Anal. Bioanal. Electrochem., Vol. 2, No. 2, 2010, 67 - 78

Analytical & Bioanalytical Electrochemistry

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Full Paper

Effect of Atenolol on the Interaction between Direct Red 16 or Direct Orange 26 and TTAB

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Received: 13 February 2010 / Accepted: 15 May 2010 / Published Online: 30 June 2010

Abstract- A simple, low-cost and sensitive method has been used to investigate the interaction between a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), two anionic dyes, C.I. Direct Orange 26 (DO26) and C.I. Direct Red 16 (DR16), and a drug, Atenolol (ATN). The methods used to study the interaction were electromotive force (EMF) measurements involving a surfactant–selective electrode and spectrophotometry. This method was also used to investigate the interactions of Atenolol (ATN). The interaction between TTAB and DO26 was found to be stronger than that of TTAB and DR16. TTAB only showed a weak interaction with ATN at a high drug concentration. Therefore, when ATN was added to a mixture of TTAB and the dye, ATN was found to first interact with the dye and, when ATN saturated, a higher concentration of TTAB interacted with the dye.

Keywords- Direct Orange 26, Direct Red 16, tetradecyltrimethylammonium bromide (TTAB), Atenolol, Ion-Selective Electrode, Spectrophotometry

1. INTRODUCTION

Dyes are extensively used for dyeing, printing and several other coloring purposes in industries with about 50% of the dyes used being azo dyes [1,2]. Azo dyes, characterized by nitrogen-to-nitrogen double bonds (N=N) and have been widely used in many industries, such as the production of textiles, paint, ink and cosmetics [3,4]. Surfactants are widely used in household and industrial cleaners, cosmetics, research laboratories and as leveling,

dispersing and wetting agents in the dyeing process [5]. The investigations into the behavior of different dyes in surfactant aqueous solutions can, among other things, give useful information about the mechanisms according to which surfactants operate as leveling agents and information on the influence of dye–surfactant interactions on the thermodynamics and kinetics of dye process [6].

Although much work has been carried out involving dye–surfactant interactions, the studies in this area are still important and interesting for the theory and technology of dyeing [7]. Interaction of surfactants with dyes has investigated using various techniques. Experimental methods mostly used were Uv/Vis spectroscopy [8,6], conductometry [9,10], surface tension measurements [11] and potentiometry [6,12].

Atenolol is a β-blocker drug, named chemically as 4-(2-hydroxy-3-isopropyl-aminopropoxy) phenylacetamide (ATN) [13]. It is a hydrophilic β1-receptor blocking agent. β-blockers are exceptionally toxic and have a narrow therapeutic range [14]. A β-blocker is a drug commonly used in the prevention of heart disease, specifically for anginapectoris, cardiac arrhythmias, and management of hypertropic obstructive cardiomyopathy, and control of somatic manifestations of anxiety or stress [13]. A number of drugs have been observed to aggregate or form micelles in aqueous solution [15]. Most therapeutic drugs are selected or designed to be amphiphilic in order to penetrate cells and tissues and to favor the interaction of drug molecules with receptor sites.

The mixed aggregates (MA) which is based on the measurement of the critical micelle concentration (CMC), is used to determine amphiphiles. When the charges of the surfactant and dye are opposite, then the attractive forces between the dye and surfactant lead to dye-surfactant complex formation in solution [16]. When an amphiphilic compound is added to the dye-surfactant mixture, it causes a decrease in the dye-surfactant binding degree and therefore causes an increase in the interaction between the amphiphile (analyte) and surfactant (reactant) molecules [17].

In spectrophotometric analysis, when surfactants are added to the solution, the spectral band shifts and the absorbance value changes. The spectral changes depend on the chemical structure of the dye, drug, and surfactant. The results show that the hydrophobicity of the alkyl chain of the surfactant plays an important role in complex formation [18].

