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Electromotive force studies about some dyes–cationic surfactants interactions in aqueous solutions

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Abstract

Surfactants have been widely used as auxiliaries in many areas of textile finishing. The nature of the interactions between dyes and surfactants is one of the basic pieces of information for understanding the process of dyeing and finishing of textile material.

The interactions of Orange II and Direct Red 80, anionic azo dyes, and also Indigocarmine with *n*-dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (HTAB) in submicellar concentration ranges have been investigated by a potentiometric technique using DTAB and HTAB membrane selective electrodes. The detection limits for HTAB and DTAB electrodes are 8×10^{-7} and 5×10^{-7} mol dm^{-3}, respectively. The data show that significant binding takes place and the critical concentrations associated with the saturation of the dyes with bound surfactant have been determined. It has also been shown that free micelles occur in solution before the dyes become fully saturated with bound surfactant. The results also show that under the same experimental conditions the complex formation between HTAB and Orange II takes place at more less surfactant concentration than between DTAB and Orange II. EMF data and comparison between calibration and binding curves showed that interaction between HTAB and Orange II is more than that between Direct Red 80 and Indigocarmine.

Keywords: Membrane selective electrode; Dyes–cationic surfactants interactions; Micelle

1. Introduction

Surfactants are widely used in household and industrial cleaners, cosmetics, research laboratories and as leveling, dispersing and wetting agents in the dyeing process [1]. Extensive research has already been carried out on surfactant–dye interactions. The studies in this area are still very important and interesting in the context of the theory and technology of dyeing [2–8]. The investigations of dye–surfactant interactions may directly affect the increase in the quality of dyeing, which is one of the aims of textile finishing. In recent years, these interactions have been studied, mostly spectroscopically [8–13]. These researchers have detected spectral changes of ionic dyes when the oppositely-charged or nonionic surfactants are added to aqueous dye solutions. The change in adsorption band accompanied by the change of the color of the dye can be explained as the result of dye–surfactant interactions. In previous works also the interactions between surfactant and polymers and other macromolecules were investigated by ion-selective electrodes [14–20]. In the present work, a potentiometric titration was used to obtain the results of interactions between two cationic surfactants, dodecyltrimetylammonium bromide (DTAB) and hexadecyltrimetylammonium bromide (HTAB) and three dyes, Orange II, Indigocarmine and Direct Red 80.

From the measured electromotive force (EMF) data and also the variation of monomer (m_1) surfactants' concentration with total added surfactants (C_1), various

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critical concentrations associated with the binding process have been determined. These include the value of the total DTAB and HTAB concentrations corresponding to (i) onset of binding (T_1), (ii) the saturation of the dye with bound DTAB and HTAB (T_2), and (iii) the formation of free micellar (T_f). In addition, binding isotherm and a parameter which is a measure of the relative extent of binding have been determined.

2. Experimental

2.1. Materials

In this work DTAB and HTAB were used as received from Aldrich, and also the dyes Orange II, Indigocarmine and Direct Red 80 as received from Fluka were used without further purification. The structures of the dyes and surfactants used in this study are shown in Fig. 1.

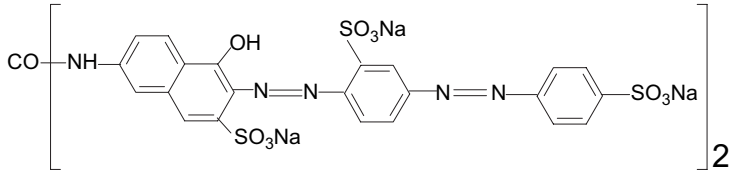
2.2. EMF measurements

Surfactant membrane electrodes selective to DTAB and HTAB were constructed in the laboratory [21] and used to determine the concentrations of monomers DTAB and HTAB by measuring their EMF relative to a commercial sodium ion (corning 476211) selective electrode. The cells used for these measurements and the procedures to calculate the respective monomer concentrations have been described elsewhere [16–20]. In the EMF experiments a concentrated surfactant solution is titrated into 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 surfactant concentration for the solutions with and without the dyes, the latter being the binding experiment.

