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Rhodamine B adsorption on anodic porous alumina in sodium dodecyl sulfate solutions

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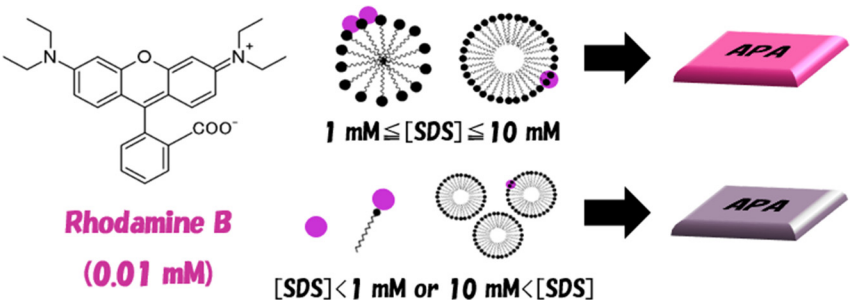
GRAPHICAL ABSTRACT



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ABSTRACT

Anodic porous alumina (APA) with its positively charged surface can be dyed by electrostatic interactions with negatively charged dye molecules. In this study, an anionic surfactant, sodium dodecyl sulfate (SDS) was found to allow such use of cationic dyes as well, using rhodamine B (RB) as a test. By dipping APA in the RB-SDS solutions, RB was successfully adsorbed to the APA surface to create a uniform pink color. The amount of adsorbed RB first increased with [SDS] up to around 3 mM, and then decreased to almost zero with the corresponding color change in the APA surface. A bath pH of 6–7 was suitable for dyeing APA in the RB-SDS solutions. From the absorption and fluorescence studies, we concluded that RB is dominantly adsorbed on APA as a zwitterionic form in non-fluorescent H-dimers in the dye-rich induced micelles and SDS micelles. Surface analysis studies of the dyed APA showed that RB is entrapped in the pores of APA with the average pore diameter of 17 nm up to about 600 nm in depth.

1. Introduction

For almost a century, anodic porous alumina (APA), which is formed by the anodization of aluminum in an acidic electrolyte, has been used mainly for protective purposes as well as coloring the aluminum surface [1,2]. APA is conveniently dyed by dipping in a bath containing an organic dye or pigment. A key factor in the dyeing process is the dye-bath pH. At an ideal pH in the range of 3–5, the APA surface is positively charged due to $Al(H_2O)_4(OH)_2^+$ or $Al(OH)_2^+$ species. The positively charged surface is mainly dyed by electrostatic interactions with negatively charged dye molecules, such as those containing SO_3^- and OH^- groups [1]. This means that cationic and neutral dyes generally cannot be used here.

In recent years, APA has also served as functional nanostructured materials for optical and other applications [2–7]. For example, nanocomposites featuring tris(8-hydroxyquinoline)aluminum (Alq_3) entrapped in the pores of APA have been studied in the field of organic light-emitting diodes. Nanocomposites of APA are expected to have

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great potentials as optical materials. However, not all molecules of interest in these applications are negatively charged, and so novel methods are required to adsorb molecules on APA regardless of the charge.

Our group had previously studied the adsorption of non-charged complexes and molecules to the APA surface, including Alq_3, tris(dibenzoylmethane)mono(1,10-phenanthroline)europium (Eudp), and pyrene by using sodium dodecyl sulfate (SDS) micellar solutions [8]. The adsorption of Alq_3 and Eudp achieved in SDS micellar solutions was about three times larger than those in *N*,*N*-dimethylformamide solvent. Also, pyrene could only be adsorbed when dissolved in the SDS micellar solution. These results suggested that the negatively charged SDS micelles containing dissolved non-charged molecules were successfully adsorbed on the APA surface.

Rhodamine dyes including rhodamine B (RB) and rhodamine 6G (R6G) are well-studied functional dyes with various applications, such as in active optical materials [9], chemosensors [10], and optical memory materials [11]. Silina et al [12]. studied the adsorption of hydrophilic dyes including R6G on APA films for pH sensing. They obtained a stable, homogenously saturated pink film of R6G only after prior modification of the APA by oleic acid. RB is a rhodamine dye with a high fluorescent yield. RB has various species depending on the pH and solvent nature (Fig. 1), including cationic RBH^+, zwitterionic $RB^{\pm}$, and lactone RB^o forms (the content of RB^o is negligibly small in water) [13,14]. Moreover, RB molecules are known to form non-fluorescent H-dimers with a sandwich structure and fluorescent J-dimers with an oblique geometry [15–17].

