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Study of interaction between a cationic surfactant and two anionic azo dyes by ion-selective electrode technique and spectrophotometry

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Abstract

Interaction between a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB), and two anionic azo dyes, C.I. Direct Orange 26 (DO26) and Direct Red 16 (DR16) has been investigated using surfactant-selective electrode and spectrophotometry techniques. In ion-selective electrode technique an HTAB surfactant-selective membrane electrode has been used. The electromotive force versus total surfactant concentration has been plotted for the systems of HTAB/DR16 and HTAB/DO26 in 1×10^{-4} and 1×10^{-3} mol dm^{-3} NaBr at 25 °C. The concentrations of free and bound surfactant and also dye–surfactant complex constant, K, could be obtained from the experimental data. The data show that significant binding takes place and the critical concentration associated with the saturation of the dyes with bound surfactant has been determined. The results also indicate that in the DO26/HTAB system, where more hydrophobic dye DO26 is used, the dye–surfactant interaction is stronger than in DR16/HTAB system, which shows the importance of hydrophobic forces in the interaction.

Keywords: HTAB; Direct Orange 26; Direct Red 16; Surfactant-selective electrode

1. Introduction

Surfactants are used to assist in dyeing, by wetting and leveling or dispersing dyes of low solubility and in household and industrial cleaners, cosmetics and for research laboratories, and also as plasticizers in the cement and concrete chemistry [1–3]. The study of dye–surfactant interaction is important and interesting from point of view of the theory and technology of dyeing. The investigation of the behaviour of different dyes in surfactant aqueous solutions can give useful information about the mechanisms according to which surfactants operate as leveling agents and information on the thermodynamics and kinetics of dyeing [4,5].

A lot of research work focused on dye–surfactant interactions including the interactions between ionic dyes and ionic surfactants of the opposite and the same charges [3–11], between ionic dyes and nonionic surfactants [12–15], as well as between nonionic dyes and ionic or nonionic surfactants [16] in the submicellar and micellar concentration ranges of surfactants. Experimental methods mostly used were uv/vis spectroscopy, conductometry, surface tension measurements and potentiometry. In this paper, we used surfactant-selective electrode and uv/vis spectroscopy to study the interaction between two anionic azo dyes, C.I. Direct Orange 26 (DO26) and Direct Red 16 (DR16), and a cationic surfactant hexadecyltrimethylammonium bromide (HTAB). In ion-selective electrode method, from the measured electromotive force (EMF) data and also from the variation of monomer (m_1) surfactants' concentration with total added surfactants (C_1), various critical concentrations associated with the binding process have been determined. These include the value of the total HTAB concentrations corresponding to the onset of binding (T_1), the saturation of the dye with bound HTAB (T_2), and the formation of free micelles (T_f) [17–22].

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In spectrophotometric method, when surfactants are added to the solutions, the spectral band of the dye shifts and the value of absorbance changes. The spectral changes of the dyes depend on the chemical structure of both dye and surfactant. The results indicate that for association between cationic surfactant and anionic dyes both electrostatic and hydrophobic forces are important [23–25].

2. Experimental

2.1. Materials

In this work, HTAB, THF, and NaBr are from Merck and PVC containing SO_3H (0.1%) and also dyes, DO26 and DR16, are from Sigma and were used without further purification. Elvaloy 742 is from Dupont. The structures of the dyes and surfactant used in this study are shown in Fig. 1.

2.2. Apparatus

The apparatus that were used in this work are as follows: Unicam UV/vis series Spectrometer, pH meter (type 1.691.001) and a commercial sodium ion (corning 476211) reference electrode, from Metrohm. The surfactant membrane electrode selective to HTAB was constructed in the laboratory.