The interaction between a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB) and two anionic azo dyes, DR16 and DO26 have been previously investigated by our group [19] with ion selective electrode and spectrophotometry methods. In other work, we used the ion-selective electrodes [20] to investigate the interactions between surfactant and dyes. However, to the best of our knowledge, no publications about the surfactant-selective investigation of ATN in the presence of dyes exist in the literature.

In this paper, we used a simple, low-cost and sensitive surfactant-selective electrode and UV/Vis spectrophotometry to study the interaction between two anionic azo dyes, DO26,

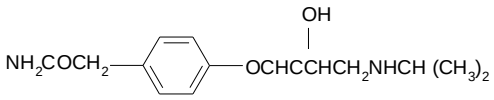
DR16, one cationic surfactant, TTAB, and a drug, ATN. Spectrophotometry was then used to prove the interactions.

2. EXPERIMENTAL

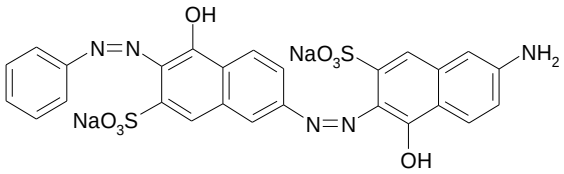
2.1. Materials

TTAB (MW=316.08), tetrahydrofuran (THF) and NaBr were obtained from Merck. PVC containing SO_3H and two dyes, DO26 (MW=746) and DR16 (MW=632), were purchased from Sigma. ATN (MW=266.336) was obtained from the Sina Daru Company in Iran and Elvaloy 742 is from Dupont. All other materials were of analytical reagent grade. All measurements were carried out at room temperature. The structure of the dyes, surfactant and drug used in this research are shown in Figure 1.

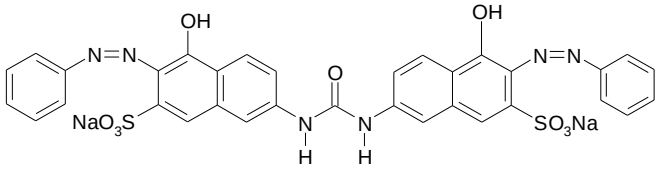
Atenolol



DR16



DO26



TTAB

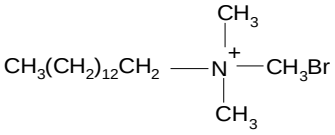


Fig. 1. Structures of the used dyes, surfactant and drug

2.2. Apparatus

The equipment used for this study consisted of a pH meter (Model 162 from Fanavary Tajhizat Sanjesh), a commercial Calomel reference electrode, a working electrode and a UV/Vis spectrometer (Model UV2-200 from Unicam Company, England).

2.3. Preparation of the PVC Membrane Electrode

The surfactant-selective membrane electrode was prepared according to our previous work [20]. For this, 180 mg of polymeric plasticizer, Elvaloy 742 were dissolved in 30 ml of double distilled THF and stirred until total dissolution. Then, 120 mg of TTAB-PVC complex were added very slowly with stirring until no gel was left in the solution. The filtered solution was then placed into a Petri dish (55 mm in diameter), the THF was allowed to evaporate, and the filtrate was completely dried. The membrane was then separated from the dish, cut and pasted to a PVC tube (Tip).

2.4. Measurements

2.4.1. Ion Selective Electrode

The ion selective electrode was used in the experimental method. A TTAB-selective electrode was used to determine the concentration of free TTAB in solution. The cells used for these measurements and procedures to calculate the respective monomer concentration have been described elsewhere [21,22]. In the EMF experiments, a concentrated surfactant solution was added to an aqueous solution containing a constant amount of dyes and drug. After each titration, the EMF of the solution was measured. The EMF data were then plotted as a function of surfactant concentration for the solution with and without the dyes and drug, the latter being the binding experiment

2.4.2. Spectrophotometry

The visible absorption spectra of DO26/ATN/TTAB and DR16/ATN/TTAB were recorded at room temperature. The concentration of the dyes and drug were kept constant during the whole process and different concentrations of TTAB were used over a range of 0-5×10^{-4} mol L^{-1}.