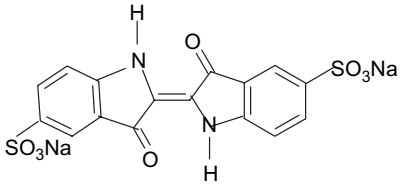
Typical EMF data are shown in Fig. 2 for the DTAB/dyes system at 1×10^{-4} mol dm^{-3} NaBr. Normally, when binding is taking place the EMFs are different for each corresponding titration for the solution with and without dyes.

3. Results and discussion

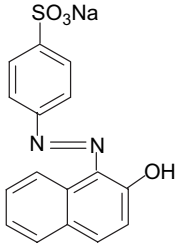
In the present work on DTAB and HTAB/dye systems, the methods used to determine the critical



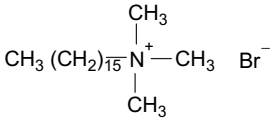
Direct Red 80



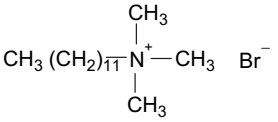
Indigocarmine



Orange II



Hexadecyltrimetylammonium bromide (HTAB)



Dodecyltrimetylammonium bromide (DTAB)

Fig. 1. Structures of the dyes and surfactants.

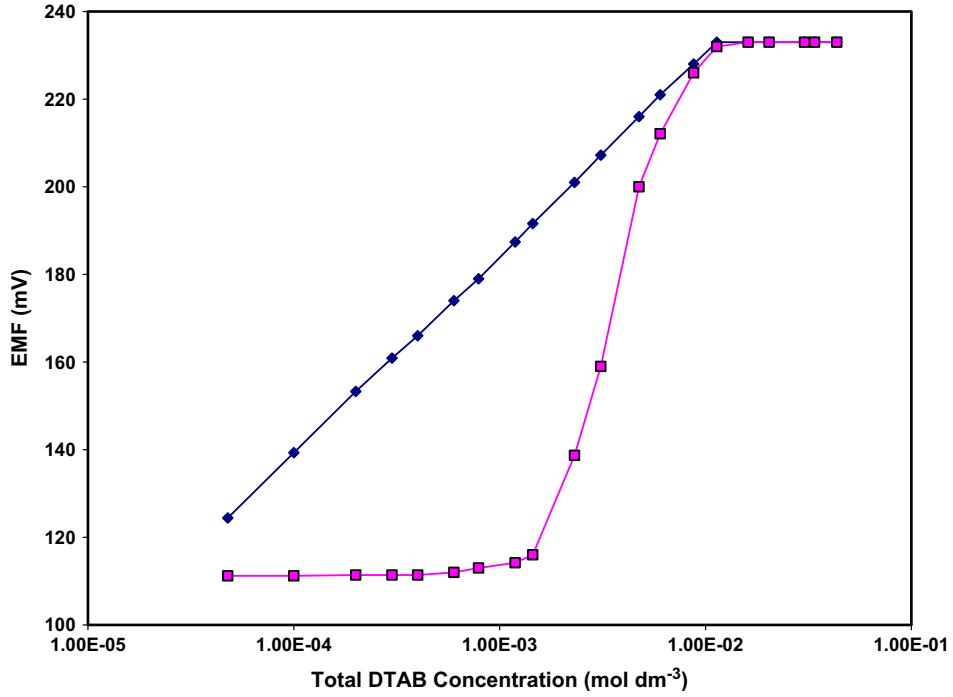


Fig. 2. Plot of the EMF of the DTAB electrode (reference Na+) as a function of the total DTAB concentration for the DTAB/Orange II system in 1×10^{-4} mol dm^{-3} NaBr: (♦) pure DTAB; (■) DTAB + Orange II (0.1% w/v).

