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A study of anionic dye–cationic surfactant interactions in mixtures of cationic and nonionic surfactants

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Abstract

Interactions between anionic azo dye C.I. Acid Red 88 (AR88) and cationic surfactant dodecyltrimethylammonium bromide (DTA) in mixtures of DTA and nonionic surfactant Triton X-100 (TX100) at 25 °C have been quantitatively investigated by means of potentiometry based on the DTA surfactant cation-selective electrode. For this reason the treatment of mononuclear complex formation in aqueous solution has been used. Association constants K_1 for the formation of DTA–AR88 complex in the TX100 solutions of different concentrations in its micellar concentration range have been determined and compared to those obtained in the binary mixtures. It has been observed that the addition of TX100 into the mixture of DTA and AR88 causes a significant decrease of K_1, suggesting that the stability of DTA–AR88 complex is reduced in the presence of TX100 micelles. The results show that the decrease of the value of K_1 is directly affected by the DTA-TX100 and AR88-TX100 interactions in the solution. Since the solubilization of the DTA-AR88 complexes has been appeared in the TX100 solution our results support the conclusion that adding TX100 influences the hydrophobic–hydrophylic balance of the studied complexes. Comparison of the stability of DTA–AR88 complexes to that obtained between DTA and the anionic azo dye C.I. Acid Orange 7 (AO7) without added TX100 shows that under the same experimental conditions DTA strongly interact with AR88 than with AO7. Such behaviour can be explained as a consequence of more hydrophobic character of AR88 compared to AO7. The addition of TX100 into DTA-AO7 mixtures significantly affects the nature of the binding process.

Keywords: Dye–surfactant interactions; Anionic dye; Cationic–nonionic surfactant mixtures; Complex formation; Association constants; Potentiometry

1. Introduction

Although a lot of research work has already been done into dye–surfactant interactions the studies in this area are still important and interesting for the theory and technology of dyeing. The investigations into the behaviour of different dyes in surfactant aqueous solutions can, among other thinks, give useful information about the mechanisms according to which surfactants operate as levelling agents and information on the influence of dye–surfactant interactions on the thermodynamics and kinetics of dyeing process. This may directly affect the increase in the quality of dyeing, which is one of the goals of textile finishing, from technological, ecological and economical points of view.

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According to the structures of dye and substrate, surfactants used as levelling agents operate by different mechanisms. Consequently, a great deal of research work focused on dye–surfactant interactions in binary mixtures including the interactions between ionic dyes and ionic surfactants of the opposite and the same charges [1–12], ionic dyes and nonionic surfactants [6,12–18] as well as between nonionic dyes and ionic or nonionic surfactants [19] in the submicellar and micellar concentration ranges of surfactants. Experimental methods mostly used were spectroscopy, tensiometry, conductometry and potentiometry. In spite of the fact that the surfactant mixtures as levelling agents are of great practical importance because of their synergistic behaviour, investigations into intermolecular interactions between dyes and surfactants in mixed surfactant systems are rare [12,20]. Therefore, the aim of our research work was to find out a suitable experimental method, a procedure and an appropriate theoretical model for the quantitative study of dye–surfactant interactions in systems where two surfactants are present in aqueous dye solutions.

The following paper gives the results of an investigation into interactions between anionic azo dye C.I. Acid Red 88 (AR88) and cationic surfactant dodecyltrimethylammonium bromide (DTA) in the solution of nonionic surfactant Triton X-100 (TX100) at different concentrations of the dye and surfactants. The association constants determined for the DTA–AR88 complex formation in the presence of TX100 in its reverse micellar media were calculated and compared to those obtained when TX100 is not added. By studying the influence of the hydrophobic character of the dye on the dye–surfactant interactions as well as the effects of the TX100 on the nature of the binding process, the dye–surfactant interactions were also studied in the presence of the anionic azo dye C.I. Acid Orange 7 (AO7). We also discussed the nature of the interactions between selected species. This work was done with the use of the potentiometric method, based on the use of surfactant cation-sensitive membrane electrodes. This experimental method was not chosen by chance but based on the previous inspections of the benefits derived from the potentiometric measurements. Since the high selectivity of the ion selective membrane electrode, permit the detection of the concentration of free primary ions at any total concentration in the presence of other ions to which the electrode is not selective, potentiometry has already been used succesfully for studying the binding of ionic surfactants to ionic dyes [8,10], polyelectrolites [21–25] and nonionic surfactants [26,27] in binary mixtures.