3. RESULTS AND DISCUSSION

Typical EMF data is shown in Figure 2 for TTAB/dye with different dye concentrations and in Figure 3 for TTAB with different drug concentrations in 1×10^{-4} mol L^{-1} NaBr. Normally, when binding takes place, the EMF is different for each corresponding titration for the solution with and without dyes and drugs.

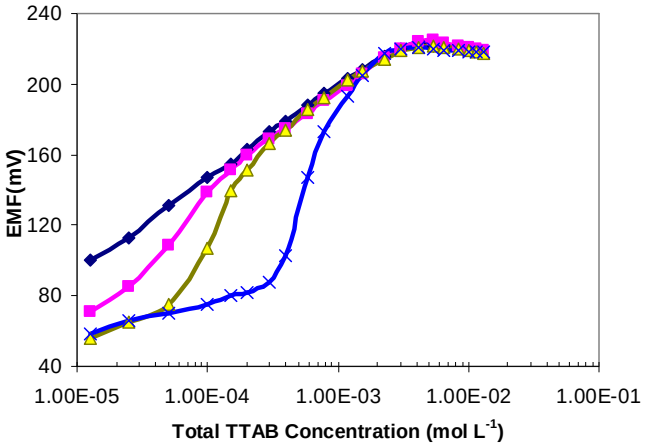


Fig. 2. EMF versus total concentration of TTAB in the presence of DR16: (♦) 0.00 mol L^{-1} DR16, (■) 0.0001 mol L^{-1} DR16, (▲) 0.0005 mol L^{-1} DR16, (×) 0.001 mol L^{-1} DR16

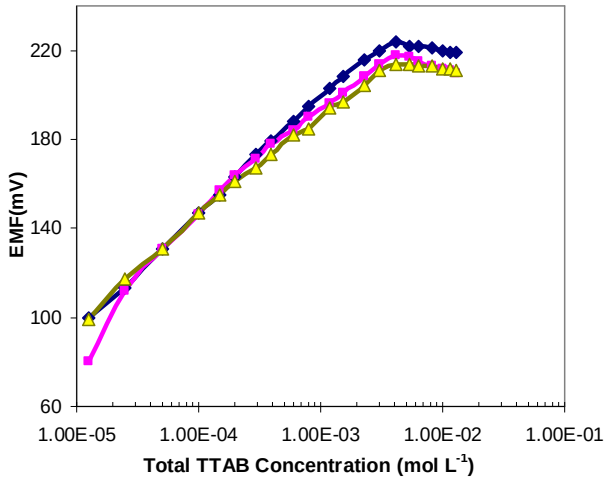


Fig. 3. EMF versus total concentration of TTAB in the presence of ATN: (■) 0.00 % ATN, (▲) 0.05% ATN, (×) 0.01% ATN

The experimental results for the systems show that there are interactions between TTAB and DO26 (1×10^{-4} mol L^{-1}) (Figure 4) and interactions between TTAB and DR16 (1×10^{-4} mol L^{-1}) (Figure 2).

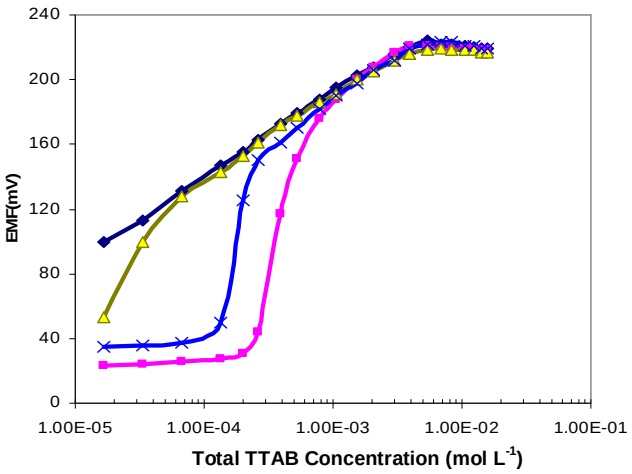


Fig. 4. EMF versus total concentration of TTAB in the presence of DO26: (♦) 0.00 mol L^{-1} DO26, (▲) 0.0001 mol L^{-1} DO26, (×) 0.00025 mol L^{-1} DO26 (■), 0.0005 mol L^{-1} DO26

