Asian Journal of Chemistry; Vol. 23, No. 2 (2011), 729-732

ASIAN JOURNAL OF CHEMISTRY

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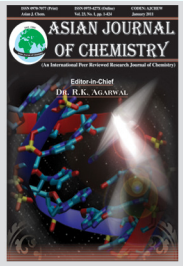

Spectroscopic Studies of the Interaction between Methyl Orange and Gemini Surfactant

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(*Received*: 15 March 2010; *Accepted*: 30 September 2010) AJC-9149

The influence of two kinds of cationic surfactants on spectral properties of methyl orange in aqueous solutions has been investigated by means of UV-vis spectroscopy in various pH values and concentration range. For the Gemini14-methyl orange (MO) solutions, a hyperchromic shift was observed from 509-403 nm with the decrease of spectra absorption by increasing the pH values. Spectral behaviour of dye-surfactant solutions with varying concentrations of surfactants confirmed that electrostatic hydrophobic interactions between dye and surfactant played an important role. An H-type aggregation appeared in the concentration ratio 1:2 for Gemini14 and methyl orange, but in the CTAB solutions, the ratio was 1:1. The initial decrease of the absorbance resulted from dye-surfactant complex formation. It can be concluded that the amount of the cationic groups plays an important role in the complex formation.

Key Words: Gemini surfactant, Methyl orange, Absorption spectroscopy, Dye-surfactant interaction.

INTRODUCTION

The interactions between dye and surfactant are subjects of numerous investigations[1-7]. Dye-surfactant interactions in aqueous buffered systems have been the subjects of many research topics due to their industrial applications[8] and pertinence to biological process[9,10]. From their several applications, analytical interest arises from their role in solubilization processes, since they can replace the use of organic solvents or co-solvents. 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[11-13].

Many techniques were used for qualitative description of dye-surfactant interactions, *i.e.*, potentiometry[14,15], conductometry, tensimetry, voltammetry[16] or ion selective electrodes[17]. Spectrophotometric methods are, in general, highly sensitive and are as such suitable for studying dye-surfactant solution. In the presence of surfactant new bands in the electronic absorption spectra of many dyes can appear and the stronger the mutual interaction between dye and surfactant the greater change is observed[18]. The changes of dye visible absorption spectra in the presence of surfactant at different concentrations result from the equilibrium between surfactant monomers, micelles, dye aggregates, dye-surfactant premicellar complex and dye particles incorporated into the micelles[19,20]. The aggregation of oppositely-charged dyes with surfactants is strongly dependent on non-coulombic interactions. As a result of the attraction forces, the ionic pair of the dye-surfactant was formed in the solution.

Gemini surfactants are composed of two monomeric surfactant molecules chemically bonded together by a spacer. There are two hydrophilic and hydrophobic groups in their molecules. The advantages of the 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].

The aim of the work is to study the complex formation between opposite-charged dye and the Gemini cationic surfactant which has been synthesized surfactant particles by means of UV-vis spectroscopy. Meanwhile, the spectra of the anionic dye in CTAB solutions were for comparison with it in Gemini cationic surfactant.

EXPERIMENTAL

Methyl orange was obtained from Aldrich. Hexadecyltrimethylammonium bromide (CTAB) from Merck, Germany, was used as surfactant. Deionized water from reverse osmosis was used as a solvent. The chemical structures of the chemicals were shown in Fig. 1.

Synthesis: The intermediate *bis*(2-bromoethyl)ether was synthesized from diglycol and phosphorus tribromide. The surfactant labeled as Gemini 14 was obtained by *bis*(2-bromo-

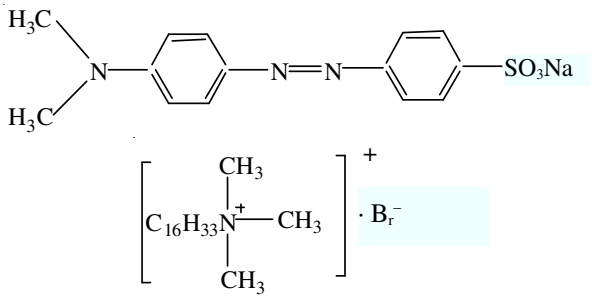

Fig. 1. Chemical structures of (a) methyl orange, (b) hexadecyltrimethylammonium bromide (CTAB)

ethyl) ether with N,N-tetradecyl-N,N-dimethylamine in isopropanol at 78 ºC for 48 h. 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 was shown in Fig. 2.

