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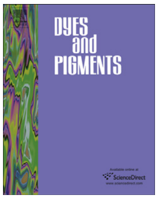

Toluidine blue-sodium lauryl ether sulfate complexes: Influence of ethylene oxide length

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ABSTRACT

Sodium Lauryl Ether Sulfates (SLES) are an increasingly important and versatile type of surfactants. The complexation between ortho-Toluidine blue (TBO) and a homologous series of SLES, including Sodium Lauryl Sulfate (SDS) without Ethylene Oxide (EO), has been investigated using visible spectrophotometry. Upon increasing the molar surfactant-dye-ratio (S/D), three TBO organization regimes can be identified from the absorption spectra: (i) Ion-pair formation, (ii) Pre-micellar aggregation and (iii) Micellar aggregation. The limited solubility of SDS-TBO ion pairs, leading to precipitation of ion-pair clusters, causes a decrease of the TBO monomeric peak height when S/D is increased. The better solvability of TBO-SLES ion-pairs causes the onset of precipitation to occur at higher S/D when the EO-block length increases. In an intermediate S/D range, metachromasy is observed as a result of dye-stacking onto the SDS arranged in a pre-micellar state at surfactant concentrations well below the critical micelle concentration (CMC). For SDS, the S/D range showing pre-micelles depends on TBO concentration but seems independent of variation of ionic strength (phosphate buffer, pH = 7.0, $C_{buffer} = 0.1–10$ mM), whereas the metachromatic peak height increases with decreasing ionic strength. The pre-micellar region for all SLES-TBO is located at the same S/D range but the maximum metachromatic peak height follows the trend: $EO_2 > EO_4 > SDS > EO_{12} \approx EO_{30}$. The onset of the micellar range, in which TBO is again present in monomeric form, is shown to coincide with the CMC. These findings could proof helpful in either formulation or analysis of SLES. Likewise, understanding the dyes' interactions may facilitate formulation of dyeing solutions for optimal performance, or alternatively, as part of the textile plant effluent treatment to remove, and possibly recycle, dyes.

1. Introduction

Ortho-Toluidine blue (TBO), a cationic phenothiazinium dye (CI 52040) [1], discovered by William Henry Perkin in 1856, was the first synthetic organic dye. Next to being a dyeing agent, nowadays, it is widely used for a variety of other practical applications, including specific staining in histology [2], clinical use [3,4] and as a reagent in analytical chemistry [5–8]. TBO owes its use in clinical and analytical applications, as an indicator for the presence of polyanions, to a visible colour change when interacting with these species; this phenomenon is called metachromasy [9]. Metachromasy, in the case of TBO the appearance of a typical hypsochromic, or blue shifted, change in its absorbance spectrum, is the result of self-organization of TBO via stacking. To allow for such stacked organization, TBO needs to electrostatically bind to a suitable template which has multiple anionic charges at regularly spaced positions in order to fit the stacked TBO assemblies. The stacking of dye molecules, which involves bringing the charged groups into close proximity, is driven by both hydrophobic interactions as well as the overlap of the conjugated double bond π-orbitals of adjacent dye molecules. Polyanions, either synthetic [5,7,8,10,11] or natural [12], offer such a template and this is employed both in specific staining of cell organelles (rich in polyanions like e.g. heparin [13]) and in chemical analysis. Metachromasy is not unique for TBO but is observed for many other cationic azo dyes. Similarly, anionic dyes such as methyl orange,

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show metachromasy in the presence of polycations [14]. Most dyes, or their degradation products, are toxic [16] and their presence in effluents from textile dyeing plants is therefore a major concern. Understanding the interactions of a dye may help applying these compounds more effectively in the textile dyeing process, e.g. by tuning their optical properties, or alternatively, as part of the textile plant effluent treatment to remove, and possibly recycle, them.

TBO also forms complexes with anionic surfactants, this has been studied for SDS [15], but the resulting absorption characteristics depend on surfactant concentration and molar surfactant-to-dye ratio and seem to reflect more complicated structures formed than those of polyanion-TBO complexes. At low surfactant concentration, TBO molecules form 1:1 ion-pairs with oppositely charged surfactants and no metachromasy is observed. When the ion-pairs exceed their solubility limit they may precipitate. Upon further increase of the surfactant concentration, but still below the critical micelle concentration of the surfactant, the ion-pair precipitates transform into an organized structure. In such structures surfactants can provide a suitable template for the binding of stacked formations of adjacent TBO ions, which show metachromasy. This organization of the surfactant has been denoted as pre-micellar aggregation [15]. Upon further increase of the surfactant concentration, the critical micelle concentration (CMC) is attained, and the dye molecules distribute themselves as monomers over these micelles [15]. In the scarce literature on TBO interactions with surfactants [15], the solution conditions were rarely controlled by use of a buffer; most work was done in ultrapure water. In such aqueous solutions minor quantities of salts, acids and bases, present as impurities in either of the reagents, may cause substantial differences in observed pH and ionic strength.