2. Experimental

2.1. Materials

The anionic azo dyes C.I. Acid Red 88 (AR88), C.I. Acid Orange 7 (AO7), the cationic surfactant *n*-dodecyltrimethylammonium bromide (DTA) and the nonionic surfactant polyoxyethylene *tert*-octyl phenol, Triton X-100 (TX100), were Aldrich-Chemical Company's commercial products. AR88 and AO7 were purified by repeated recrystallization from aqueous acetone solution and from the *N*,*N*′-dimethylformamide-benzene. DTA was purified by four recrystallizations from acetone while TX100 was used as obtained, without further purification. Sodium dodecylsulphate (SDS) (Aldrich-Chemical Co.), which was used for the preparation of the ion-exchange complex, was also purified by four recrystallizations from acetone. All solutions were prepared in double distilled water by weighing and expressed in molal concentrations.

2.2. Measurements

2.2.1. Potentiometry

The potentiometric titrations were used as an experimental method. The use of the DTA-selective electrode, which included the DTA cation–SDS anion complex incorporated in a poly(vinyl chloride) gel membrane [28], enabled us to determine the concentration of free DTA surfactant cations in solution. Potentiometric measurements were carried out in the following electrode cell:

Ag I AgCl I reference solution; $1 \cdot 10^{-4}$ mol/kg DTA + 0.1 mol/kg NaCl, I polymer membrane I test solution; m_S II KCl (satd.) I Hg_2Cl_2 I Hg. An ammonium nitrate salt bridge was used to connect the membrane electrode with the reference calomel electrode. The addition of $5{\cdot}10^{-3}$ mol/kg NaBr provided the constant ionic strength of test solutions.

The relationship between the e.m.f. (E) of the cell and the DTA concentration (m_S) was measured in the concentration range $6.0{\cdot}10^{-6}$ to $4.0{\cdot}10^{-2}$ mol/kg at 25 °C. The calibration curves represent plots of E versus m_S of DTA without the addition of the surfactant TX100 or the dyes AR88 and AO7. Titration curves were obtained when measurements of E versus m_S of DTA were carried out in the presence of constant concentration of TX100 higher than c.m.c. [29] ($5.0{\cdot}10^{-3}$, $1.0{\cdot}10^{-2}$ and $5.0{\cdot}10^{-2}$ mol/kg), or AR88 ($1.0{\cdot}10^{-4}$ and $5.0{\cdot}10^{-4}$ mol/kg), or in mixtures of TX100 and AR88, in which the dye and surfactant concentrations represented above are used in combinations. The potentiometric measurements of E versus m_s of DTA in $1.0{\cdot}10^{-4}$ and $5.0{\cdot}10^{-4}$ m solutions of AO7 performed with and without added TX100 in $5.0{\cdot}10^{-2}$ m concentration.

2.2.2. Spectrophotometry

The visible absorption spectra of AR88-TX100 and AO7-TX100 solutions were recorded at 25 °C on a Varian Cary 1E UV-Visible Spectrophotometer using 1 cm cells. The dye concentrations were $5.0{\cdot}10^{-5}$ mol/kg for AR88 and $4.0{\cdot}10^{-5}$ mol/kg for AO7. Different concentrations of TX100 surfactant were used over a range of $5.0{\cdot}10^{-3}$–$5.0{\cdot}10^{-1}$ mol/kg.

3. Results and discussion

Figs. 1–4 show plots of the e.m.f. (E) of the cell versus the logarithm of DTA concentration, log m_S, with and without the addition of TX100 and AR88 or TX100 and AO7. As seen from the figures, the calibration curves are linear over the concentration range of $4.1{\cdot}10^{-6}$–$8.8{\cdot}10^{-3}$ mol/kg with a slope of +59.6 mV per decade at 25 °C, and that the titration curves obtained in DTA–TX100, DTA–AR88, DTA–AR88–TX100 and DTA–AO7–TX100 solutions deviate from Nernstian behaviour over the whole measured concentration range [30]. Since they lie below the calibration curve, this indicates that at any measured concentration of DTA the concentration of free surfactant cations, which can be detected by the DTA-selective electrode, is lower than the total concentration. This suggests the formation of dye–surfactant and surfactant–surfactant complexes in the studied solutions, in which the DTA cations are associated and can not, therefore, be selected by the electrode. The concentration of DTA cations bound into complexes increases with the increase of TX100 and AR88 or AO7 concentrations. It is also evident from the Fig. 4 that in comparison with other studied systems the titration curves obtained in DTA–AO7 solutions of low DTA concentrations are linear and lie on the calibration curve. In this concentration range m_S is equal to $m_{S,F}$, indicating that there are no dye-surfactant interactions in the solution. Above the critical DTA concentration, $m_{S,\mathrm{crit}}$, which is much lower than the c.m.c. ($1.6{\cdot}10^{-2}$ mol/kg) of DTA [27], the complexes between DTA and AO7 are present in the studied mixtures, which results in the deviation of titration curves from the linearity. Since the $m_{S,\mathrm{crit}}$ decreases with the increase of the AO7 concentration, it indicates that the increase of the dye concentration promotes the formation of dye–surfactant complexes. At the same time it must be emphasised that the shapes of titration curves obtained in DTA–AO7–TX100 mixtures are very similar to those obtained in DTA–AR88–TX100 mixtures under the same measuring conditions.

