Psi F + \Delta G_{tr}(\text{H}^+)}{RT \ln 10} \quad (4)$$

Further, the modern expression for $\text{p}K_a^{\text{app}}$, i.e., the aforesaid HMFF equation, is as follows, Eq. (5):

$$\text{p}K_a^{\text{app}} = \text{p}K_a^w + \frac{\Delta G_{tr}(\text{A}^-) - \Delta G_{tr}(\text{HA})}{RT \ln 10} = \text{p}K_a^i - \frac{\Psi F}{RT \ln 10} \quad (5)$$

Here K_a^w is the thermodynamic ionization constant in water, K_a^i is called “intrinsic” constant. The spectroscopic method gives the ratio of equilibrium concentrations of HA and A^- forms, not activities. However, because the Stern region is actually a concentrated electrolyte solution, the ratio of concentration activity coefficients is expected to be close to unity, and the corresponding logarithmic term is as a rule supposed to be negligible, taking into account the character of the dependence of ionization constants of indicators and other acids in aqueous media on ionic strength [23].

The Ψ value may be calculated via Eq. (6) using the experimentally determined $\text{p}K_a^{\text{app}}$ value of an indicator if some reasonable way to estimate the $\text{p}K_a^i$ value is available.

$$\Psi = \frac{RT \ln 10}{F} (\text{p}K_a^i - \text{p}K_a^{\text{app}}) \quad (6)$$

For instance, the $\text{p}K_a^i$ value of an indicator in ionic micelles may be equated to the $\text{p}K_a^{\text{app}}$ value of the same compound in micelles of non-ionic surfactants [21,24,25]. Some other procedures are also recommended in the literature, including those using water-organic mixed solvents [17,18,23,26,27].

The “apparent ionization constant” approach was used by different authors [28–30]; the collection of data obtained up to 1989 was presented by El Seoud [31]. Gaboriaud and co-workers [28] and Drummond, Grieser, and Healy [24,32,33] developed the above electrostatic model. Also, some reviews were devoted to this problem [23,31,32].

Such approach is applicable to microemulsions [26,27], bilayers of phospholipids [34], and monolayers [35,36].¹

In order to obtain a satisfactory approach to the $\text{p}K_a^i$ value of an indicator in a given ionic micelle, various aspects of solvation should be taken into account, particularly the hydrogen-bond donating ability of the medium. It is reasonable to assume that the formation of hydrogen-bonds with water, e.g., by means of the OH group of the acid and the O atom of the corresponding anion significantly contributes to the total solvation energy of the acid-base couple in the medium. Therefore, it is important to clarify the microenvironment of the equilibrium dye forms in the micellar interfacial region.

Hence, the key point in such studies is the locus of the molecular probes or, more precise, of their ionizing groups [39–41]. As a rule, the last-named are considered to be situated in the Stern layer of ionic micelles, except the case when they are forcibly immersed into the bulk phase using spacers [42]. In general, the models of dye location developed by different authors may be rather contradictory, as it can be seen in the studies of rose Bengal B in cationic micelles [43,44]. A verified method is the application of NMR spectroscopy [25,45–47]. For instance, according to the ¹H NMR data, the COOH group of the 4-octadecyloxy-1-naphthoic acid is primarily located in the head group region of both cetyltrimethylammonium bromide, CTAB, and sodium *n*-dodecylsulfate, SDS, micelles, and around the first ether linkage away from the hydrocarbon center of the non-ionic surfactant $\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$ [25]. A recent study of phenol in CTAB micelles by means of ¹H NMR and NOESY techniques [48] demonstrated that the locus of the phenolate ion is similar to the above-mentioned for naphthoates and benzoates [45,46]. But the OH group of the neutral phenol molecule is exposed to more extent to the aqueous phase, while the phenyl portion is just between the cationic head groups [48]. The El Seoud group [47] used the NMR spectroscopy in order to clarify the locus of solvatochromic betaine dyes in micelles.

Besides experimental determination of the location of molecular probes within the micelles, the comparison of the Ψ values estimated with indicators and those theoretically calculated is of importance [24,49]. For the last-named calculations, the Ohshima–Healy–White equation [50] is usually used.

Evidently, it is of special interest to examine the locus of the acid-base couple of the indicator within the micellar pseudophase via molecular dynamics (MD) simulation. Indeed, the MD simulation method has already been applied to the standard solvatochromic Reichardt's dye in the environment of non-ionic block-copolymers [51]. Other examples of MD modeling of dyes in surfactant environment are the studies of rhodamine-labeled phospholipid incorporated into a lipid bilayer [52] or sulforhodamine in SDS layers on water-air interface [53]. Recently, we used the MD modeling for revealing the localization and orientation of both zwitter-ionic and protonated (cationic) forms of several Reichardt's dyes in micelles of SDS and CTAB [54–56]. The results agree in outline with the experimental solvatochromic data, which allows assuming that modern theoretical approaches open the possibility of revealing the character of molecular orientation in surfactant micelles. It is important that the location of the zwitter-ionic and cationic forms is markedly different [54–56]. This should be taken into account because this solvatochromic dye is also used as an acid-base probe for determination of the Ψ values [23,32].

Therefore, it seems to be worthwhile to examine in the same manner the most popular indicator dyes, which are applied for monitoring of interfacial electrical properties of cationic and anionic micelles. The present article is aimed to revisit the problem of location of the Hartley–Roe indicator, historically first used for such purpose, via MD modeling. We examined the surfactants used by these authors [10],

¹ In some studies, such approach is used even for the indicator on the water/air interface, without any surfactant ions [37]. However, in such case not the effective pH or Ψ value, but the stabilization of neutral form of indicators and destabilization of their ionic form probably play crucial role [27], in accord with the results by Eisenthal [38].

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