concentrations associated with the binding of DTAB and HTAB to the dyes using the DTAB and HTAB selective electrodes are described below. The experimental results for the system whose experimental data behave ideally, namely, DTAB/Orange II in Fig. 2, show how EMF data from some of the other systems have been interpreted. Fig. 2 shows that binding occurs even at very low DTAB concentrations and the process continues until the dye is fully saturated with bound DTAB. This point is reached when the EMF data for

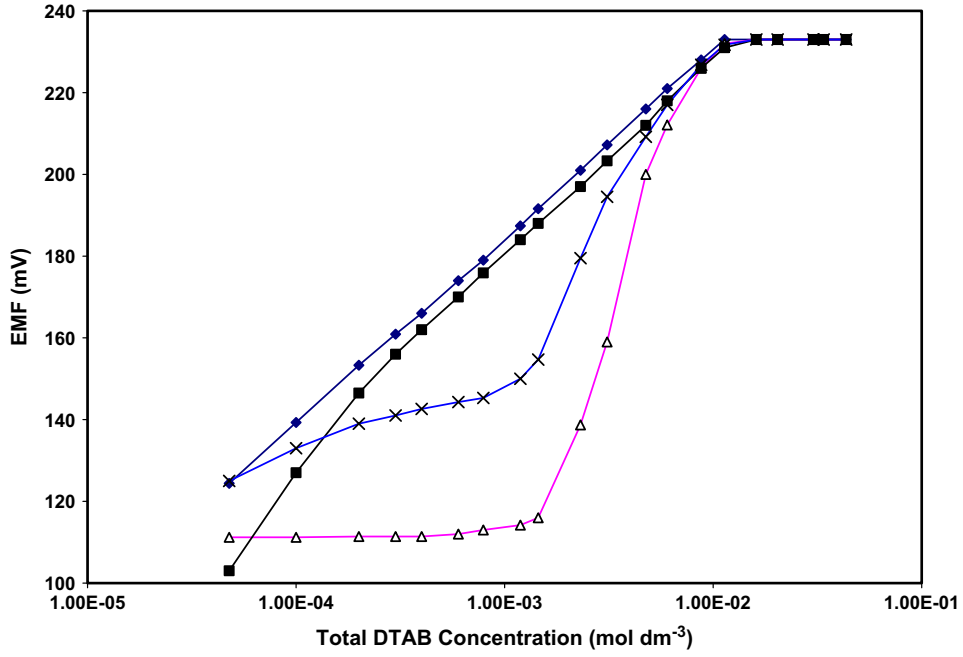


Fig. 3. Plot of the EMF of the DTAB electrode (reference Na+) as a function of the total DTAB concentration for DTAB/dye (0.1% w/v) systems in 1×10^{-4} mol dm^{-3} NaBr: (♦) pure DTAB; (△) DTAB + Orange II; (■) DTAB + Indigocarmine; (×) DTAB + Direct Red 80.