In the e.m.f. range where linear behaviour of the DTA calibration curve was obtained (below the c.m.c of DTA), at any measured value of E the total DTA concentration, m_S, was obtained from the titration curve and an appropriate concentration, $m_{S,F}$ of free DTA cations from the calibration curve. The concentration of DTA cations which formed the complexes is equal to (m_S—$m_{S,F}$).

To detect if the AR88–TX100 and AO7–TX100 interactions exist in the studied systems apart from the DTA–AR88, DTA–AO7 and DTA–TX100 interactions, the visible spectra of the AR88 and AO7 solutions in the presence of TX100 micelles were recorded (Figs. 5 and 6). The results of our previous work [31] showed that the potentiometric method is not suitable for studying the dye–nonionic surfactant micelles interactions. It can be seen from the Fig. 5 that the absorption spectrum

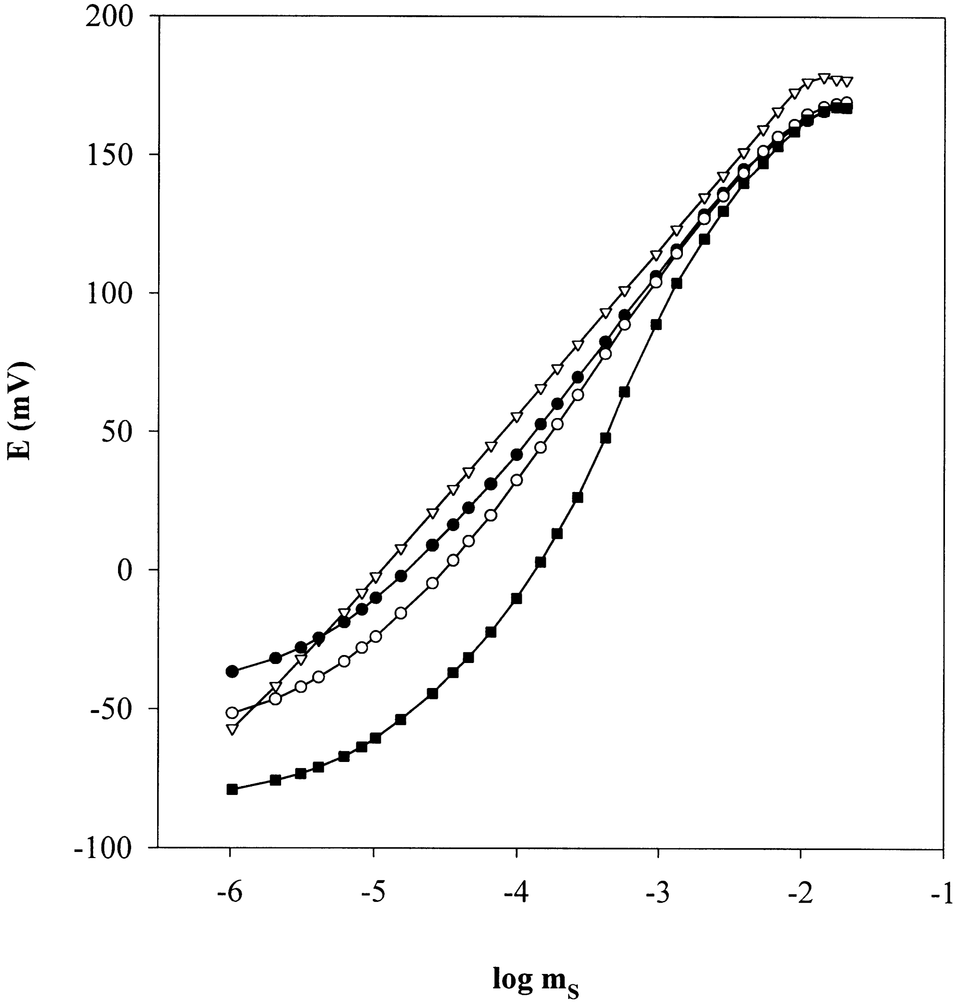

Fig. 1. Plots of e.m.f. (E) of the cell versus the logarithm of the molal concentration (log m_S) of DTA in TX100 and AR88 solutions of different concentrations at 25 °C.-▽-▽-: calibration curve,-●-●-: $5.0{\cdot}10^{-3}$ mol/kg TX100,-○-○-: mixture of $5.0{\cdot}10^{-3}$ mol/kg TX100 and $1.0{\cdot}10^{-4}$ mol/kg AR88,-■-■-: mixture of $5.0{\cdot}10^{-3}$ mol/kg TX100 and $5.0{\cdot}10^{-4}$ mol/kg AR88.