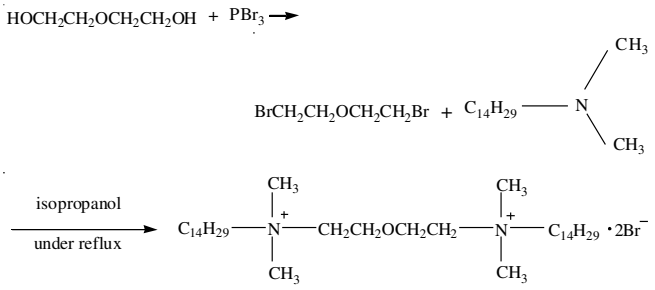

Fig. 2. Synthetic procedure of Gemini 14 surfactant

Spectral characteristics for Gemini14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 6H), 1.28-1.30 (m, 44H), 1.7 (m, 4H), 3.65 (t, 4H), 3.46 (s, 12H), 4.06 (s, 4H), 4.37 (s, 4H).

Preparation of mixed surfactant solutions: The methyl orange solution was obtained by dissolving 0.0336 g of methyl orange in a 1 L volumetric flask and diluted with deionized water up to mark line. The stock solutions of surfactants (Gemini14 and CTAB) were prepared by dissolving certain amounts in water. All 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. Dye-surfactant mixed systems were prepared as molar surfactant concentration and kept for at least 0.5 h for equilibrium in a thermostat bath at 25 ºC before spectroscopic measurements.

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 350-600 nm for methyl orange was performed with ChemStation program (Agilent Technologies), running under Windows XP.

RESULTS AND DISCUSSION

Spectra of methyl orange in surfactant solutions at various pH values: The absorption spectra of methyl orange in pure water at various pH values were recorded. In order to investigate the influence of the conventional cationic surfactant (CTAB) and Gemini cationic surfactant (Gemini 14) in acidity solutions, a series of experiments were run at different surfactant concentrations (1.64×10^{-5}, 2.05×10^{-5} and 4.1×10^{-5} M of surfactant to water). Sample spectrums of the indicator at different pH values in pure water-surfactant mixtures were shown in Fig. 3.