Therefore, the increase of the hydrophobicity, either of the surfactant or the dye, increases the tendency to associate [20]. If a surfactant is added at a submicellar concentration to a dye solution, both the surfactant monomer and the dye aggregate at concentrations far below the normal CMC. Interactions between dye and surfactant molecules bearing a charge of the opposite sign result in the formation of a mixed dye-surfactant aggregate. The results in Figure 3 show that there is no interaction between TTAB and ATN or there is very little interaction between them. From a comparison between Figures, 2 or 4 and 3, we find that the interaction mechanisms between TTAB and dyes and also between TTAB and ATN are completely different. The interaction between TTAB and 0.05% ATN is very low and there is no observable interaction between TTAB and 0.01% ATN. On the other hand, the calibration and binding curves at first are approximately the same and no interaction exists. When the binding curve starts, a small deviation from calibration curve is seen, this shows that a weak interaction occurs. From Figure 2, the deviation of binding curve starts at the first stages of addition of TTAB. This shows that binding occurs between the dye and the monomer of TTAB.

When the binding curves lay below the calibration curve, at any measured concentration of TTAB, the concentration of the free surfactant, which can be detected by the TTAB-selective electrode, is lower than the total TTAB concentration. This suggests the formation of a dye-surfactant complex and the formation of a complex in ternary systems like a dye-surfactant-drug complex. When the EMF data with and without dye merge, they indicate that the dye becomes fully saturated with bound surfactant.

A mixture of ATN at a concentration of 0.01% and DR16 at three concentrations was titrated by TTAB; the results are shown in Figure 5. Furthermore, mixtures of ATN at

different concentrations and DR16 at a concentration of 0.001 mol L^{-1} were titrated by TTAB; the results are shown in Figure 6.

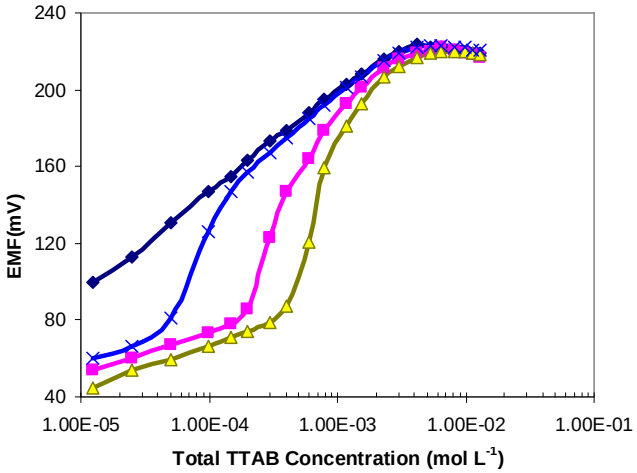


Fig. 5. EMF versus total concentration of TTAB in the presence of ATN and different concentrations of DR16: (♦) 0.00 mol L^{-1} ATN + 0.00 M DR16, (×) 0.01 % ATN + 0.0001 mol L^{-1} DR16, (■) 0.01 % ATN + 0.0005 mol L^{-1} DR16, (▲) 0.01 % ATN + 0.001 mol L^{-1} DR16