of $5.0{\cdot}10^{-5}$ m AR88 solution shows the absorption maximum at 504 nm and that all the dye spectra obtained in TX100 solutions of the concentrations above the c.m.c. cause the decrease in absorbance with batochromic spectral shift at 515 nm. Furthermore, all spectra pass through two isosbestic points. All this supports the formation of 1:1 complex between AR88 and TX100 micelle in the absence of DTA. The existing interactions between AO7 and the nonionic micelles of TX100 are evident from Fig. 6. In spite of the fact that no isosbestic point is evident in the absorption spectra, the batochromic spectral shift at 523 nm can be detected in all dye spectra obtained in TX100 solutions. This absorption maximum is determined precisely when the solution of AO7 whose concentration is the same to that of free dye anions in the mixture is subtracted as the reference.

When describing the complex formation process it can be assumed that only mononuclear complexes are formed in the studied mixtures. This is characteristic of a large number of systems, especially of diluted solutions [32]. According to this treatment, the DTA was considered the ligand and AR88,

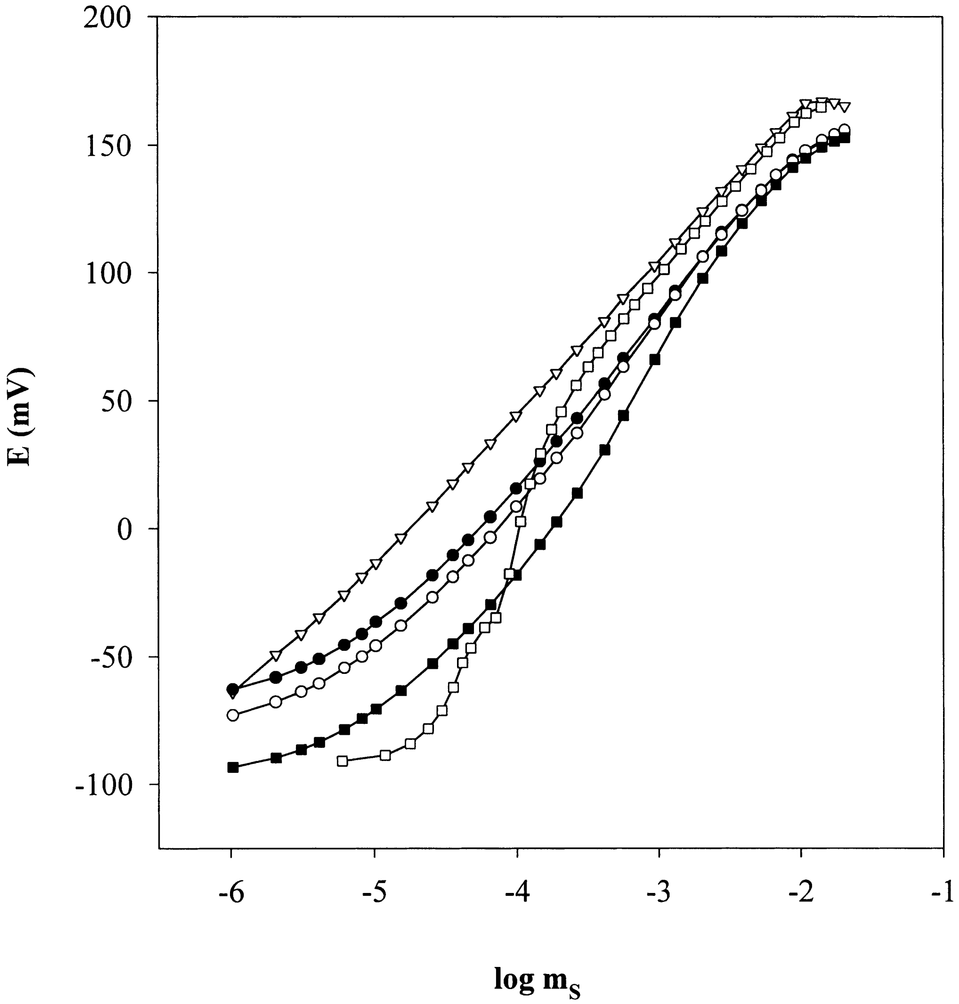

Fig. 2. Plots of e.m.f. (E) of the cell versus the logarithm of the molal concentration (log m_S) of DTA in TX100 and AR88 solutions of different concentrations at 25 °C.-▽-▽-: calibration curve, -●-●-: 1.0·10^{-2} mol/kg TX100, -□-□-: 1.0·10^{-4} mol/kg AR88, -○-○-: mixture of 1.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AR88, -■-■-: mixture of 1.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88.

