



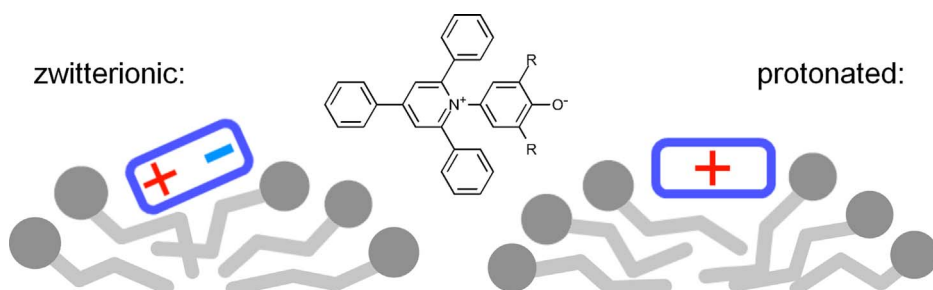
Solvatochromic betaine dyes of different hydrophobicity in ionic surfactant micelles: Molecular dynamics modeling of location character



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GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the locus and hydration character of three solvatochromic pyridinium-*N*-phenolate dyes in ionic surfactant micelles were examined using molecular dynamics modeling. These dyes, also called 'betaine dyes', are of various hydrophobicity due to different substituents in 2,6-positions of the phenolate moiety. They are as follows: 4-(2,4,6-triphenylpyridinium-1-yl)phenolate, 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, and 2,6-di-*tert*-butyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate; the abbreviations are BD-H, BD-Cl, and BD-tBu, respectively. The results were compared with those obtained previously with the so-called Reichardt's standard betaine dye, 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate, or BD-Ph. The aggregates of widely used ionic surfactants, sodium dodecyl sulfate, SDS, and cetyltrimethylammonium bromide, CTAB, were selected as the most typical micellar media. The results of modeling shed some light on the state of the solvatochromic dipoles within the micellar pseudophase. Though the location of the dyes is rather similar, with the phenolate oxygen atom directed toward the Stern layer, the more hydrophobic dyes, BD-tBu and BD-Ph, appeared to be immersed somewhat deeper as compared with BD-H and BD-Cl. The average compositions of the local microenvironments of the dye molecules and the hydration of the oxygen atom were estimated. The last finding confirms the higher values of the E_T parameter of the interfacial micellar region of SDS as against those of CTAB, in line with experimental data. The versatile information concerning the dye locus was compared with the NMR data available in the literature. Also, the same studies were performed with the protonated colorless forms of the betaine dyes, keeping in mind that these compounds are also often used as acid-base indicators in micellar media. Noteworthy, for all of the dyes under study, and in both micelles, the protonated colorless forms are oriented somewhat different as compared with the corresponding colored dipolar molecules. This should be taken into account when utilizing these compounds as interfacial pH-probes, in particular, for estimating the surface electrical potential of micelles and other colloidal species.

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1. Introduction

Acid-base and solvatochromic indicators are indispensable tools for examining surfactant micelles and related colloidal species. The abovementioned molecular probes of the first kind normally serve for determining of the surface electrical potential, Ψ , of micelles [1–7], lipid monomolecular films [8], and surfactant monolayers on water–air interface [9]; for review of the problem, see ref. [10–12], whereas the second ones allow estimating the polarity of the pseudophase [13–18]. Pyridinium *N*-phenolate dyes are known as the most powerful solvatochromic indicators [19,20] often used for exploration of oil/water and air/water interfaces [21,22] and micellar solutions, microemulsions, etc. [4,11,12,15,20,23–33], and at the same time they act as acid-base indicators, which is also utilized in the same field of research [4,11,12,34–39]. The general formula and protolytic equilibrium of these dyes is shown in Scheme 1.

The cationic form, ${}^+DH$, is colorless, while the neutral, or more precise, zwitterionic one, ${}^+D^-$, is colored. The solvatochromic scale of polarity based on these dyes is established using the maximum of the charge-transfer absorption band of ${}^+D^-$. The energy of the charge-transfer band, E_T , expressed in kcal mol $^{-1}$ may be calculated via Eq. (1):

$$E_T = hc\tilde{\nu}N_A = 2.8591 \times 10^{-3} \tilde{\nu}_{\max} = 28591/\lambda_{\max} \quad (1)$$

Here h is the Plank constant, c is the velocity of light in vacuum, $\tilde{\nu}$ and λ_{\max} are the wavenumber of the band maximum in cm $^{-1}$ and the wavelength maximum in nm, respectively, and N_A is the Avogadro constant. For the standard Reichardt's dye ($R^1 = R^2 = R^3 = C_6H_5$), the corresponding value is called $E_T(30)$, in accordance with the number 30 of this dye within the set of compounds in the initial paper [19]. Nowadays, the dimensionless parameter E_T^N is mainly used (Eq. (2)):