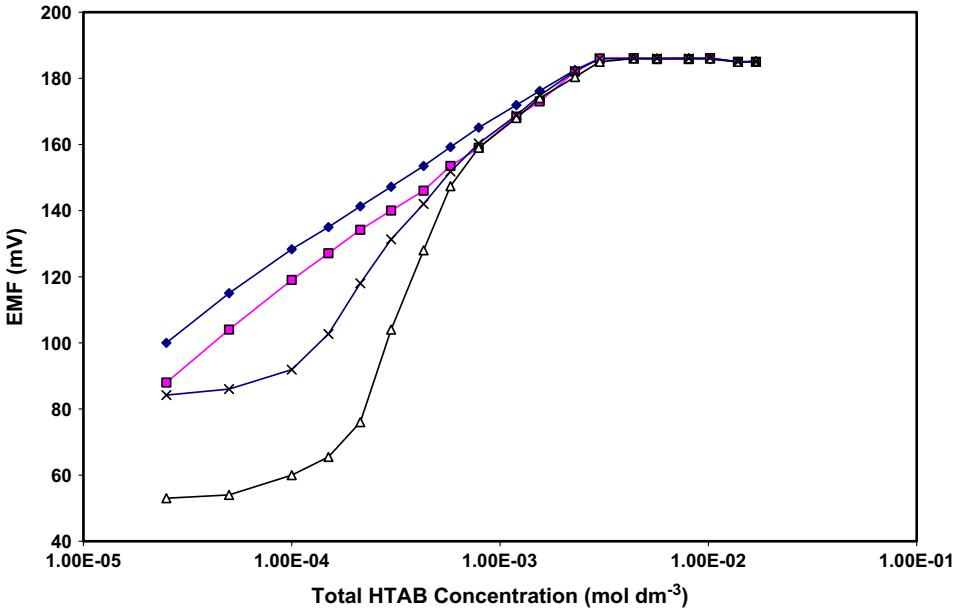


Fig. 4. Plot of the EMF of the HTAB electrode (reference Na+) as a function of the total HTAB concentration for HTAB/dye (0.01% w/v) systems in 1×10^{-4} mol dm^{-3} NaBr: (♦) pure HTAB; (△) HTAB + Orange II; (■) HTAB + Indigocarmine; (×) HTAB + Direct Red 80.

the solutions with and without dyes merge in the micellar range. This is a result that Wyn-Jones and coworkers have obtained previously in connection with the binding of SDS to linear polymers and dendrimers and the inclusion of SDS into cyclodextrins [19].

When the EMF of the DTAB electrode merge it shows that the dye is no longer involved in any further binding with DTAB or alternatively the dye can be regarded to be saturated with bound DTAB. At DTAB concentration in excess of this point the dye is no longer involved in any further interaction with DTAB.

The DTAB concentration corresponding to the merger is denoted T_2. This is not an easy concentration to pinpoint accurately from the experimental data in the sense that the EMF data for the solutions containing dye become asymptotic to the data in the absence of polymer. As a result T_2 must be regarded very much in the same way as the CMC of a surfactant, i.e. it takes place over a narrow range of surfactant concentrations. The same results obtained for DTAB/Indigocarmine and Direct Red 80 and also for HTAB/Orange II, Indigocarmine and Direct Red 80 are shown in Figs. 3 and 4, respectively.

From comparison between Figs. 3 and 4, it can be concluded that interactions between HTAB/dyes are much more than those between DTAB/dyes with the same dye concentrations.

These results arise probably because HTAB is bigger and therefore it is easier to obtain dyes than with DTAB. The values of T_2 estimated from the present EMF data are shown in Tables 1 and 2.

In this work also we can obtain T_f, DTAB and HTAB concentrations at which free micelles occur in solution. The variation in the concentrations of the monomers DTAB and HTAB with the overall DTAB and HTAB concentrations is a very useful guide which may be used to distinguish between different mechanisms of binding and/or DTAB and HTAB aggregation.

The concentration of the monomers DTAB and HTAB, denoted m_1, has been evaluated from the electrode data and is shown as a function of total DTAB concentration, C_1, in Fig. 5. An increase in m_1 with increasing C_1 is exactly the behavior expected when DTAB and HTAB exclusively bind to a dye. When m_1 decreases with increasing C_1 it signifies the formation

Table 1
Summary of the interaction between HTAB and dyes (0.001% w/v) 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 g^{-1})	[HTAB]/[dye] at T_2 (mol mol^{-1})
Orange II	350.33	0.003	0.0008	0.08	28
Direct Red 80	1373.09	0.0023	0.0005	0.05	69
Indigocarmine	466.36	0.0023	0.0001	0.01	5

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

Table 2
Summary of the interaction between DTAB and dyes (0.01% w/v) 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})	[DTAB]/[dye] at T_2 (mol g^{-1})	[DTAB]/[dye] at T_2 (mol mol^{-1})
Orange II	350.33	0.0161	0.0048	0.048	17
Direct Red 80	1373.09	0.0113	0.0034	0.034	48
Indigocarmine	466.36	0.0113	0.0001	0.001	0.5

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

of free micelles in solution. Furthermore, when the maximum in m_1 (denoted T_f) and T_2 occur at the same total DTAB concentration then the dye is fully saturated with bound DTAB before free micelles occur in solution. At DTAB concentrations exceeding T_2 the EMFs and monomer concentrations for solutions with and without the dyes are the same. The values of T_2 and T_f listed in Tables 1 and 2 are very close, showing that all the dyes become fully saturated with bound DTAB before free micelles occur in solution.