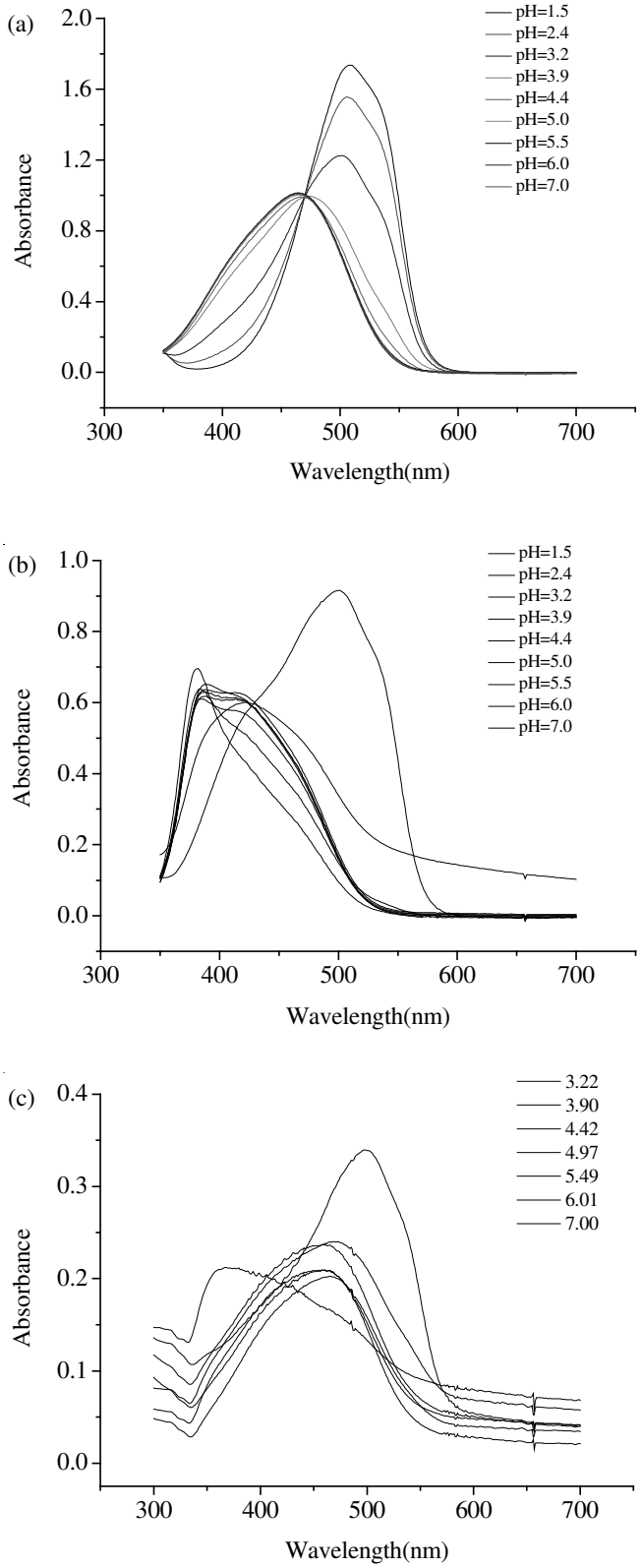

Fig. 3. Absorption spectra for methyl orange (4.1×10^{-5} M) in (a) pure water, (b) Gemini14 (4.1×10^{-5} M) and (c) CTAB (4.1×10^{-5} M) at different pH values

The acidity constant values of these indicators were investigated in pure water and two different water-surfactant mixtures spectrophotometrically at 25 ºC. Fig. 3a showed the absorption spectra of 4.1×10^{-5} M methyl orange at different pH values in pure water. The absorption spectrum of methyl orange showed an absorption band which has an absorption maximum at 509 nm. This absorption band was attributed to the acidic form of methyl orange. With the increasing pH, the absorption at 509 nm for acidic form gradually decreased whereas the absorption at about 467 nm increased at pH = 3.9. A sharp isobestic point was observed in Fig. 3a. Fig. 3(b, c) showed the sample spectra of methyl orange in different surfactant media with the concentrations of 4.1×10^{-5} M of surfactant. In Fig. 3b, it can be the indication that the solution containing methyl orange and Gemini14 1:1 complex was formed as a result of dye-surfactant complex formation.

In the presence of the surfactants, the absorbance of band decreased weakly and a new band at 379 nm appeared (hyperchromic shift) when the pH was 3.22. But the absorption band at 530 nm did not shift at this pH in pure water and CTAB solution. Different kinds of complexes in the solution can be expected. Although the dye and surfactant were individually hydrated in the solution, they can sometimes meet each other in aqueous solution and the long-range electrostatic and short-range hydrophobic forces caused the formation of dye-surfactant complexes. There were strong indications that two methyl orange molecules with one surfactant molecule were arranged in a parallelway (H-type aggregation). It meant the complex was 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).

Fig. 3b showed the absorption spectra of 4.1×10^{-5} M methyl orange at different pH values in Gemini14 solution at 4.1×10^{-5} M. With the increasing of the pH value, the absorption at 501 nm for acidic form gradually decreased whereas the absorption at about 430 nm increased. This shift was caused by the change of the resonance forms of the methyl orange (Fig. 4). The similar changes appeared in the CTAB-MO solutions, where the absorption band shifted from 503-463 nm. However the band shifted at pH = 3.9 to 470 nm in the pure water and CTAB solution. But for Gemini14 solution, the absorption band shifted when the pH was 2.4. It can be seen from Fig. 3(b,c), the changes both in absorption band shift and absorbance of MO were larger for Gemini14 solution that contains two cationic groups. It can be concluded that the tendency to form dye-surfactant complex increases with increasing amount of cationic groups of surfactant. With increasing amount of cationic groups, hydrophobic interaction increased, micellization begins at the lower surfactant concentration. The results indicated that hydrophobicity of cationic groups played an important role in complex formation. Also it can be concluded that Gemini 14 can broaden the indicator range of the MO, but this role for CTAB was not very clear.

