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Interaction between 4-chloro-(2′-hydroxylphenylazo)rhodanine and cetyltrimethyl ammonium bromide

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Abstract

The interaction between 4-chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR) and cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was investigated by surface tension, absorption spectra, resonance light scattering (RLS) spectra and transmission electron microscopy. It can be concluded from the experimental results that the hydrophobic forces cannot be neglected, even though the electrostatic interaction between ClHPAR and CTAB plays an important role. The RLS spectral behavior of ClHPAR changes in the presence of CTAB. The efficiency and the effectiveness of ClHPAR–CTAB mixture to decrease the surface tension of water are higher than those of any single component, i.e. CTAB and ClHPAR. As one might expect, NaCl and urine have different effects on the interaction between ClHPAR and CTAB and their interaction also depends on pH.

Keywords: Interaction; Cetyltrimethyl ammonium bromide (CTAB); Dye; Surfactant; 4-Chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR)

1. Introduction

Dye–surfactant interactions are of great importance due to their industrial applications, pertinence to biological process and analytical chemistry [1–3]. For instance, surfactant is often used as a wetting agent, a suspending agent, and a solubilizer for water insoluble dye in various dyeing processes such as textile dyeing, photography and printing ink [4]. Therefore, the interaction between them has been studied quite extensively for many years by different methods including potentiometry, conductometry, voltammetry, tensiometry, etc. [5–14].

Considerable research has confirmed that surfactants can affect the spectra of the solutions of many dyes [15–17], due to aggregation of the dye molecules or dye–surfactant ion pairs and charge transfer between dye and surfactant molecules [18]. This property has been used in spectroscopic determination of metal ions, inorganic substances and biological macromolecules and to improve spectral characteristics of colored systems [19–24]. Hence, it is necessary to probe the mechanism of interaction between the dye and the surfactant.

In our previous work, the aggregation behaviors of sodium bis(2-ethylhexyl)sulfosuccinate and sodium bis(2-ethylhexyl)-phosphate surfactants were studied via the energy transfer between acridine orange and rhodamine B dyes [25]. In this work, surface tension, absorption spectra, resonance light scattering (RLS) spectra and transmission electron microscopy (TEM) techniques were used to investigate the interaction mechanism between 4-chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR) and cetyltrimethyl ammonium bromide (CTAB). In order to investigate the effect of hydrophobicity of the surfactant upon interaction, tetradecyltrimethyl ammonium bromide (TTAB) and dodecyltrimethyl ammonium bromide (DTAB) were also used. In addition, the effects of pH, NaCl and urea on the interaction between ClHPAR and CTAB are probed.

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2. Experimental

2.1. Apparatus

Absorbance measurements were performed on a Hitachi UV-4100 spectrophotometer, appropriately equipped with 1.0 cm quartz cells.

The RLS spectra were scanned synchronously at the same wavelength of excitation and emission in the range of 300–600 nm by Perkin Elmer LS-55 spectrofluorimeter with a 1.0 cm quartz cell. The excitation and emission slits are 10 and 2.5 nm, respectively.

Surface tension measurements were made on Processor Tensiometer-K12 (Krüss Company, Germany) using the Wilhelmy dipping plate method at 25.0 ± 0.2 °C. The average values of surface tension were obtained by repeating three times.

The morphology and size of products were characterized directly by transmission electron microscopy (JEM100-CXII electron microscope, Japan). Staining was achieved by treating the samples with 1% phosphotungstic acid aqueous solution.

2.2. Reagents

The cationic surfactants, dodecyltrimethyl ammonium bromide (DTAB), tetradecyltrimethyl ammonium bromide (TTAB) and cetyltrimethyl ammonium bromide (CTAB), were obtained from Ameresco and their critical micelle concentrations (CMC) were 15, 3.0, and 0.8 mmol L^{-1} [26], respectively. ClHPAR was purchased from East China Normal University. It has a planar aromatic and heterocyclic structure as is presented in Fig. 1.

NaCl and urine were supplied from Xilong Chemical Factory, Guangdong. Tris–HCl buffer (pH 7.85) was used to control the acidity. Water used in the experiments was triply distilled by a quartz water purification system.