Maximum binding capacity of the dyes is also obtained from the data. The values of $T_2 - m_1$, where m_1 is the concentration of the monomers DTAB and HTAB at T_2, are listed in Tables 1 and 2. These values represent the maximum amount of DTAB and HTAB that the dyes can bind. At DTAB and HTAB concentrations approaching the end of binding (T_2) the complex involves one dye containing 0.5–69 bound monomers of DTAB and HTAB depending on the size and type of dyes.

3.1. Binding region

A more accurate and informative guide to the binding behavior can be obtained from the EMF data where the ratio of bound DTAB and HTAB ($C_1 - m_1$) per mole dye (C_d) (the binding ratio) is evaluated as a function of DTAB and HTAB concentrations in the binding region. Typical data for DTAB/dyes are shown in Fig. 6 depicting the binding ratio plotted against C_1.

The plot of binding ratio against m_1 for DTAB/dyes is shown in Fig. 7. These data show that in the early stages the binding ratio can be as small as 5 whereas at T_2 the highest value is 69. This clearly implies that at least two modes of binding are taking place. As stated earlier, the m_1 as a function of C_1 plots provides excellent guidelines to distinguish between different binding mechanisms. As shown in Fig. 5, the m_1 versus C_1 plots can be clearly divided into two regions at DTAB and HTAB concentrations up to T_2 which are represented by two straight lines whose slopes ($d \ln m_1 / d \ln C_1$) are

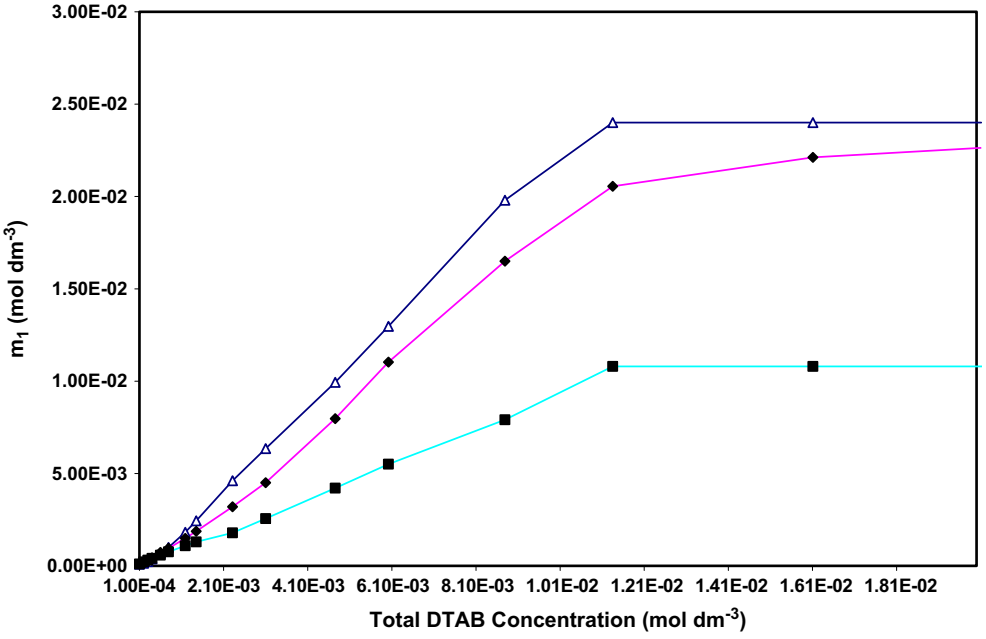


Fig. 5. Plot of the DTAB monomer concentration (m_1) as a function of the total DTAB concentration for DTAB/dye (0.01% w/v) systems in 1×10^{-4} mol dm^{-3} NaBr: (△) DTAB + Orange II; (■) DTAB + Indigocarmine; (♦) DTAB + Direct Red 80.