AO7 and TX100 were referred to as the central group. The binding of DTA cations to dye anions and TX100 micelles can be presented as a set of multiple equilibria:

$$\begin{aligned} &S^+ + D^- \overset{K_1}{\longleftrightarrow} DS \\ &S^+ + DS \overset{K_2}{\longleftrightarrow} DS_2^+ \\ &\ldots \\ &S^+ + DS_{n-1}^{+(n-2)} \overset{K_n}{\longleftrightarrow} DS_n^{+(n-1)} \end{aligned} \qquad (1)$$

and

$$\begin{aligned} &S^+ + M \overset{K_1}{\leftrightarrow} MS^+ \\ &S^+ + MS^+ \overset{K_2}{\leftrightarrow} MS_2^{+2} \\ &\ldots \\ &S^+ + MS_{n-1}^{+(n-1)} \overset{K_n}{\leftrightarrow} MS_n^{+n} \end{aligned} \qquad (2)$$

where S^+, D^- and M refer to the free DTA cation, the free AR88 or AO7 anion and TX100 micelle, $DS_n^{+(n-1)}$ and MS_n^{+n} to complexes with different

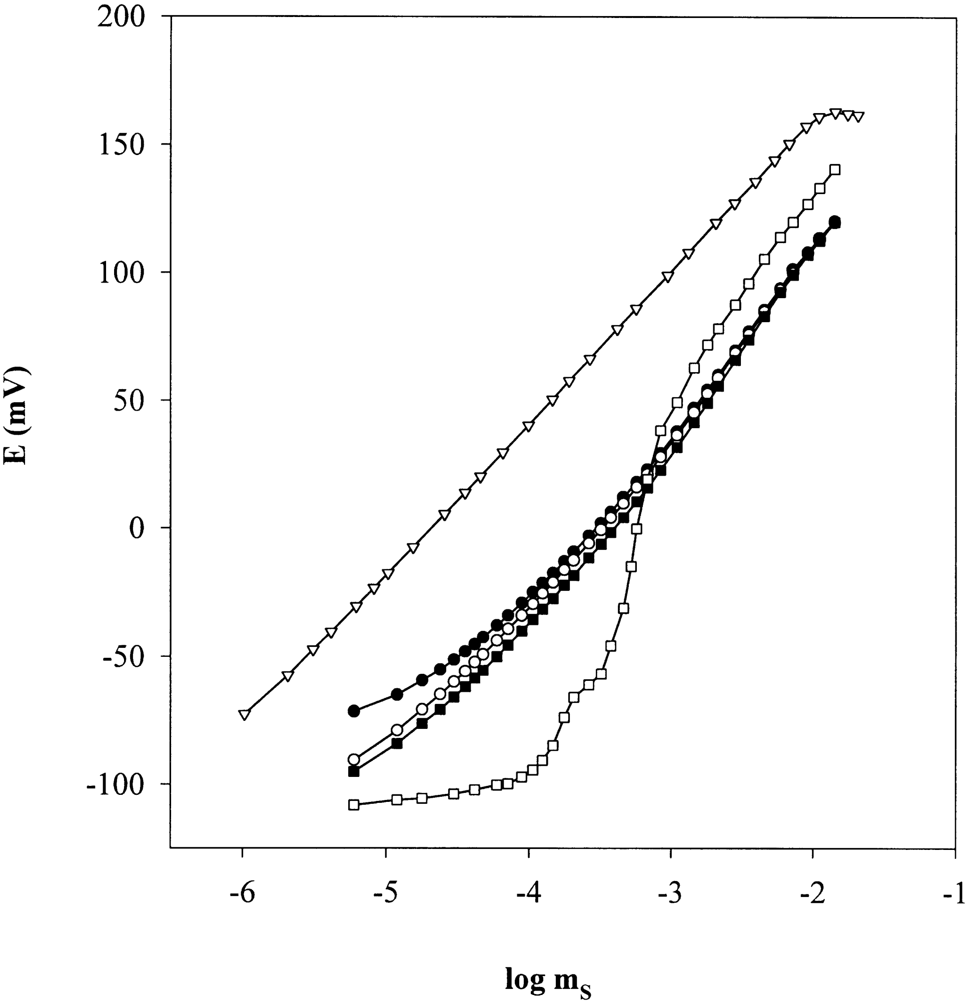

Fig. 3. Plots of e.m.f. (E) of the cell versus the logarithm of the molal concentration ($\log m_S$) of DTA in TX100 and AR88 solutions of different concentrations at 25 °C.-▽-▽-: calibration curve, -●-●-: $5.0 \cdot 10^{-2}$ mol/kg TX100, -□-□-: $5.0 \cdot 10^{-4}$ mol/kg AR88, -○-○-: mixture of $5.0 \cdot 10^{-2}$ mol/kg TX100 and $1.0 \cdot 10^{-4}$ mol/kg AR88, -■-■-: mixture of $5.0 \cdot 10^{-2}$ mol/kg TX100 and $5.0 \cdot 10^{-4}$ mol/kg AR88.

numbers of bound DTA cations, n, and K_1, K_2,..., K_n and κ_1, κ_2,..., κ_n are the corresponding stoichiometric equilibrium constants.

