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Studies on The Interaction of Gemini Surfactant With Anionic Azo Dyes by Absorption Spectroscopy

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The interactions of two anionic azo dyes, methyl orange and methyl red, with a kind of gemini surfactant in aqueous solution have investigated by means of UV-Vis spectroscopy. It was observed that the aggregation of surfactant and dye takes place at surfactant concentrations far below the critical micelle concentration of the surfactant. Aggregations with anionic dyes were reflected by hypsochromic shifts with a decrease in the intensity of absorption band. The results show the absorption spectrum of methyl orange at 510 nm for acidic form gradually decreased whereas the absorption at about 430 nm increased with the increasing of pH. For methyl red, bathochromic shifts take place from 525 to 420 nm with the increasing pH.

Key Words: Gemini surfactant, Methyl orange, Methyl red, Absorption spectroscopy.

INTRODUCTION

Azo dyes are a versatile class of coloured organic compounds which have been extensively used in the dyeing of synthetic fibers as well as in the formulation of many industrial pigments. Dye-surfactant interactions in aqueous buffered systems have been the subject of many research topics due to their industrial applications[1] and pertinence to biological process[2-4]. The investigations into the behaviour of different dyes in surfactant aqueous solutions can give useful information for understanding the thermodynamics and kinetics of the dyeing process and the finishing of textile material[5-8]. Many researchers have studied acid-base equilibria at dye-surfactant systems with both the acidic and basic forms of the dye completely bound to micelles by different methods[9-12]. UV-Vis spectroscopy, conductometry and using surfactant selective electrodes are among the most widely used measurement methods for studying this subject[13-15].

The spectral changes of a dye observed in the presence of various amounts of surfactants are consistent with sequential equilibria involving surfactant monomers, micelles, dye aggregates, premicellar dye-surfactant complex and dye incorporated into micelle.

The investigation of cationic surfactant-anionic dyes has shown that the importance of long-range electrical forces is basically to bring the dye anion and the surfactant

cation close enough to enable the action of short-range noncoulombic attractive van der Waals forces and hydrophobic interactions. The importance of hydrophobic interactions is supported by the fact that the addition of ethanol to water reduces dye-surfactant ion pair formation. So, the long-range electrical forces as well as short-range attractive forces are responsible for the dye-surfactant ion pair formation[16,17].

The aggregation of oppositely-charged dyes with surfactants is strongly dependent on noncoulombic interactions. So, the hydrophobicity increase of the surfactant or the dye, increases the binding energy[18]. It has been reported that the type of head group of surfactants has no large influence on the aggregation process[19,20].

Gemini surfactants are composed of two monomeric surfactant molecules chemically bonded together by a spacer. There are two hydrophilic and two hydrophobic groups in their molecules. The advantages of gemini surfactants in comparison with corresponding conventional ones are higher surface activity, much lower values of the concentration C_{20}, lower critical micelle concentration (CMC), lower Krafft temperature and useful viscoelastic properties such as effective thickening[21].

In this study a kind of gemini cationic surfactant has been synthesized and the interactions of them with two anionic azo dyes, methyl Orange (MO) and methyl red (MR) in aqueous solution have been investigated by means of UV-Vis spectroscopy.

EXPERIMENTAL

Methyl red and methyl orange were obtained from Aldrich. The methyl orange solution was obtained by dissolving 0.0164 g of methyl orange in a 100 mL volumetric flask and diluted with double distilled water up to mark line. The stock solution of methyl red was prepared by dissolving 0.0202 g of methyl red in 50 mL of ethanol and then diluted up to 100 mL with double distilled water up to mark line. The stock solutions of surfactants were prepared by dissolving certain amounts of water. The critical micelle concentration of Gemini16 is 1.4×10^{-4} mol/L. All of the test solutions were prepared by diluting the respective stock solutions. Standard buffered solutions such as citric acid/citrate and acetic acid/acetate used were also of reagent grades.

Synthesis: The intermediate *bis*(2-bromoethyl) ether was synthesized from diglycol and phosphorus tribromide. The surfactant labeled as Gemini16 were obtained by refluxing the *bis*(2-bromoethyl) ether with N-N-hexadecyl-N,N-dimethylamine in isopropanol at 78 ºC for 48 h[22]. Solvent was removed under vacuum from the reaction mixture and the solid thus obtained was recrystallized three times from ethyl acetate-ethanol solvent mixture (volume ratio is 2:1). The synthetic procedure is shown in Fig. 1.

Spectral characteristics for Gemini16: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, 6H), 1.26-1.28 (m, 52H), 1.69 (m, 4H), 3.45 (s, 12H), 3.62 (t, 4H), 4.03 (s, 4H) 4.36 (s, 4H).