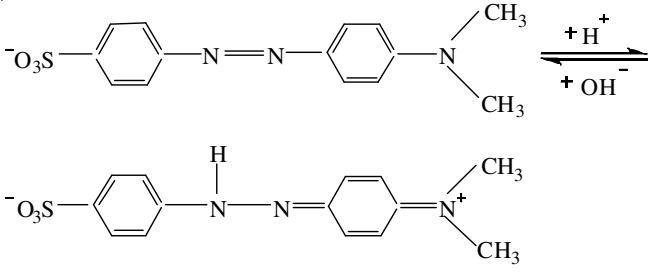

Fig. 4. Resonance forms of the methyl orange

Spectra of methyl orange in various concentrations of surfactant solutions: Changes of absorption spectra for methyl orange in the presence of the surfactants were shown in Fig. 5. In the solution containing MO and Gemini14 at the concentration of 1.64×10^{-5} M, the dye exhibited a new maximum absorption band at 377 nm and a shoulder at 463 nm (Fig. 5a), with the decreasing of the absorption band. At this time, there were two forms of MO in the solution at this concentration, MO monomer and surfactant-dye dimer. The two different molecules formed of MO caused this bimodal with the change of the chromophoric group of the methyl orange. When the concentration ratio was 2:1 of MO and Gemini14, there was only dye-surfactant complex by the effect of electrostatic force in the solution, causing the hyperchromic shift of the absorption band. In Fig. 5b, when the concentration ratio was 1:1 for CTAB and MO, only the absorption intensity decreased without hyperchromic shift. But when the concentration ratio was 1:2 for Gemini14 and MO, a sharp decrease of the absorption intensity resulting from the dye-surfactant complex formation was observed (Fig. 5a) and a strong hyperchromic shifted from 465-383 nm.

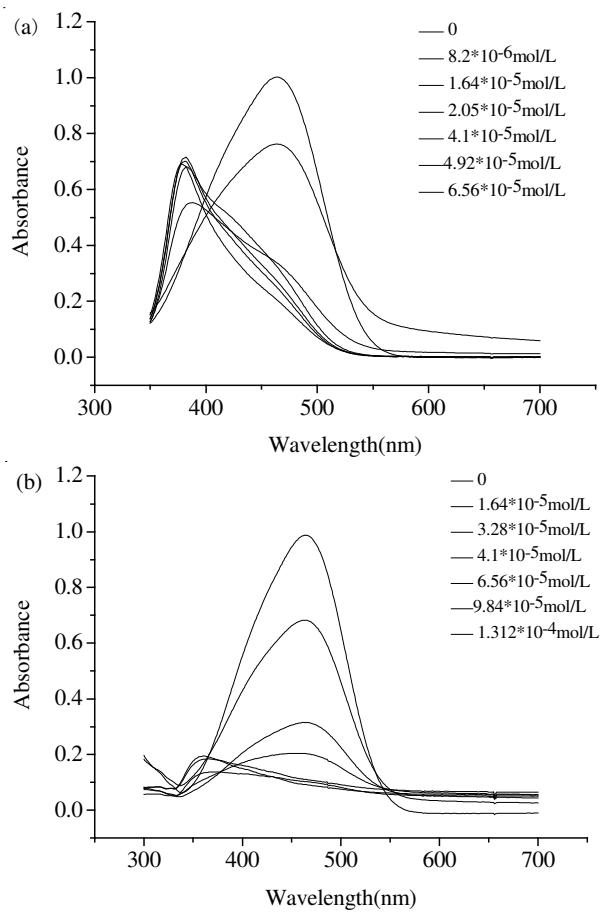

Fig. 5. Absorption spectra of methyl orange in (a) Gemini14 solution, (b) CTAB solution at various concentrations in pure water

Fig. 6 showed the absorbance changes of 4.1×10^{-5} M MO with increasing surfactant concentrations at the pH of 3.22. As seen in Fig. 6a, in the solutions containing MO and Gemini14 at the concentrations ranging from 0-2.05×10^{-5} M the intensity of the absorbance decreased with the appearance of a new band at 379 nm. The intensity of the band gradually increased, as the Gemini14 concentration increased to 6.56×10^{-5} M with a bathochromic shift at 426 nm. But no absorption band shifted in solutions containing MO and CTAB at the concentration ranging from 0-6.56×10^{-5} M. The increasing concentration of CTAB was only caused the diminishing of the absorption intensity. Until the concentration increased to 9.84×10^{-5} M, a new band appeared at 360 nm (hyperchromic shift). These phenomena showed that lower concentration of Gemini14 caused the shift of the absorbance band for MO solutions than that was in CTAB solutions. This case was similar as it in the solutions of Gemini14 and CTAB with different concentrations in pure water (Fig. 5). But in Fig. 6a, a new maximum absorption band appeared at 426 nm, as the Gemini14 concentration increased near to critical micelle concentration (CMC). Because of the electrostatic force and hydrophobic interactions in the solutions at pH = 3.22, MO molecules dissociated from the complex, with the destroying of the H-type complex. And the methyl orange molecules joined the surfactant micelle gradually. But in the pure water, methyl orange molecules existed with negative charge, which made the combination between MO and Gemini14 firmly. So it was difficult for MO to dissociate from the surfactant-dye complex. Meanwhile, there was no bathochromic shift for methyl orange solutions with the Gemini14 concentration increasing to 6.56×10^{-5} M.