2.3. Measurements

2.3.1. Ion-selective electrode

The surfactant ion-selective electrode was used in experimental method. The use of HTAB-selective electrode enables us to determine the concentration of free HTAB surfactant cations in the solution. The cell used for these measurements was constructed as follows and the procedures to calculate the respective monomer concentrations have been described elsewhere [17–22].

$$\mathrm{Ag/AgBr}\left|\begin{array}{c}10^{-4}\ \mathrm{mol\ dm^{-3}\ NaBr\ and}\\ 10^{-5}\ \mathrm{mol\ dm^{-3}\ HTAB}\end{array}\right\|\ 10^{-4}\ \mathrm{mol\ dm^{-3}\ NaBr}\ \Big|\ \text{Sodium reference electrode}$$

↑
HTAB Membrane

In the EMF experiments a concentrated surfactant solution is titrated with an aqueous solution containing a constant amount of dye. After each titration, the EMF of the solution is measured. The EMF data are then plotted as a function of the total surfactant concentration for the solutions without and with the dyes, the latter being the binding experiment.

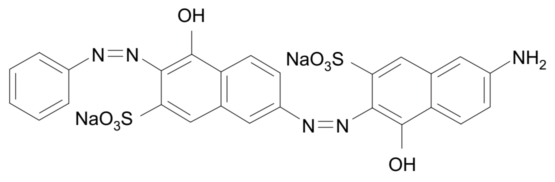
Typical EMF data are shown in Fig. 2 for the HTAB/DO26 and HTAB/DR16 systems in 1×10^{-4} mol dm^{-3} NaBr. Normally, when binding is taking place, the EMFs are different for each corresponding titration for the solution with and without dye, because the surfactant-selective electrode is sensitive to free surfactant ions; the experimental results allow the direct determination of the concentration of monomer surfactant ions as well as the concentration of surfactant ions bound in the dye–surfactant complex indirectly.

2.3.2. Spectrophotometry

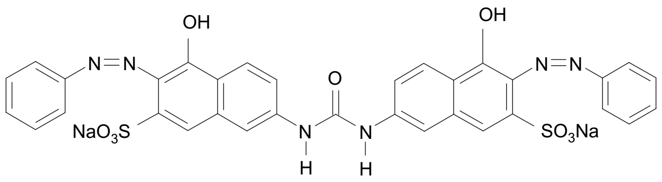
The visible absorption spectra of DO26/HTAB and DR16/HTAB were recorded at 25 °C. The concentrations of DO26 and DR16 were kept constant (1×10^{-4} mol dm^{-3}) during the whole process and different concentrations of HTAB were used over a range of 1×10^{-5}–5×10^{-2} mol dm^{-3}.

3. Results and discussion

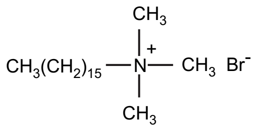
Figs. 2 and 3 show typical plots of EMF of the cell versus the logarithm of HTAB concentration, log *c*, with and without the dye, and the NaBr concentrations in these experiments are



Direct Red 16 (DR16)



Direct Orange 26 (DO26)



Hexadecyltrimetylammonium bromide (HTAB)

Fig. 1. Structures of the dyes and the surfactant.

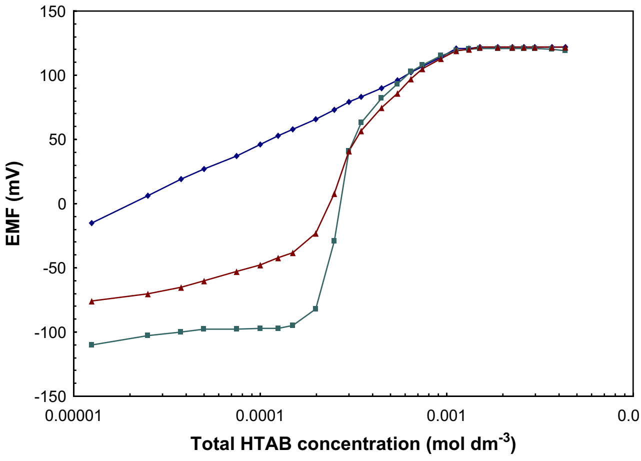


Fig. 2. Plot of the EMF of the HTAB electrode (reference Na^+) as a function of the total HTAB concentration for the HTAB/dye (1×10^{-3} mol dm^{-3}) systems in 1×10^{-4} mol dm^{-3} NaBr: (◆) pure HTAB; (■) HTAB + Direct Orange 26; (▲) HTAB + Direct Red 16.