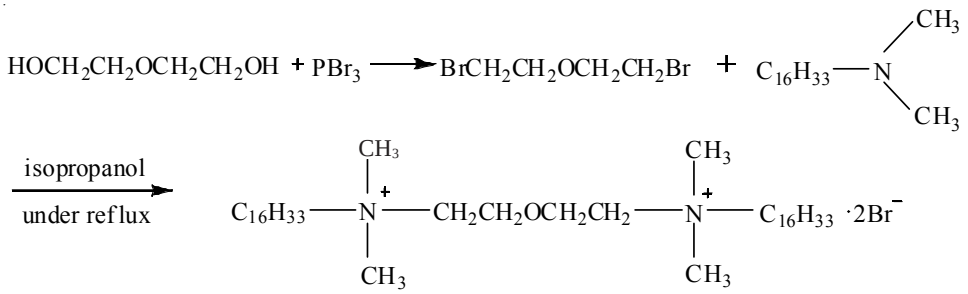

Fig. 1. Synthetic procedure of Gemini surfactant[16]

Instrumentation and software: A Hewlett-Packard 8453 diode array spectrophotometer controlled by a Hewlett-Packard computer and equipped with a 1 cm path length quartz cell was used for UV-Vis spectra acquisition. Data acquisition between 360-580 nm for methyl orange was performed with UV-Vis ChemStation program (Agilent Technologies), running under Windows XP.

RESULTS AND DISCUSSION

Methyl orange-surfactant interactions: The position of the long-wavelength absorption band of azo dyes is sensitive to medium effects, therefore, they can be used as solvatochromic micropolarity reporter molecules. For example, the wavelength of maximum absorption of methyl orange is position at 463 nm in water, whereas it is situated at 417 nm in ethanol. Similarly, upon binding of azo dyes to hydrophobic aggregates, a shift in absorption maximum occurs to shorter wavelength.

Fig. 2 shows the effect of different concentrations of Gemini16 on the absorption spectrum of methyl orange. In submicellar regions, the dye forms a sparingly soluble precipitate but it becomes soluble as the Gemini16 concentration reaches the CMC. Different kinds of complexes in the solution can be expected. Although the dye and surfactant are individually hydrated in the solution, they can sometimes meet each other in aqueous solution and the long-range electrostatic and short-range hydrophobic forces cause the formation of dye-surfactant complexes. There are strong indications that the dye molecules are arranged in a parallelway (H-type aggregation). It means the complex is a monomer involving electrostatic interaction between the positive charge of cationic surfactant and negatively charged sulphonate group, with the alkyl chain of cationic surfactant in close contact with the rest of the dye molecule and particularly, the azo group (the chromophoric unit). Some of these complexes can aggregate and precipitate in the solution which is in equilibrium with the precipitates. The loss of absorbance in dye solution in submicellar region is partly due to the precipitation of dye in the solution. Bathochromic shift of about 65 nm occurs at CMC of about 1.5×10^{-4} mol/L. Further addition of Gemini16 leads to hyperchromic shift which is characteristic of methyl orange bound to cationic micelles. It is obvious that association of surfactant molecules occurs with increase in concentration. This phenomena can increase the solubility of methyl orange,

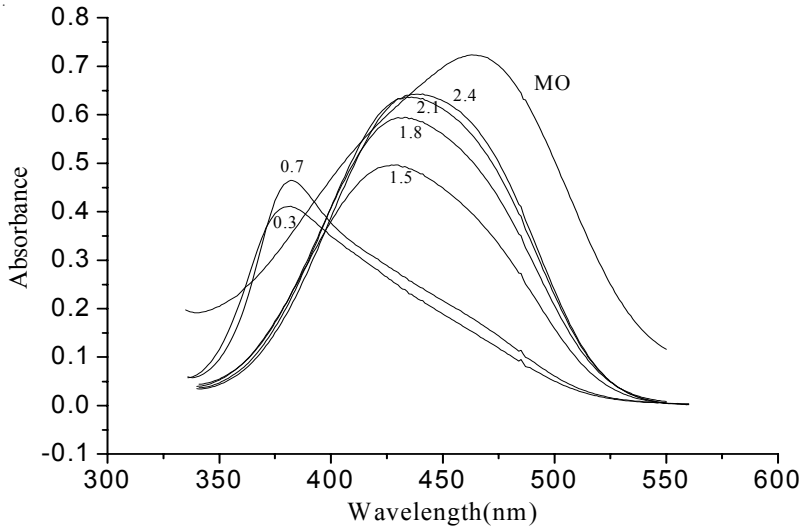

Fig. 2. Effect of Gemini16 on absorption spectrum of methyl orange (MO) (at 25 ºC, [MO] = 20 µM). The numbers represent the concentration of Gemini16 in 10^{-4} M

dye-surfactant aggregates and precipitates in the solution. So, bathochromic shift along with an increase in the intensity of absorbance can be seen in UV-Vis spectra. The gemini cationic surfactant shows larger hypsochromic shift (75-110 nm). This difference in the hypsochromic shift can be attributed to stronger charge density and hydrophobic forces of geminis in comparison to CTAB and it is obvious that every gemini molecule can bind and complex with two methyl orange molecules.