Since the concentration of free DTA cations as a function of the total concentrations of DTA, AR88, AO7 and TX100 is obtained as a result of the potentiometric measurements, the extent of mononuclear complex formation can be expressed in terms of the degree of binding, β. In this case the average number of DTA cations bound to each dye anion or TX100 micelle may be calculated from the relationships [32]:

$$\beta_D = \frac{m_s - m_{S,F}}{m_D} \tag{3}$$

and:

$$\beta M = \frac{m_S - m_{S,F}}{m_M} \tag{4}$$

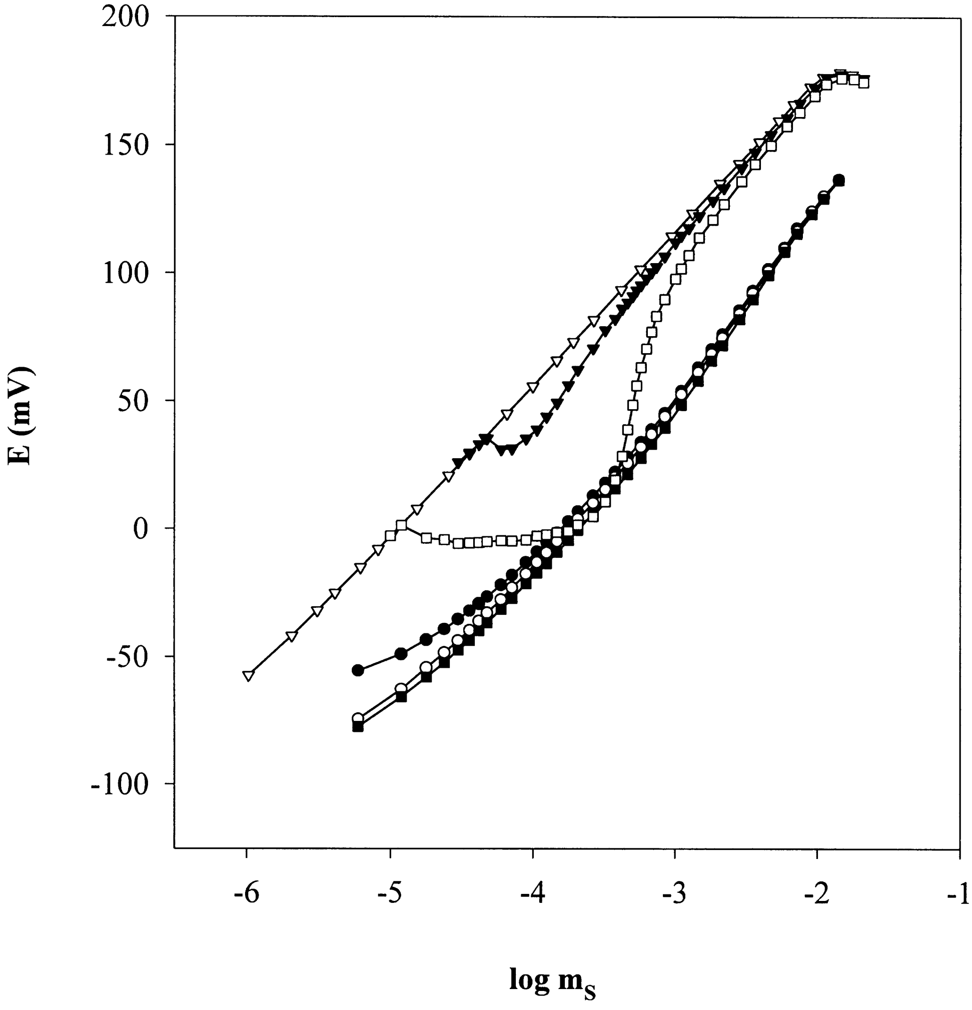

Fig. 4. Plots of e.m.f. (E) of the cell versus the logarithm of the molal concentration (log m_S) of DTA in TX100 and AO7 solutions of different concentrations at 25 °C.-▽-▽-: calibration curve, -●-●-: 5.0·10^{-2} mol/kg TX100, -▼-▼-: 1.0·10^{-4} mol/kg AO7, -□-□-: 5.0·10^{-4} mol/kg AO7, -○-○-: mixture of 5.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AO7, -■-■-: mixture of 5.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AO7.