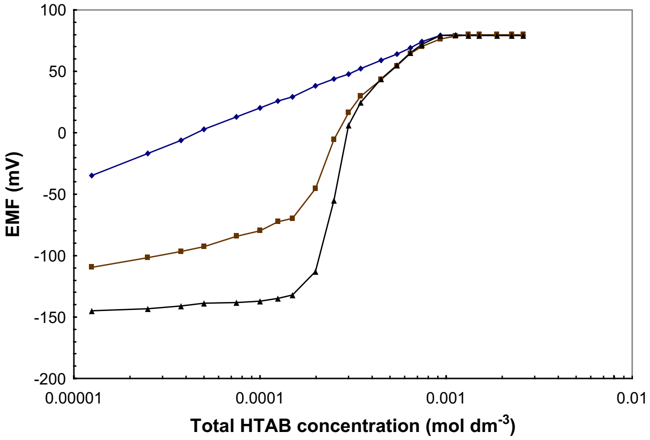


Fig. 3. Plot of the EMF of the HTAB electrode (reference Na^+) as a function of the total HTAB concentration for the HTAB/dye (1×10^{-3} mol dm^{-3}) systems in 1×10^{-3} mol dm^{-3} NaBr: (◆) pure HTAB; (▲) HTAB + Direct Orange 26; (■) HTAB + Direct Red 16.

1×10^{-4} and 1×10^{-3} mol dm^{-3}, respectively. Comparison between Figs. 2 and 3 shows that the CMC value of HTAB in 1×10^{-3} mol dm^{-3} NaBr is less than it is in 1×10^{-4} mol dm^{-3} NaBr. When more NaBr concentration is used, repulsion between the head groups in micelles is less; therefore micelles are formed easily and also interaction between micelles and dyes increased.

Titration curves obtained in HTAB/DO26, HTAB/DR16 solutions deviate from Nernstian behaviour over the whole measured concentration range. Since they lie below the calibration curve, this indicates that at any measured concentration of HTAB, the concentration of free surfactant cations, which can be detected by the HTAB-selective electrode, is lower than the total concentration. This suggests the formation of dye–surfactant complex.

When the EMF data with and without the dye merge, it indicates that the dye becomes fully saturated with bound surfactant. The HTAB concentration corresponding to the merger is denoted as T_2.

The concentration of the monomers HTAB, denoted as m_1, has been evaluated from the electrode data and is shown as a function of total HTAB concentration, C_1, in Fig. 4. In first part of Fig. 4 it has been shown that with increasing C_1, m_1 are almost constant showing that interaction occurs between monomer surfactant and dye (until 2×10^{-4} mol dm^{-3} HTAB). Following the onset of binding, the monomer concentration increases with C_1, reaches a maximum and then merges with the data for the pure surfactant at T_2. An increase in m_1 with increasing C_1, is exactly the behaviour expected when HTAB binds exclusively to a dye. Eventually m_1 decreases or remains almost constant with increasing C_1 which signifies the onset of the formation of free micelles (denoted T_f). The results in Fig. 4 confirm the data obtained from Fig. 2.

The quantity $(T_2 - m_1)$ for the systems, where $T_f = T_2$ can be regarded as a very useful binding parameter/indicator to measure the relative scale of the binding process. Therefore the dyes reached its maximum capacity to bind a surfactant at T_2, and also $T_2 - m_1$ represents the maximum amount of the bound surfactant. The values of $T_2 - m_1$, where m_1 is the concentration of the monomer HTAB at T_2, are listed in Table 1.

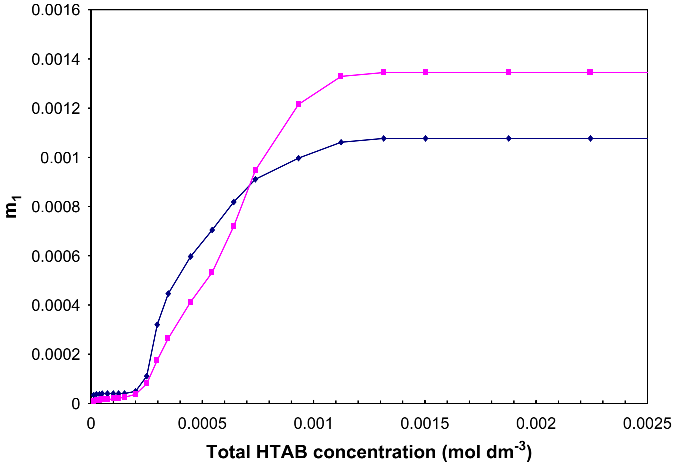


Fig. 4. Plot of the HTAB monomer concentration (m_1) as a function of the total HTAB concentration for the HTAB/dye (1×10^{-4} mol dm^{-3}) systems in 1×10^{-4} mol dm^{-3} NaBr: (■) HTAB + Direct Red 16; (◆) HTAB + Direct Orange 26.