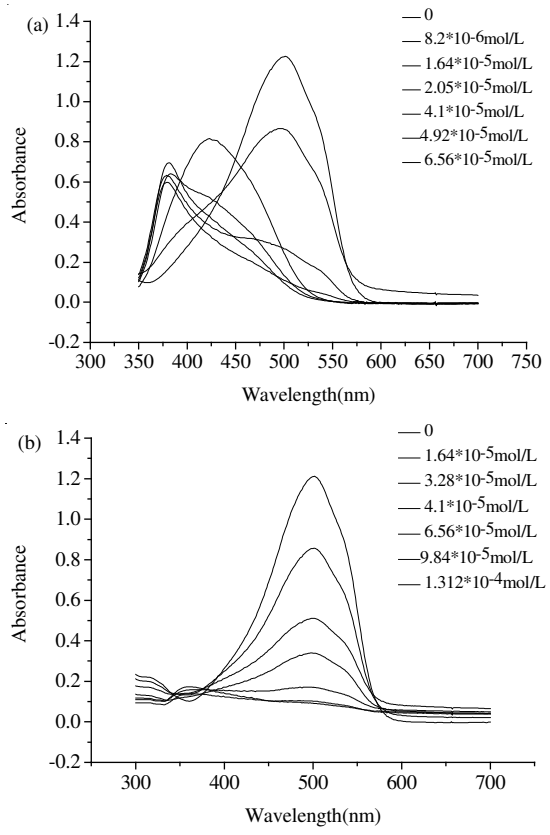

Fig. 6. Absorption spectra of methyl orange in (a) Gemini14 solution, (b) CTAB solution at various concentrations at pH = 3.22

Both in Figs. 5b and 6b, no bathochromic shift appeared when the CTAB concentration increased to 1.3124×10^{-4} M. There were two forms for methyl orange in MO solutions, azo-type and quinoid-type. No matter what form it was, the combination force between CTAB and MO was larger than the force between Gemini14 and MO. The quinoid-type was on the role of repulsion for Gemini14 with two cationic groups. There was greater repulsion for Gemini14 than CTAB with methyl orange. Therefore the MO-Gemini14 complex was vulnerable to damage, releasing the methyl orange molecules. Gradually, in the solutions containing surfactant at the concentration near CMC first an adhesion of ionic pairs on the surfaces of micelles formed in the system took place and then dye particles were incorporated into the micelles. In the solutions containing methyl orange and CTAB at the concentration ranging from 6.56×10^{-5}-1.312×10^{-4} M, more over than the concentration of the MO of 4.1×10^{-5} M, the intensity of the band at 460 nm diminished with the appearance of a new band at 357 nm (Figs. 5b and 6b). The lower Gemini 14 concentration caused the decrease of the absorbance of the methyl orange, with a new absorption band appearing.

Conclusion

The interactions of two cationic surfactants in solutions with anionic azo dye, methyl orange have been studied by UV-vis spectroscopy. The increasing of pH values led the hyperchromic shift and the decrease of the absorption intensity for the methyl orange spectra both in Gemini14 and CTAB solutions. This phenomenon was caused by the change of the resonance forms of the methyl orange. The interaction of cationic surfactant with methyl orange was occurred at low surfactant concentration and continued until the dye occupies the micelle of the surfactant. At low surfactant concentrations, the decrease in spectral values indicated dye-surfactant complex formation. This was resulted from the strong interactions between dye's sulfonate groups and head groups of surfactant. Therefore, for the interaction between cationic surfactants (Gemini14, CTAB) and anionic dye (methyl orange) both hydrophobic and electrostatic forces were important. The results indicated that the amount of the cationic groups also plays an important role in the complex formation.

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