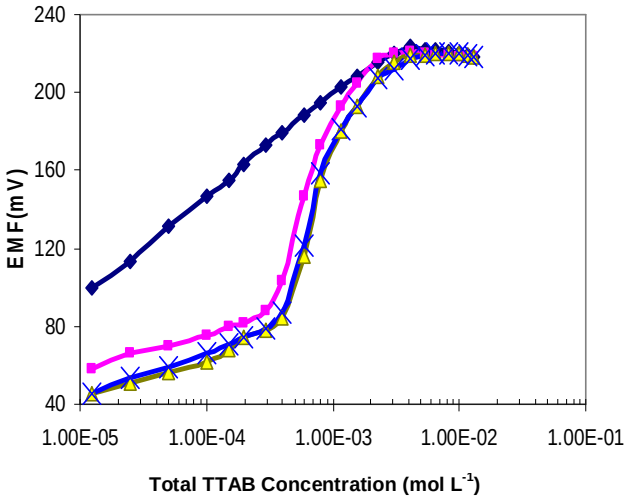


Fig. 6. EMF versus total concentration of TTAB in the presence of different concentrations of ATN and DR16: (♦) 0.00 % ATN + 0.00 mol L^{-1} DR16, (■) 0.00 % ATN + 0.001 mol L^{-1} DR16, (▲) 0.05 % ATN + 0.001 mol L^{-1} DR16, (×) 0.01 % ATN + 0.001 mol L^{-1} DR16

The interaction between TTAB and DR16 (5×10^{-4} mol L^{-1}) in the absence and presence of ATN (0.01%) is compared in Figures 2 and 5. When ATN is absent, the binding and calibration curves merged in 7×10^{-4} mol L^{-1} TTAB (Figure 2), but they merged at 3×10^{-3} mol L^{-1} in the presence of ATN (Figure 5). When the concentration of DR16 is 1×10^{-3} mol L^{-1}, in the absence of ATN, both the binding and calibration curves merged at 2×10^{-3} mol L^{-1} (Figure 2) On the other hand, in the presence of 0.01% ATN, the merge occurs at 5×10^{-3} mol L^{-1}, as shown in Figure 5.

From Figure 3, it is understood that there is no interaction between TTAB and ATN; therefore, we can say that there was an initial interaction between the drug and the dye (DR16). Indeed, ATN prevents the interaction between the dye and the surfactant at first, but if we add more TTAB, it causes the dye to separate from the drug and interact with TTAB. Thus, more TTAB is needed for the saturation of the dye and the merge occurs at a higher concentration of TTAB. The above results are supported by Figure 6.

From a comparison of the binding curves of DR16 (1×10^{-3} mol L^{-1}) and TTAB with DR16 (1×10^{-3} mol L^{-1}) and ATN and TTAB in Figure 6, the merge occurs when the concentration of TTAB is 4×10^{-3} mol L^{-1}. The same results also are shown for the binding of TTAB/DO26 and ternary mixtures of TTAB/DO26/ATN, respectively, in Figure 7.

The comparison of the UV/Vis spectra of a mixture of the dye/drug and the dye/drug/surfactant aqueous solution at various concentrations confirms that the mixed dye/drug interact with the TTAB (Figures 8,9).

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

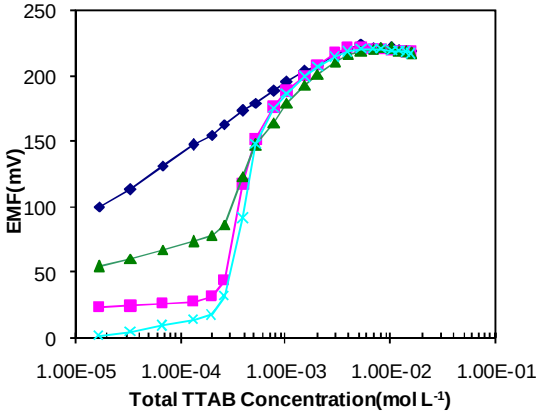


Fig. 7. EMF versus total concentration of TTAB in the presence of different concentrations of ATN and DO26: (♦) 0.00 % ATN + 0.00 mol L^{-1} DO26, (■) 0.00 % ATN + 0.0005 mol L^{-1} DO26, (▲) 0.01 % ATN + 0.0005 mol L^{-1} DO26, (×) 0.05 % ATN + 0.0005 mol L^{-1} DO26