However, the long-range electrostatic forces and short-range hydrophobic interactions are not only the reason for dye-surfactant aggregation. Thus, other factors such as conformation, mobility and dispersivity of surfactant's molecule, different pH may also play important roles for dye-surfactant aggregation. The formation of parallel complexes of dye and surfactant molecules in the solution and different kinds of aggregates may depend on the pH values in solution. Fig. 3 shows the absorption spectra of 2.0×10^{-5} M methyl orange at different pH values in pure water. The absorption spectrum of methyl orange shows an absorption band which has an absorption maximum at 510 nm. This absorption band is attributed to the acidic form of methyl orange. With the increasing of pH, the absorption at 510 nm for acidic form gradually decreased whereas the absorption at about 430 nm increased. This shift is caused by the change of the contribution of the resonance forms (Fig. 4). A sharp isobestic point is observed in Fig. 3.

Methyl red-Surfactant interactions: Fig. 5 shows the absorption spectra of 3.0×10^{-5} M methyl red at different concentrations of Gemini16 at pH 2.98 in pure water. The absorption spectrum of methyl red shows an absorption band which has an absorption maximum at 525 nm. This absorption band is attributed to the acidic form of methyl red. With the increasing of concentrations of Gemini16, the absorption

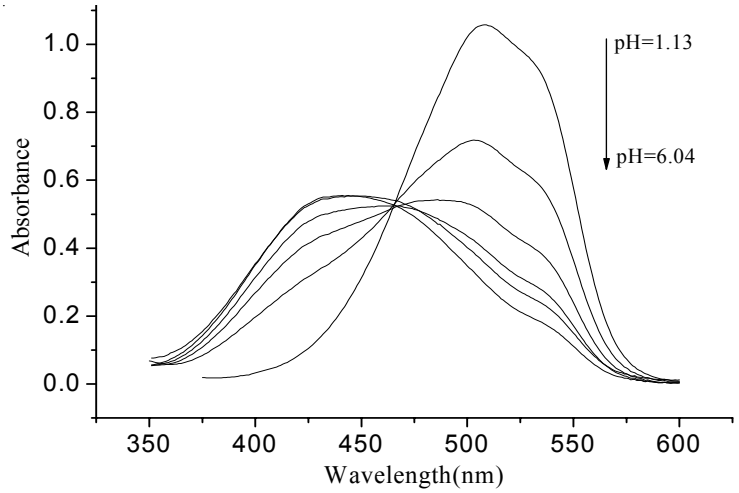

Fig. 3. Effect of pH values on absorption spectrum of methyl orange (MO) (at 25 ºC, [MO] = 20 μM, [Gemini16] = 2.5×10^{-5}). pH values are varying at 1.13, 2.08, 3.17, 4.09, 5.22, 6.04, respectively