The photophysical and photochemical properties of organic molecules in organized assemblies have been extensively studied [18,19]. An interesting finding is the electrostatic interaction between cationic dyes and anionic SDS, allowing them to form complexes that change the characteristics of the micelles and the dye. Especially, cationic dye-SDS systems exhibit an interaction below the critical micellar concentration (CMC, 8.2 mM) in the so-called pre-micellar region [18]. In the lower part of the pre-micellar region where SDS is approximately 1–4 mM, pre-micellar aggregates are formed by the surfactant and dye. The aggregates become the “dye-rich induced micelles” in the higher pre-micellar region [18] near the SDS concentration of 4 mM. Then, above the CMC they become ordinary micelles solubilizing the dyes. Junqueira et al. [19] also reported similar results in the methylene blue (MB^+)-SDS system, where a small volume of the “micelle pseudo-phase”, *i.e.*, the dye-rich induced micelles [18] was formed at ~3 mM SDS concentration. Remarkably, the CMC of SDS decreased from ~7 mM to ~70 μM when the MB^+ concentration increased from 0 to 45 μM due to a strong interaction between MB^+ and SDS, suggesting that MB^+ can facilitate micelle formation at a lower surfactant concentration. We thus consider that the micellar aggregates formed in cationic-SDS systems below the original CMC value (8.2 mM) each contained fewer SDS molecules, and they are essentially the same as the dye-rich induced micelles or the micelle pseudo-phase. Similar behaviors were also observed for RB in SDS solutions [13,14,20,21]. When the concentration of SDS increased from 1 to 4 mM, critical changes in absorption and fluorescence occurred at approximately 4 mM [21]. Above 4 mM, the RB molecules are solubilized into micelles. It is generally believed that the hydrophobic xanthene skeleton of RB is located in the interfacial region between the micelle and water [13,14,20,21].

In this paper, we studied the effects of SDS concentration and pH on the absorption and fluorescence properties of RB in aqueous solutions. We also examined the adsorption of RB to the APA surface using the same SDS solutions, which dyed the APA surface to a pink color. The adsorption mechanism was discussed in relation to the spectroscopic data.

2. Experimental

2.1. Materials

An Al plate (purity 99.59%) was purchased from Nilaco Co., Ltd. Japan. RB (> 98%), SDS (> 95%), perchloric acid (60 wt%, $HClO_4$), ethanol (99.5 vol%, C_2H_5OH), sulfuric acid (95 wt%, H_2SO_4), hydrochloric acid (35 wt%, HCl), and ammonia aqueous solution (30 wt%, NH_3) were purchased from Wako Pure Chemical Industries Ltd., Japan. All chemicals were used without further purification.

2.2. APA preparation and dyeing

According to our previous method [7], APA samples were prepared by a one-step anodization process. An Al plate (1-cm^2) was electropolished in a mixed solution of $HClO_4$ and C_2H_5OH (1:4 v/v) under a constant voltage of 20 V for 30 s below a temperature of 1 °C.

The polished plate was anodized in 1.5 M H_2SO_4 solution at a constant voltage of 15 V for 30 min at ~20 °C. The dyeing process was conducted using the same condition as in the alizarin red S adsorption treatment [22]. The prepared APA samples were immersed in aqueous solutions containing RB ([RB] = 0.01 mM) and SDS ([SDS] = 0–100 mM) at about 50 °C for 5 min with different pH values (2–10), as adjusted with HCl and NH_3.

2.3. Instrumental analysis

Scanning electron microscope (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were observed by an SEM Quanta 3D 200i (FEI Co., Oregon, USA) equipped with EDS analyzer (EDAX Co., Tokyo, Japan). Absorption spectra of RB in the SDS aqueous solutions and diffuse reflectance spectra for the dyed APA samples were recorded by an ultraviolet-visible spectrophotometer V-570 (JASCO Co., Tokyo, Japan). The reflectance spectra were transformed to absorption spectra using the Kubelka–Munk function. Fluorescence spectra were obtained with a fluorescence spectrophotometer FP-8500 (JASCO Co., Tokyo, Japan).

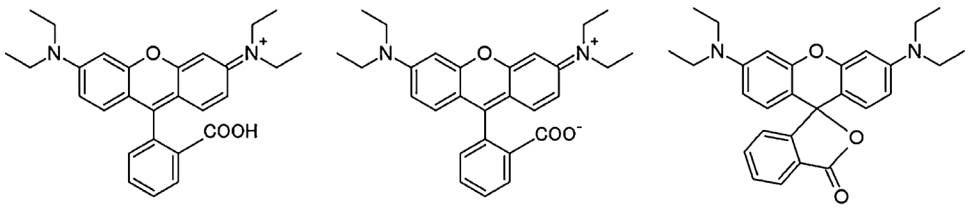

Fig. 1. Different forms of RB.