The ratio of bound HTAB, $C_1 - m_1$, per mole of dye, C_d, is called the binding ratio, $(C_1 - m_1)/C_d$, which is a more accurate and informative guide to the binding behaviour.

The interaction between the dye anion, D^-, and the surfactant cation, S^+, where, 1:1 molecular complex is formed can be represented by the equilibrium in the first approximation [8].

$$S^+ + D^- \overset{K}{\leftrightarrows} S^+D^-$$

with the complex formation constant, K, equal to:

$$K = \frac{[S^+D^-]}{[S^+][D^-]} = \frac{C_1 - m_1}{m_1\{C_d - (C_1 - m_1)\}} \Rightarrow \frac{C_d}{C_1 - m_1} = \frac{1}{K}\frac{1}{m_1} + 1$$

Fig. 5 shows the plot of $C_d/(C_1 - m_1)$ against $1/m_1$, the complex formation constant, K, could be obtained using the slope of the line. When $C_d = 1 \times 10^{-4}$ mol dm^{-3}, for the DO26/HTAB system $K = 1 \times 10^5$ and for the DR16/HTAB system $K = 0.5 \times 10^5$. These data indicate that in the DO26/HTAB system, the dye–surfactant interaction is stronger than that in the DR16/HTAB system.

The comparison of the UV/vis spectra of individual and mixed dyes–surfactant aqueous solutions in various concentration ranges confirms that the dyes interact with the HTAB.

By adding the surfactant to the solution of the dyes the value of the absorbance changes and the spectral band of the dyes shifts. The changes can be attributed to the chemical and structural characteristics of dyes and surfactant.

The variations in the visible absorption spectra of DO26, on addition of HTAB of various concentrations are shown in Fig. 6. On addition of HTAB, when the concentrations of the HTAB were below the CMC, the value of the absorbance decreased and when the concentrations of the HTAB were

Table 1
Summary of the results of the interaction between HTAB and dyes (1×10^{-3} mol dm^{-3}) in 1×10^{-4} mol dm^{-3} NaBr

Dye	MW (g mol^{-1})	T_2 (= T_f) (mol dm^{-3})	($T_2 - m_1$) (mol dm^{-3})	[HTAB]/[dye] at T_2 (mol mol^{-1})
Direct Orange 26	746	1.12×10^{-3}	6×10^{-5}	1.06
Direct Red 16	632	1.08×10^{-3}	2×10^{-5}	1.32

[HTAB] refers to the concentration of bound HTAB (=$T_2 - m_1$).

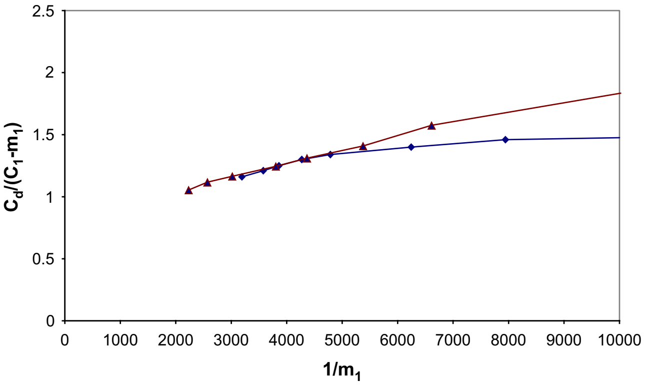


Fig. 5. Plot of $C_d/(C_1 - m_1)$ versus $1/m_1$ for (1×10^{-4} mol dm^{-3}) DO26/HTAB and (1×10^{-4} mol dm^{-3}) DR16/HTAB.

above the CMC, a new absorption band, with maximum absorption at 480 nm was observed and also the value of the absorbance increased.