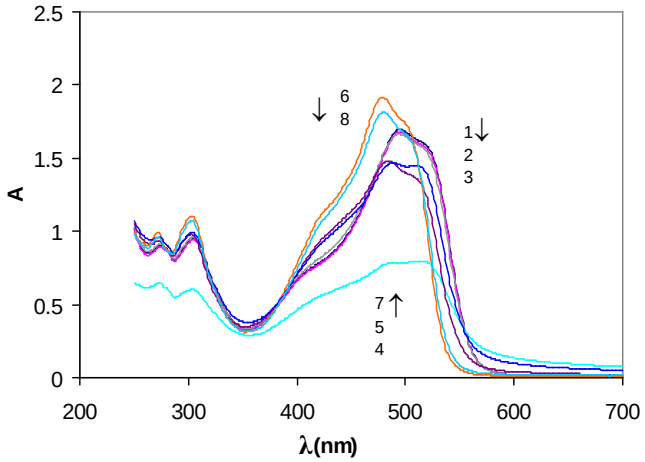


Fig. 8. Visible absorption spectra of ATN/DO26, (ATN, 0.01% and DO26, 1×10^{-4} mol L^{-1}) in the presence of TTAB, [TTAB] (mol L^{-1}):1(0.0), 2(1×10^{-6}), 3(1×10^{-5}), 4(1×10^{-4}), 5(1×10^{-3}), 6(1×10^{-2}), 7(5×10^{-4}), 8(5×10^{-3})

The variation in the visible absorption spectra of ATN/DO26, upon addition of TTAB at various concentrations, is shown in Figure 8. When the concentration of TTAB was below the CMC, the value of the absorbance decreased. On the other hand, when the concentration of TTAB was above the CMC, a new absorption band, with a maximum absorption at 480 nm, was observed and the value of the absorbance increased (curves 6, 7 and 8 in Figure 9).

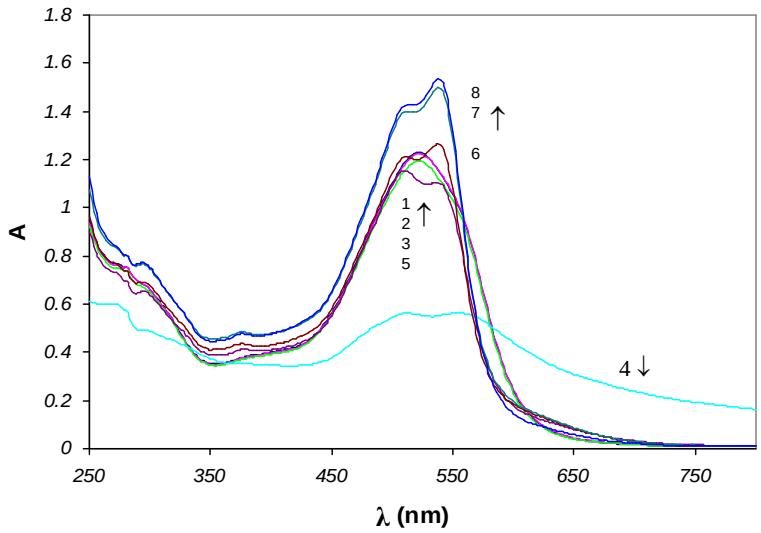


Fig. 9. Visible absorption spectra of ATN/DR16, (ATN, 0.01% and DR16, 1×10^{-4} mol L^{-1}) in the presence of TTAB, [TTAB] (mol L^{-1}): 1(0.0),2 (1×10^{-6}), 3(1×10^{-5}), 4(1×10^{-4}), 5(1×10^{-3}), 6(5×10^{-3}), 7(1×10^{-2}), 8(5×10^{-2})

The band of ATN/DO26 at a concentration of TTAB below its CMC can be attributed to the surfactant-dye and surfactant-drug interaction. The 480 nm band can be attributed to the interaction of ATN/DO26 with the TTAB micelles, where the micelles begin forming at around the CMC in presence of the dye/drug.