where m_S is the total concentration of DTA, m_D is the total concentration of AR88 or AO7 and m_M is the total concentration of the TX100 micelle which equals to (m_N—c.m.c.)/v; m_N represents the stoichiometric concentration of TX100 and v its micellar aggregation number [16]. Assuming that in studied solutions only mononuclear complexes can be formed, the total DTA, AR88, AO7 and TX100 concentrations may be expressed as a summa of the free ligand or the central group concentration and the concentrations of complexes of different sizes. Therefore the Eqs. (3) and (4) can be converted into the forms:

$$\beta_D = \frac{m_{DS} + 2m_{DS_2} + 3m_{DS_3} + \ldots + nm_{DS_n}}{m_{D,F} + m_{DS} + m_{DS_2} + m_{DS_3} + \ldots + m_{DS_n}} \tag{5}$$

$$\beta_M = \frac{m_{MS} + 2m_{MS_2} + 3m_{MS_3} + \ldots + nm_{MS_n}}{m_{M,F} + m_{MS} + m_{MS_2} + m_{MS_3} + \ldots + m_{MS_n}} \tag{6}$$

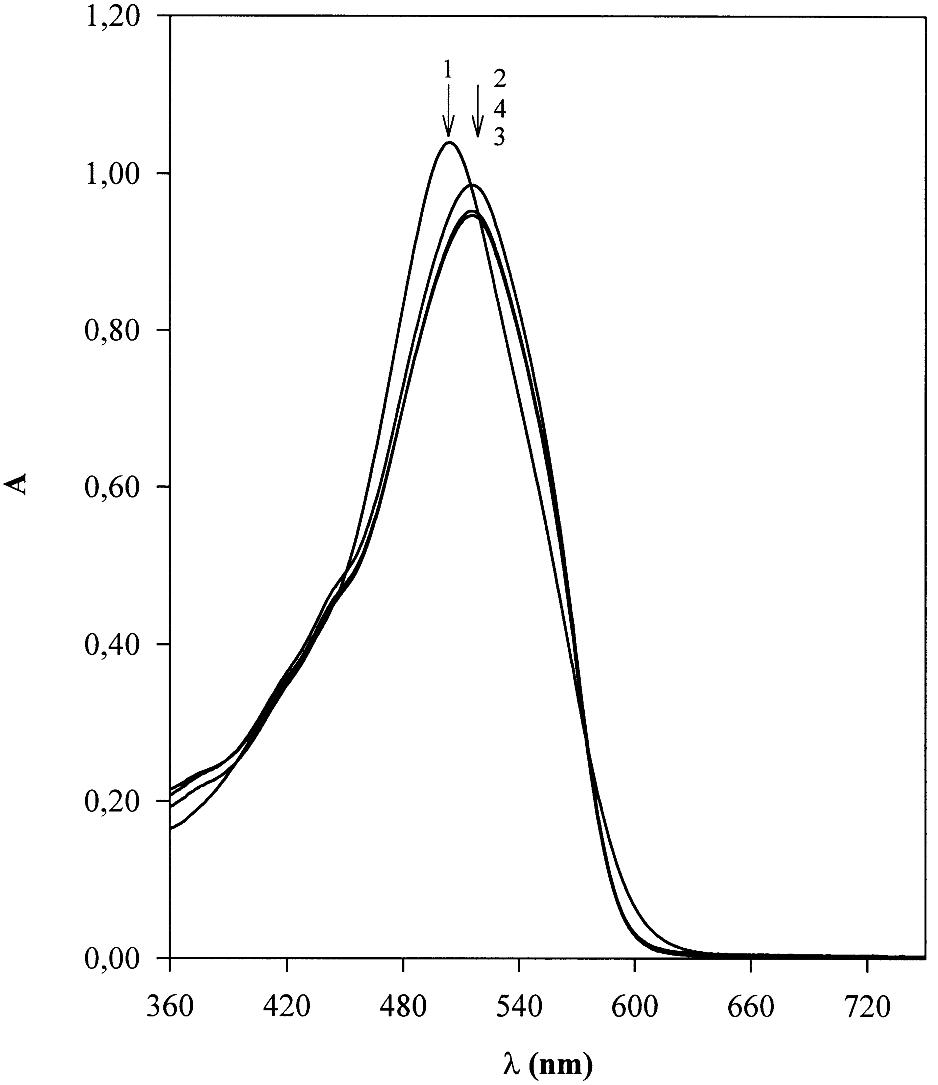

Fig. 5. The visible absorption spectra of AR88 and TX100 in water at 25 °C. Concentration of AR88: $5.0 \cdot 10^{-5}$ mol/kg, concentration of TX100: (1) 0.0 mol/kg, (2) $5.0 \cdot 10^{-3}$ mol/kg, (3) $1.0 \cdot 10^{-2}$ mol/kg, (4) $5.0 \cdot 10^{-2}$ mol/kg.