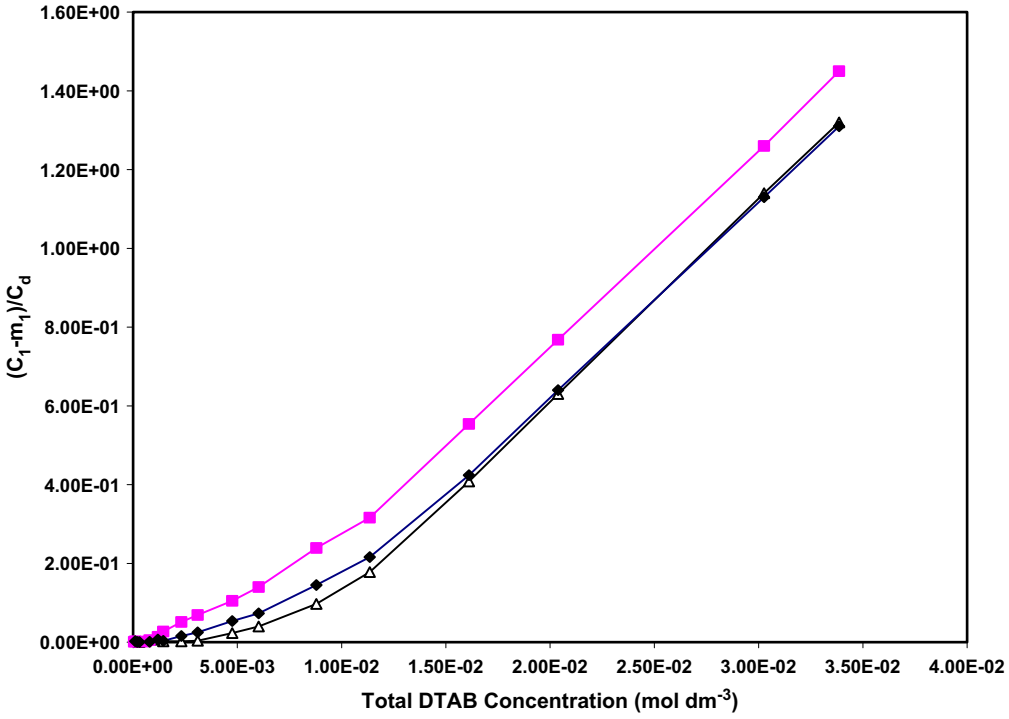


Fig. 6. Plot of binding ratio of DTAB/dyes as a function of the total DTAB concentration for DTAB/dye (0.01% w/v) systems in 1×10^{-4} mol dm^{-3} NaBr: (△) DTAB + Orange II; (■) DTAB + Indigocarmine; (♦) DTAB + Direct Red 80.

significantly different. The transition from the first straight line to the second is a gradual process that takes place over a small range of added DTAB and HTAB. In the early stage of binding the slope ($\mathrm{d}\ln m_1/\mathrm{d}\ln C_1$) is small which indicates that the binding is a non-cooperative process. Furthermore the numbers involved when we consider the amount of bound DTAB and HTAB per mole dye denoted $(C_1 - m_1)/C_\mathrm{d}$ are of

