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Reporter molecules for nanosized lyophilic dispersions. 2,6-Dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate in aqueous micellar solutions of colloidal surfactants

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The behavior of a reporter molecule, the solvatochromic dye 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, was studied in aqueous micellar solutions of anionic, nonionic, and cationic surfactants. The possibility of utilization of this molecular probe as a combined indicator for monitoring of polarity and electrical potential of interfaces in lyophilic nanosized dispersions was demonstrated.

Исследовано поведение репортерной молекулы, сольватохромного бетаинового красителя 2,6-дихлор-4-(2,4,6-трифенилпиридиний-1)фенолята, в водных мицеллярных растворах анионного, неионного и катионного поверхностно-активных веществ. Показана возможность использования данной молекулярной пробы в качестве комбинированного индикатора для мониторинга полярности и электрического потенциала на межфазных границах в лиофильных наноразмерных дисперсиях.

For gaining inside into the characteristics and organization of nanosized lyophilic dispersions, effective molecular probes (reporter molecules) are necessary. Pyridinium *N*-phenolate betaine dyes exhibit the largest range of solvatochromism among up-to-now known organic dyes [1,2]. Therefore, they are often used for the polarity estimation of interfaces in various microheterogeneous systems, such as micellar solutions of colloidal surfactants [1-4], suspensions of liposomes [1,2,4,5], microemulsions [1-3,6], polymer microdomains [7], and dendrimers [8]. In such studies, the standard betaine dye, the Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, was used as a rule. This indicator with strong negative solvatochromism was also utilized in the examination of sol-gel systems doped with surfactants [9] and of ionic liquids [10]. Furthermore, Reichardt's dye can serve as pH-indicator for simultaneous checking of the interfacial acidity in the aforesaid disperse systems [4-6,9]. The determination of the so-called apparent dissociation constants can be used for monitoring of electrical interfacial potentials [4-6].

However, not only the standard dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate, but also other betaine dyes can serve as both solvatochromic and acid-base probes. For example, 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Fig. 1) was used for measuring polarity of micellar surfaces by some research groups [11-14].

In non-uniform nanosized particles, such as micelles (as well as microdroplets, vesicles, etc.), the absorption spectra and acid-base properties of different molecular probes can reflect rather different microenvironments, caused by different penetration depths or/and different orientation of the indicator dipole molecules within the micellar interior or palisade [6,15].

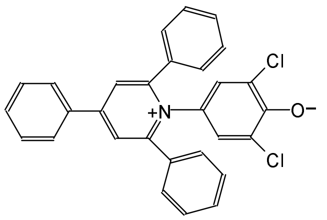

Fig.1. Betaine dye 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate ($D^{\pm}$).

Therefore, it can be expected that more reliable information concerning micelles and other nanosized particles can be obtained by using a set of different betaine dyes. In this paper, we briefly communicate the results obtained with 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Fig. 1). The sample of this dye was kindly putted to our disposal by Professor Dr. C. Reichardt.

Anionic, nonionic, and cationic surfactants used are: sodium n-dodecylsulfate (SDS), nonylphenol-12 (NP-12), and N-cetylpyridinium chloride (CPC), respectively. The absorption spectra of this dye (in form of the aforementioned dipolar structure, $D^{\pm}$) in various systems are depicted in Fig. 2. The λ_{max} values of the so-called charge-transfer band [1,2] are equal to 409 (in water), 437 (in SDS micelles), 451 (in NP-12 micelles), and 458 (in CPC micelles).

The apparent dissociation constants, K_a^a, of the colorless cation ($HD^+ \rightleftarrows D^{\pm} + H^+$) were obtained vis-spectroscopically in buffer solutions, using the common procedure [5,6,15]. The complete binding of the indicator species by the micelles was proved by variation of surfactant concentrations. The results are presented in the Table; $pK_a^a = -\log K_a^a$. The experimental details will be given elsewhere.

Our thermodynamic value in water, pK_a^w, is close to the value 4.78±0.05, obtained by Kessler and Wolfbeis [11] at ionic strength < 0.01 M and 22 °C.

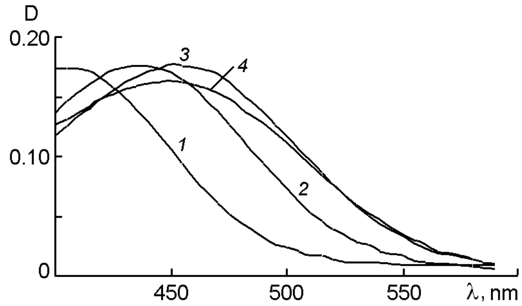

Fig. 2. Vis absorption spectra of 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (1.7×10^{-5} M) in water (*1*) and in aqueous micellar solutions (0.01 M) of SDS (*2*), NP-12 (*3*), and CPC (*4*); pH = 10-12, optical path length: 5 cm.

According to the well-known model [4-6,15], the values depend on the electrical interfacial potential, Ψ/mV: $pK_a^a = pK_a^i - -0.0169\Psi$. Here pK_a^i is the so-called intrinsic dissociation constant, which is usually equated to the pK_a^a value in non-ionic micelles, where $\Psi \to 0$.

Inspection of the Table and Fig. 2 reveals that the betaine dye studied can serve as a combined indicator for monitoring of polarity and electrical potential of interfaces. For example, the estimates of Ψ = −112 and +86 mV can be made as first approximation for SDS and CPC micellar solutions, respectively.

More detailed consideration of the behavior of a set of betaine dyes in aqueous micellar solutions of surfactants will be made in our further publications.

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Table. The indices of apparent dissociation constants of the colorless 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenol, HD^+, in micellar solutions of colloidal surfactants; bulk ionic strength: 0.05 M (NaCl + buffer mixtures); 25 °C.

System	pK_a^a	$\Delta pK_a^a = pK_a^a - pK_a^w$
Aqueous 0.01 M SDS solution	7.10±0.05	2.34
Aqueous 0.01 M NP-12	5.21±0.03	0.45
Aqueous 0.01 M CPC solution	3.75±0.02	−1.01
Water (thermodynamic pK_a^a value)	4.76±0.03	0

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Репортерні молекули для нанорозмірних ліофільних дисперсій. 2,6-Дихлор-4-(2,4,6-трифенілпіридиній-1)фенолят у водних міцелярних розчинах колоїдних поверхнево-активних речовин

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Досліджено поведінку репортерної молекули, сольватохромного бетаїнового барвника 2,6-дихлор-4-(2,4,6-трифенілпіридиній-1)феноляту, у водних міцелярних розчинах аніонної, неіонної та катіонної поверхнево-активних речовин. Показано можливість використання даної молекулярної проби як комбінованого індикатора для моніторингу полярності та електричного поверхневого потенціалу на міжфазних границях у ліофільних нанорозмірних дисперсіях.