2.3. Procedure

To a test tube, the solutions were added in the following order: buffer solution, an appropriate amount of ClHPAR and cationic surfactant solution. The mixture was diluted to the mark with water and mixed thoroughly. After 10 min, the solution was measured as mentioned above.

3. Results and discussion

3.1. Absorption spectra of mixtures of ClHPAR and cationic surfactants

The absorption spectrum of ClHPAR with and without CTAB at pH 7.85 is shown in Fig. 2. The spectrum of the dye consists of two absorption peaks at 330 and 422 nm. In the presence of CTAB (0.05 mmol L^{-1}, below CMC), the maximum absorption wavelength (λ_{max}) of ClHPAR shifts from 422 to 442 nm and the corresponding absorbance decreases from 0.593 to 0.387. The maximum absorption peak still displays a red shift and the absorbance at this wavelength increases gradually with increasing CTAB concentration. However, there is no remarkable change in the absorption peak at 330 nm, only the absorbance at 330 nm changes.

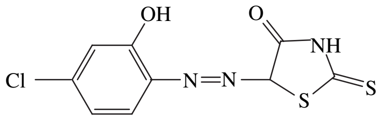

Fig. 1. The chemical structure of ClHPAR.

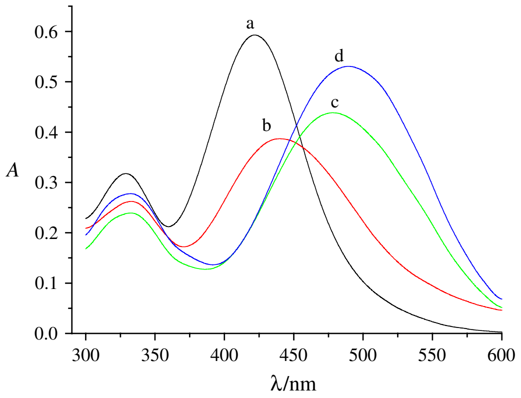

Fig. 2. Absorption spectra of ClHPAR dye (3.0×10^{-5} mol L^{-1}) in the presence of CTAB. Condition: CTAB concentration (a) 0 mmol L^{-1}; (b) 0.05 mmol L^{-1}; (c) 0.3 mmol L^{-1}; and (d) 1.2 mmol L^{-1}.

Fig. 3 shows the effect of CTAB concentration on λ_{max}. Obviously, the values of λ_{max} increase gradually with increasing CTAB concentration (below CMC). This is due to the formation of more ClHPAR–CTAB complexes. The values of λ_{max} become nearly constant as CTAB concentration is well above its CMC, which is attributed to the solubilization of a large amount of dyes in the micelles.

In order to probe the influence of hydrophobicity of the surfactant, the absorption spectra of mixtures of ClHPAR–DTAB and ClHPAR–TTAB were studied synchronously. Some experimental results like absorbance (A), λ_{max}, wavelength shift ($\Delta\lambda$) and electronic transition energy (ΔE) are summarized in Table 1. ΔE is calculated as $\Delta E = hc/(\lambda_{dye-surfactant} - \lambda_{dye-water})$, where h is Planck's constant (6.62×10^{-34} J s), c is the speed of light

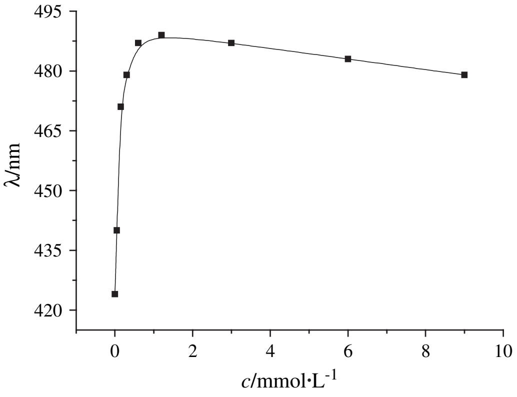

Fig. 3. Effect of CTAB concentration on the maximum wavelength of dye (3.0×10^{-5} mol L^{-1}).