The goal of this paper is to gain understanding in the effect of the presence, and size, of an EO-block adjacent to the charged head group on the complexation and self-organization of TBO onto Sodium Lauryl Ether Sulfate (SLES) surfactants. Sodium Lauryl Ether Sulfate (SLES) surfactants can be found in a number of important applications. SLES with a small EO-block, commonly 1–3 EO groups, are mostly used in shampoo or other personal care products [17]. SLES with larger EO-blocks, typically containing 3–12 EO units, are used for instance as emulsifiers in emulsion polymerization [18]. The SLES with even larger EO-blocks are used as stabilizers for emulsions and dispersions due to their combined action of the electrostatic charge of the head group and the extended and hydrated EO-chain.

The approach we took in this work is to study complexation under well controlled solution conditions of pH, ionic strength and dye concentration. To this end, and for comparison to earlier research, we initially investigate the complexation of TBO with a high purity surfactant, Sodium Dodecyl Sulfate (SDS), using visible light spectrophotometry to monitor changes in the state of TBO as a function of buffer strength and dye concentration. Next, TBO complexation is investigated with a set of industrial grade SLES surfactants, with varying EO-block size, under previously determined solution conditions. To relate spectral changes to the presence of micelles, the CMC of all tested surfactants is determined under identical solvent conditions both in the absence and presence of TBO. This knowledge may be further used in formulation of dye solutions, analytical method development for SLES and in understanding the effect of the presence of SLES in dye solutions in coloration/dyeing and in environmental remediation of textile dyeing process effluents.

2. Materials and methods

2.1. Materials

In our experimental studies, Ortho-toluidine blue, (7-amino-8-methyl- phenothiazin-3-ylidene)-dimethyl-ammonium chloride, analytical grade, further referred to as TBO, was obtained from Fluka Analytical (India). The homologous series of sodium lauryl ether sulfates (SLES) used were commercial samples of industrial grade products, kindly supplied by BASF, of Disponil® series surfactants: (1) Disponil FES 27; Sodium lauryl (EO)2 sulfate, (2) Disponil FES 32; Sodium lauryl (EO)4 sulfate (3) Disponil FES 993; Sodium lauryl (EO)12 sulfate and (4) FES 77; Sodium lauryl (EO)30 sulfate. Sodium Lauryl Sulfate (SLS), of highest purity (99.6%) available, was purchased from Merck (Germany). Scheme 1 shows the molecular structures of TBO and SLES.

Auxiliary materials used were: TEGO®trant A100: 1,3-didecyl-2-methylimidazolium chloride (DDMICl) purchased from Metrohm (Switzerland). All other chemicals were of highest purity available and were used without further purification. Ultrapure water, used throughout the investigation, was obtained using a Milli-Q Advantage A10 purification system from Millipore SA Molsheim, France.

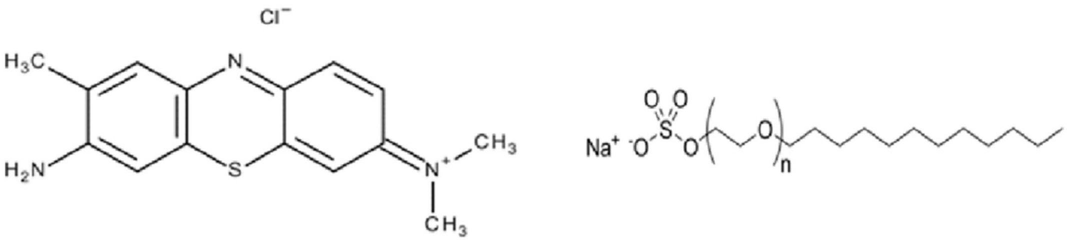
2.2. Methods

2.2.1. Reagent preparation

All reagents were prepared as stock solutions in ultrapure water. The stock solutions of surfactants were freshly prepared at a suitable concentration of at least 10 mM (the experimental verification thereof is described in the next sub-section) and stored in the dark for the duration of the study. To maintain constant pH and ionic strength, all experiments, except those in which the effect of ionic strength was investigated, were performed in a phosphate buffer at c(buffer) = 1 mM and pH = 7.0.

2.2.2. Determination and definition of surfactant concentration (S)

The surfactants used in this study were, apart from SDS, industrial grade commercial SLES samples. It is known for these



a. Ortho-Toluidine Blue (TBO) b. Sodium Lauryl Ether Sulfate (SLES)

Scheme 1. Molecular structures of TBO and SLES.