$$E_T^N = [E_T(30) - 30.7]/32.4 \quad (2)$$

The E_T^N s vary from 1.000 (water) to 0.000 (tetramethylsilane) [19]. The values of $E_T(30)$ and E_T^N for pure and mixed solvents are available in the literature [19,20]. For mixed solvents, the inspection of the dependences of polarity parameter on composition provides an insight to the phenomena of preferential solvation in these mixtures [20,40–42]. The $E_T(30)$ and E_T^N values were obtained for a plenty of surfactant micellar solutions and related systems. Besides the standard Reichardt's dye, indicators of the same family were used, e.g., the dichloro analogue ($R^1 = Cl$, $R^2 = R^3 = C_6H_5$) [14,15,34,35], the dye unsubstituted in 2,6-position of the phenolate moiety ($R^1 = H$, $R^2 = R^3 = C_6H_5$) [24,25,36], and more hydrophobic representatives ($R^1 = (CH_3)_3C$, $R^2 = R^3 = C_6H_5$ and $R^1 = R^2 = R^3 = 4-(CH_3)_3C-C_6H_4$) [35]. The betaine dyes were used for versatile examining of micellar solutions of various ionic and nonionic surfactants [4,6,11,14,20,23–25,27,28,31,34,35], zwitterionic [26] and gemini [29,30] surfactants, direct [28,36] and reversed [32] microemulsions, solutions of water-soluble polymers [33,39], mixed ionic surfactant + 1-butanol micelles [37,38], etc.

Of course, the experimental estimation of the polarity of the micellar pseudophase via solvatochromic indicators imply complete binding of these molecular probes by the micelles. Otherwise, special

study should be undertaken. The most popular way is the examining the dependence of the λ_{\max} or E_T^N value on the surfactant concentration [15,23,29]. The plateau in the corresponding curve may give evidence for complete binding, though some secondary effects may reflect the response of the completely bound indicator on the micellar transformations caused by the increase in surfactant concentration. The analysis of the vis absorption spectral band width of charge-transfer transition also allows confirming the location of the betaine dye in the surfactant micelles [31].

In some other papers [15,24–28], the vis absorption spectra and E_T^N values were determined at different concentrations of surfactants; the data were explained in terms of surfactant + dye association constants, critical micelle concentrations of surfactants, and polarity alterations of the microenvironments of the dye within the micellar pseudophase.

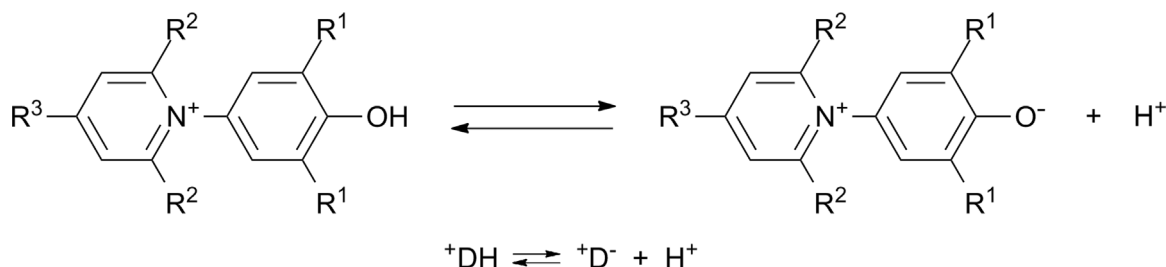
The nature of the counter-ion may display crucial role in the micellar transformations. For instance, in the case of several cationic surfactants, the introduction of some organic anions, such as tosylate, salicylate, alkyl sulfonates, returns the E_T^N values to the 'aqueous' one [43,44]; this was ascribed to the transformation of the sphere-shaped micelles to the worm-like ones. Within the course of these studies, nine pyridinium *N*-phenolate betaine dyes, including fluorinated ones, were applied [44].

Obviously, besides the problem of completeness of dye binding by micelles, the key question consists in the locus of the colored (or fluorescent) molecular probe. As a rule, the dyes bearing acidic/basic groups are supposed to be situated in the interfacial portion of ionic micelles, i.e., in the Stern layer. However, in some cases this is not so evident. Moreover, as it was shown recently [45], very small variations in the location of the ionizing group display marked changes in the Ψ value determined via the given indicator.

In our previous papers, we investigated the locus and hydration degree of the colored zwitterionic form, ${}^+D^-$, of the standard Reichardt's dye in micelles of cetyltrimethylammonium bromide, CTAB, and sodium dodecyl sulfate, SDS, [46] or sodium cetyl sulfate [47]. The results agree in general features with the experimental data. In the case of SDS, the dye is situated somewhat closer to the micellar palisade, and the oxygen atom is much more hydrated as compared with the case of CTAB micelles. This is in line with the E_T^N values of 0.827–0.842 and 0.687–0.705 determined for SDS and CTAB, respectively [4,11,23].

This observation is probably of a general character. The first measurements made with the standard Reichardt's dye have already revealed a distinct difference between the micelles of cationic alkyltrimethylammonium halide and anionic sodium alkyl sulfate surfactants [23].

In this connection, the experimental study of location character of indicators using 1H NMR spectroscopy is of particular importance. For the standard compound ($R^1 = R^2 = R^3 = C_6H_5$), Zachariasse et al. [23] have shown that, in 0.05 M CTAB aqueous solution with a surfactant:dye ratio of 20:1, the colored dye exerts the largest influence on the methyl groups of $-N(CH_3)_3^+$ and the hydrogen atoms of α and β methylene groups. Accordingly, the dye is located in the micellar surface region. Tada et al. [15] have found that the dichloro derivative ($R^1 = Cl$; $R^2 = R^3 = C_6H_5$) is rather deeply penetrated into the cationic



Scheme 1. General formula and acid-base equilibrium of the pyridinium *N*-phenolate dyes.

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