The band of DO26 at concentrations of HTAB far below its CMC can be attributed to the surfactant–dye ion pairs [9]. The 480 nm band can be attributed to the interaction of DO26 with the HTAB micelles where the micelles probably start forming at around its CMC in presence of the dye. The CMC of HTAB in the presence of the dye is probably decreased to about 8.0×10^{-4} mol dm^{-3}. The development of the 480 nm band can be attributed to the conversion of the ion pair into a charge-transfer complex between the dye and micelle.

The variations in the absorption maximum of DR16 by the addition of different concentrations of HTAB, are shown in Fig. 7. On addition of HTAB, a new absorption band, with absorption maximum at 508 nm was observed and the value of the absorbance decreased. When the concentration of the HTAB was increased above its CMC, the value of the absorbance increased with gradual decrease in the intensity of the 508 nm band.

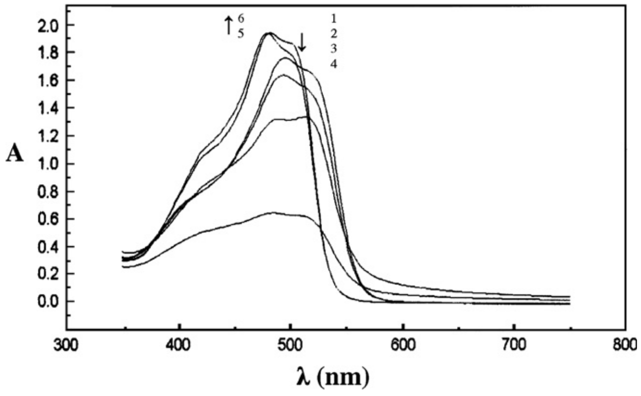


Fig. 6. The visible absorption spectra of Direct Orange 26 and HTAB in water at 25 °C. Concentration of DO26: 1×10^{-4} mol dm^{-3}, concentration of HTAB (mol dm^{-3}): (1) 0.0, (2) 1×10^{-5}, (3) 1×10^{-4}, (4) 1×10^{-3}, (5) 1×10^{-2} and (6) 5×10^{-2}.

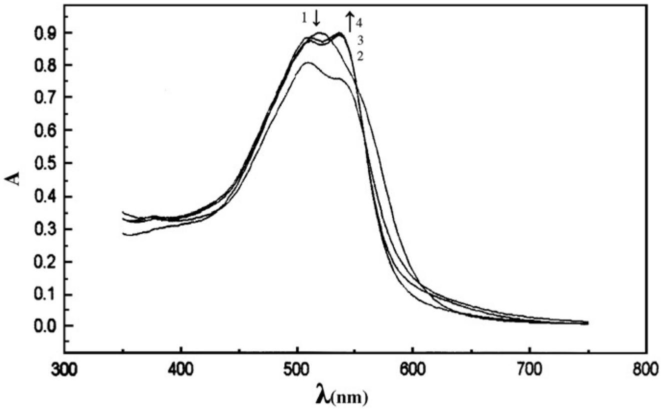


Fig. 7. The visible absorption spectra of Direct Red 16 and HTAB in water at 25 °C. Concentration of DR16: 1×10^{-4} mol dm^{-3}, concentration of HTAB (mol dm^{-3}): (1) 0.0, (2) 5×10^{-4}, (3) 1×10^{-2} and (4) 5×10^{-2}.

4. Conclusions

The HTAB-selective electrode and spectrophotometry methods show that the dyes interact with oppositely charged surfactants. Interaction occurs even at very low HTAB concentration and the binding process continues until the dye becomes fully saturated with bound surfactant, at which point the EMF data for HTAB solution with and without the dye merge, and at this point the value of the absorbance changes and the spectral band of the dyes shifts. These interactions are dependent on the chemical structure of dye and surfactant.

Our results also show that the interaction between DO26 and HTAB is stronger than that between DR16 and HTAB, because DO26 is more hydrophobic compared to DR16. Therefore, for association between ionic surfactants and ionic dyes both electrostatic and hydrophobic forces are important.

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