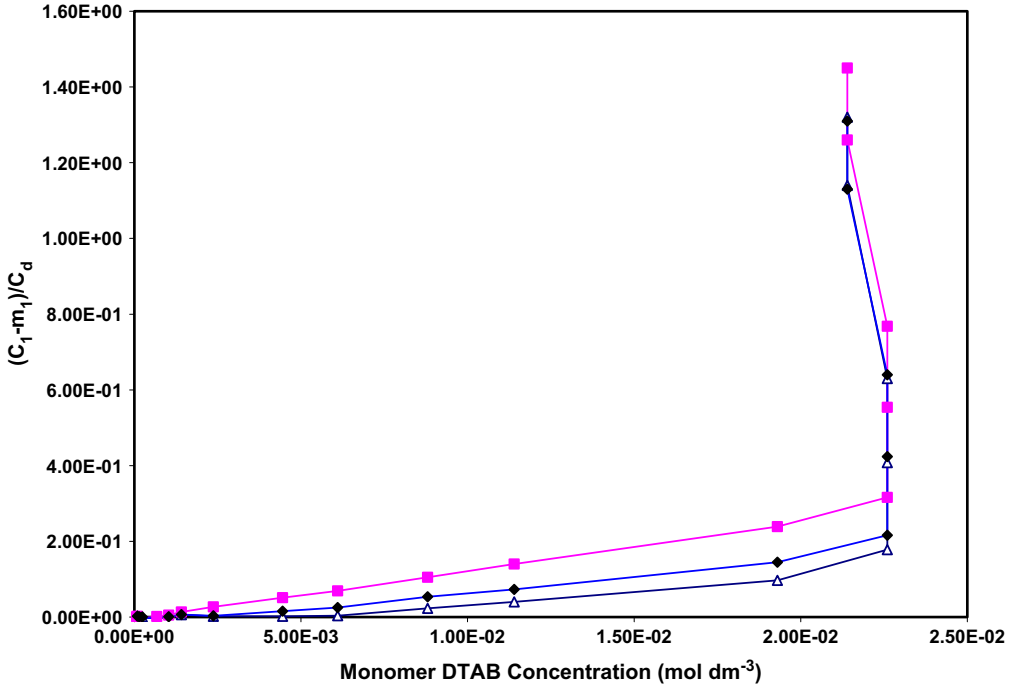


Fig. 7. Binding isotherm in the form of a plot of bound DTAB per gram of dye, $(C_1 - m_1)/C_\mathrm{d}$, as a function of monomer DTAB concentration for the system DTAB/dye in 1×10^{-4} mol dm^{-3} NaBr: (△) DTAB + Orange II (0.01% w/v); (■) DTAB + Indigocarmine (0.01% w/v); (♦) DTAB + Direct Red 80 (0.01% w/v).

the order 0.5–15 which are consistent with this conclusion. For the second binding process of DTAB and HTAB concentrations immediately proceeding T_2 the values of $(\mathrm{d}\ln m_1/\mathrm{d}\ln C_1)$ are much higher and for all the systems the values of $(C_1 - m_1)/C_\mathrm{d}$ range from $\sim$17 to values as high as 69 at T_2. This is consistent with a highly cooperative binding process.

4. Conclusions

It was found that DTAB and HTAB bind to all three dyes at surfactant concentrations lower than 1×10^{-5} mol dm^{-3}. As more DTAB and HTAB are added the binding process continues until the dye becomes fully saturated with bound surfactant, at which point the EMF data for DTAB and HTAB solutions with and without the dyes merge. The variation in monomer surfactant concentration as a function of total added surfactant is used as a probe to distinguish between different binding and/or surfactant aggregation mechanisms. At low DTAB and HTAB concentrations the binding mechanism is a non-cooperative process driven by hydrophobic interactions between the hydrocarbon chains in the dye and also electrostatic attraction between the surfactant head groups and anionic nature of dyes. As binding proceeds there is a gradual transition to a cooperative binding process in which micellar-type bound DTAB or HTAB aggregates are formed on the dyes. This continues until the dye can no longer bind any further surfactant that signals the occurrence of free regular DTAB or HTAB micelles in solution. The much more facile binding between DTAB or HTAB micelles and the dyes is driven by primary electrostatic interactions which also promote stable micellar bound DTAB or HTAB aggregates. Direct Red 80 has six SO_3^- functional groups therefore, more HTAB and DTAB bind to it.

Acknowledgement

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