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Interactions of gemini cationic surfactants with anionic azo dyes and their inhibited effects on dyeability of cotton fabric

Ali R. Tehrani Bagha [a], Hajir Bahrami [a,*], Barahman Movassagh [b], Mokhtar Arami [a], Fredric M. Menger [c]

[a] *Textile Department, Amirkabir University of Technology (Polytechnic), Tehran, Iran*
[b] *Chemistry Department, K.N. Toosi University of Technology, Tehran, Iran*
[c] *Chemistry Department, Emory University, Atlanta, GA 30322, USA*

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Abstract

The interactions of two anionic azo dyes, Methyl Orange (MO) and Congo Red (CR), with a series of gemini cationic surfactants and dodecyl trimethyl ammonium bromide (DTAB) in aqueous solution have been 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 individual surfactants. Aggregations with anionic dyes were reflected by hypsochromic shifts with a decrease in the intensity of absorption band. Further addition of surfactant results in an absorption spectrum of the dye characteristic in the presence of cationic micelles. The results also show bathochromic shifts for MO followed by sharp increase in intensity of the absorption bands at λ_{max} after the CMC points of these surfactants. Such a behavior is observed for CR solutions in higher surfactant concentrations. The inhibiting effect of cationic surfactants on dyeability of cotton fabric with CR has also been studied at three different temperatures (30, 50, 90–92 °C). Results show large differences between DTAB and gemini cationic surfactants.

Keywords: Gemini surfactants; Dye interaction; Dyeing inhibition; Methyl Orange; Congo Red

1. Introduction

The various unit operations of textile industry offer numerous opportunities for advantageous use of surface-active agents because they show interesting interfacial and bulk properties. As a consequence, a larger number of such products are used in textile processing than in any other industry [1].

Surfactants are mainly used as wetting, dispersing and levelling agents for improving dyeing process by increasing solubility, stabilizing the dispersed state and promoting uniform distribution of the dye in the textile [2].

Levelling agents act mainly by reducing the dyeing rate, increasing the rate of migration of the dye within the textile, and improving the compatibility of dyes. They can be divided into products with an affinity for dyes, and products with an affinity for fibers. According to the structures of dye and substrate, surfactants used as levelling agents operate by different mechanisms depending on the ionic type of the dye. Products with an affinity for dyes form loosely bound addition compounds with the dyes whose stability is concentration dependent and usually decreases with increasing temperature. Levelling agents with an affinity for fibers are absorbed onto the fibers in competition with the dye. The competitive reaction reduces the absorption rate of the dye and promotes migration [3].

Although, the interaction between dyes and surfactants has been studied in many papers, the studies in this area are still important and interesting for improving the dyeing process from theoretical, technological, ecological and economical points of view. The investigations into the behavior of different dyes in surfactant aqueous solutions can give useful information for understanding the thermodynamics and kinetics of the

* Corresponding author. Tel.: +98 21 645 42 680; fax: +98 21 664 00 245.
E-mail address: hajirb@aut.ac.ir (H. Bahrami).

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dyeing process and the finishing of textile material. UV–Vis spectroscopy, conductometry and using surfactant selective electrodes are among the most widely used measurement methods for studying this subject [4–16].

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 [17].

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 [9–12,18].

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 [8]. It has been reported that the type of head group of surfactants has no large influence on the aggregation process [5,6].

The choice of a particular surfactant for a particular purpose depends on its ability to interact with fibers and/or other components in the system.

Changes in the molecular structure and type of surfactant to improve upon their properties have attracted the attention of chemists. This has led to the preparation of new generation of surfactants such as geminis [19].

Gemini or dimeric surfactants are composed of two monomeric surfactant molecules chemically bonded together by a spacer. They have two hydrophilic and two hydrophobic groups in their molecules. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid, polar or non-polar [20].

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.

In terms of concentration, they are about three orders of magnitude more efficient at reducing the surface tension of water and more than two orders of magnitude more efficient in interfacial performances than conventional surfactants. The greater efficiency and effectiveness of geminis over comparable conventional surfactants make them more cost-effective as well as environmentally desirable [21].

In this study a series of gemini cationic surfactants have been synthesized and the interactions of them with two anionic azo dyes, Methyl Orange (MO) and Congo Red (CR) in aqueous solution have been investigated by means of UV–Vis spectroscopy.

2. Experimental

2.1. Material

Decyl bromide, dodecyl bromide, *N,N,N′,N′*-tetramethylethylenediamine, dodecyl trimethyl ammonium bromide (DTAB), Methyl Orange (MO), Congo Red (CR), dry acetone, diethyl ether, *N,N*-dimethyldodecylamine, absolute ethanol were obtained from Merck, Acros and Lab-Scan companies.

N,N′-didodecyl-*N,N,N′,N′*-tetramethyl-*N,N′*-butanediyl-diammonium dibromide (14-4-14) was received from Menger's research group and was used without further purification.

The structures of the azoic dyes (MO, CR) and conventional surfactant (DTAB) are shown in Fig. 1.

2.2. Synthesis

The surfactants *N,N′*-didecyl-*N,N,N′,N′*-tetramethyl-*N,N′*-ethanediyl-di-ammonium dibromide (10-2-10), *N,N′*-didodecyl-*N,N,N′,N′*-tetramethyl-*N,N′*-ethanediyl-di-ammonium

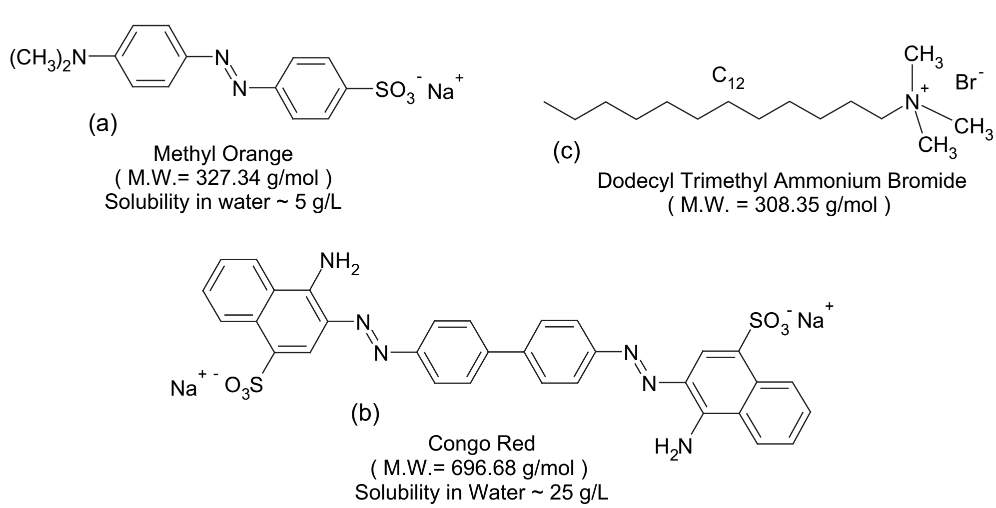

Fig. 1. Chemical structures of (a) Methyl Orange, (b) Congo Red, (c) DTAB.