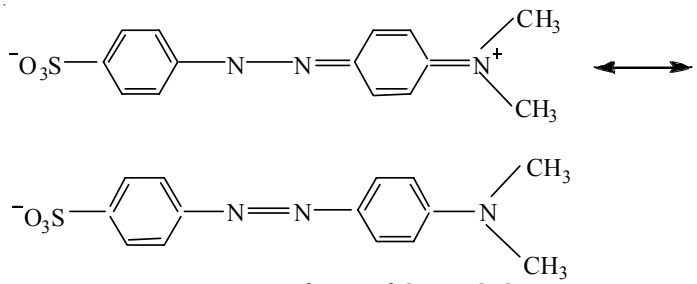

Fig. 4. Resonance forms of the methyl orange

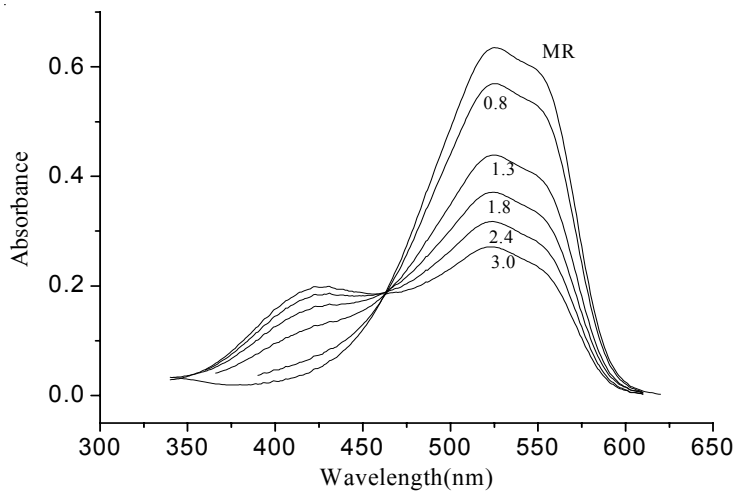

Fig.5. Effect of Gemini16 on absorption spectrum of methyl red (MR) (at 25 º, [MR] = 30 μM). The numbers Represent the concentration of Gemini16 in 10^{-4} M

at 525 nm gradually decreased and there is no absorption at 420 nm observed. It is because that the majority of the methyl red solution is at the acidic form at pH 2.98. The loss of absorbance in dye solution in submicellar could be due to the precipitation of dye-surfactant complex in the solution.

Fig. 6 shows the absorption spectra of 3.0×10^{-5} M methyl red at different pH values in pure water. The absorption spectrum of methyl red shows an absorption band which has an absorption maximum at 525 nm. This absorption band is attributed to the acidic form of methyl red. With the increasing of pH, the absorption at 525 nm for acidic form gradually decreased whereas the absorption at about 420 nm increased. This shift is caused by the change of the contribution of the resonance forms (Fig. 7). A sharp isobestic point is also observed in Fig. 6.

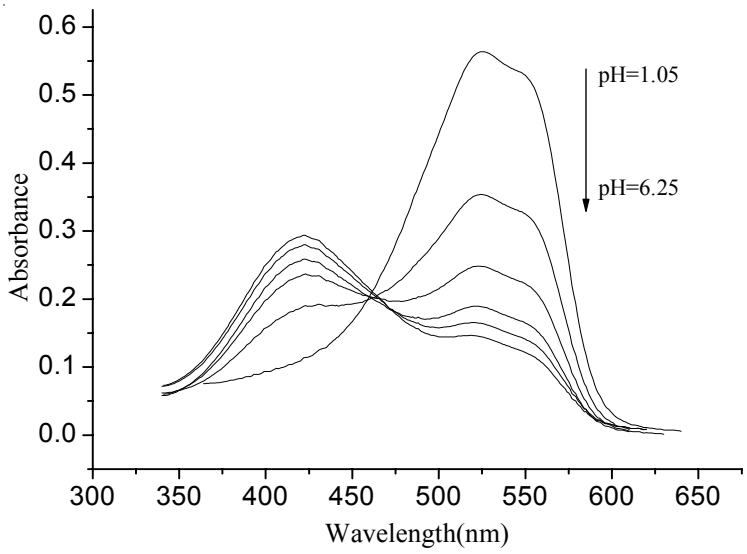

Fig. 6. Effect of pH values on absorption spectrum of methyl red (MR) (at 25 ºC, [MR] = 20 µM, [Gemini16] = 2.5×10^{-5}). pH values are varying at 1.05, 2.03, 2.96, 3.98, 4.88, 6.25, 6.60, respectively

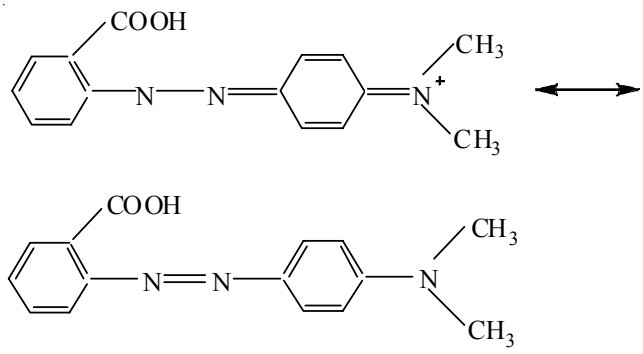

Fig. 7. Resonance forms of the methyl red

Conclusion

The interactions of a kind of gemini cationic surfactants in aqueous solution with two different anionic azo dyes, methyl orange and methyl red have been studied by UV-Vis spectroscopy. The results show that aggregation of surfactant and anionic azo dyes takes place at surfactant concentrations below the critical micelle concentration of the surfactant, their λ_{max} have considerable hypsochromic shift along with a decrease in their intensities which strongly depend on combination of bulk hydrophobic and electrostatic interactions. The results also show the absorption spectrum of methyl orange at 510 nm for acidic form gradually decreased whereas the absorption at about 430 nm increased with the increasing of pH. For methyl red, bathochromic shifts take place from 525nm to 420nm with the increasing of pH.

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