No interaction was observed between mixed ATN/DO26 (1×10^{-4} mol L^{-1}) at a surfactant concentration below its CMC (compare curves 1 and 2 in Figure 8).

If we notice the structures of ATN, DR16 and DO26, there are two OH groups and one group of free NH_2 in DR16. Therefore, the interaction between DR16 and ATN is stronger than that between DO26 and ATN. On the other hand, there are only two OH groups in DO26, which is not enough to form a strong interaction between DR16 and ATN. Hence, the interaction between DO26 and TTAB is stronger than that between DR16 and TTAB because DO26 is more hydrophobic than DR16. The results of the interaction between TTAB and ATN with DR16 and DO26 are shown in Tables 1 and 2, respectively.

The variations in the absorption maximum of ATN/DR16 by the addition of different concentrations of TTAB are shown in Figure 9. Upon addition of TTAB, a new absorption band, with an absorption maximum at 540 nm, was observed and the value of the absorbance decreased. When the concentration of the TTAB was increased above its CMC, the value of the absorbance increased with a gradual decrease in the intensity of the 540 nm band.

Table 1. Characteristics of the interaction between TTAB, DR16 and ATN

Initial Solution		Concentration of TTAB for the saturation of DR16 (mol L^{-1})
Concentration of DR16 (mol L^{-1})	Concentration of ATN (W/W %)	
1×10^{-4}	-	2×10^{-4}
1×10^{-4}	0.01	6×10^{-4}
1×10^{-4}	0.05	8×10^{-4}
5×10^{-4}	-	4×10^{-4}
5×10^{-4}	0.01	1×10^{-3}
5×10^{-4}	0.05	2×10^{-3}
1×10^{-3}	-	2×10^{-3}
1×10^{-3}	0.01	3×10^{-3}
1×10^{-3}	0.05	4×10^{-3}

Table 2. Characteristics of the interaction between TTAB, DO26 and ATN

Initial Solution		Concentration of TTAB for the saturation of DO26 (mol L^{-1})
Concentration of DO26 (mol L^{-1})	Concentration of ATN (W/W %)	
1×10^{-4}	-	-
1×10^{-4}	0.01	2×10^{-4}
1×10^{-4}	0.05	4×10^{-4}
2.5×10^{-4}	-	8×10^{-4}
2.5×10^{-4}	0.01	1×10^{-4}
2.5×10^{-4}	0.05	1×10^{-3}
5×10^{-4}	-	1×10^{-3}
5×10^{-4}	0.01	1×10^{-3}
5×10^{-4}	0.05	2×10^{-3}

4. CONCLUSION

The TTAB-selective electrode and spectrophotometry methods show that the dyes studied here interact with the surfactant. On the other hand, the drug does not interact with the surfactant, but has an effect on the interaction of the dye and the surfactant. The interaction between TTAB and the dyes occurs even at very low TTAB concentrations and the binding process continues until the dye becomes fully saturated with bound surfactant. A mixture of the drug and the dye interacts with the surfactant but, at higher concentrations of drug, the interaction is weaker so it seems that the drug and the dyes interact. Therefore, a higher concentration of TTAB is needed to interact with the dyes in the presence of the drug.

As a result, the interaction between DO26 and TTAB is stronger than the interaction between DR16 and TTAB, because DO26 is more hydrophobic compared to DR16. The electrostatic attraction between differently charged ions is not enough and the hydrophobic force also plays a role.

Acknowledgement

The authors are grateful to the Kashan University Research Councils for their financial support of the work.

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