where it is considered that each mole of complex includes n mol of bound DTA. Moreover, according to the multiple equilibria (1) and (2) the concentrations of complexes in Eqs. (5) and (6) may be expressed in terms of free DTA concentration and the association constants. In that case the degree of binding, β, can be written as:

$$\beta_D = \frac{K_1 m_{S,F} + 2K_1K_2m_{S,F}^2 + \ldots + nK_1K_2 \ldots K_n m_{S,F}^n}{1 + K_1 m_{S,F} + K_1K_2m_{S,F}^2 + \ldots + K_1K_2 \ldots K_n m_{S,F}^n} \tag{7}$$

$$\beta_M = \frac{\kappa_1 m_{S,F} + 2\kappa_1\kappa_2m_{S,F}^2 + \ldots + n\kappa_1\kappa_2 \ldots \kappa_n m_{S,F}^n}{1 + \kappa_1 m_{S,F} + \kappa_1\kappa_2m_{S,F}^2 + \ldots + \kappa_1\kappa_2 \ldots \kappa_n m_{S,F}^n} \tag{8}$$

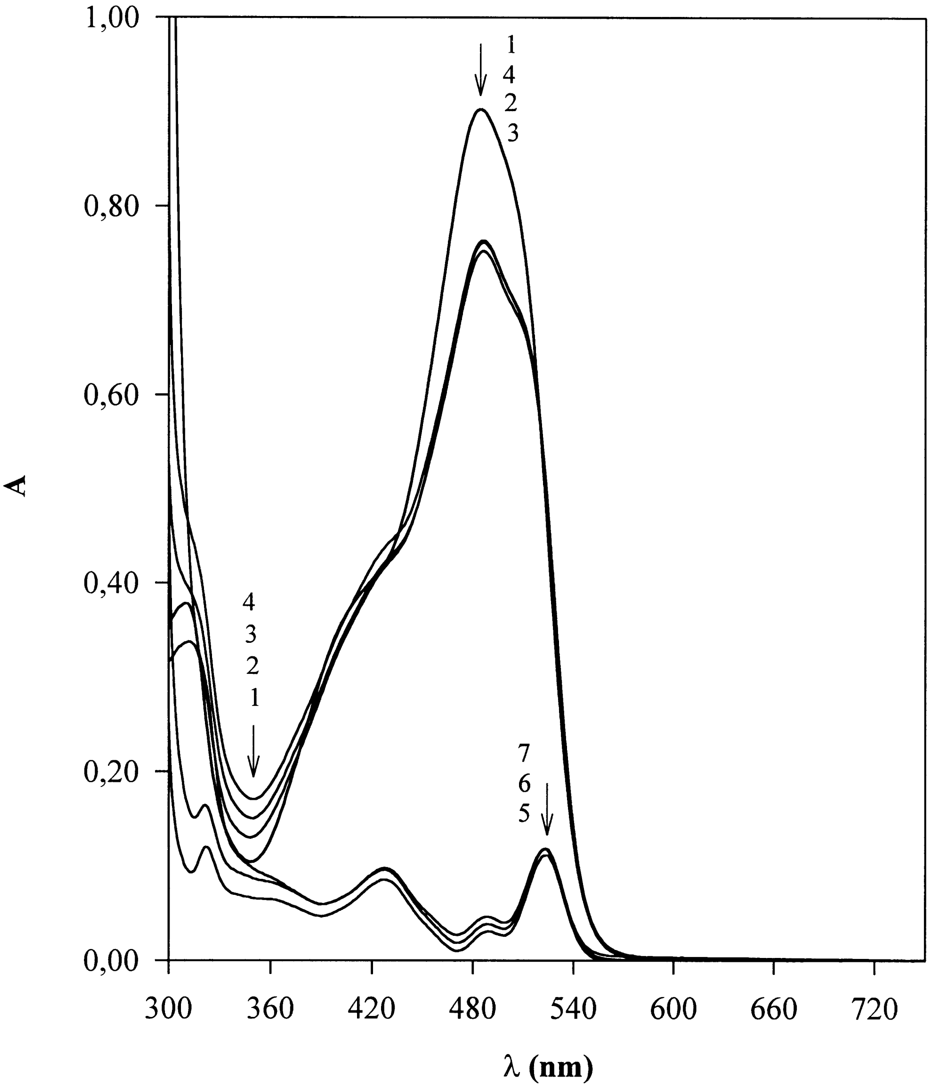

Fig. 6. The visible absorption spectra of AO7 and TX100 in water at 25 °C. Concentration of AO7: $4.0 \cdot 10^{-5}$ mol/kg, concentration of TX100: (1) 0.0 mol/kg, (2) $5.0 \cdot 10^{-3}$ mol/kg, (3) $5.0 \cdot 10^{-2}$ mol/kg, (4) $1.0 \cdot 10^{-1}$ mol/kg, (5) $5.0 \cdot 10^{-2}$ mol/kg- $3.08 \cdot 10^{-5}$ mol/kg AO7 as reference, (6) $1.0 \cdot 10^{-1}$ mol/kg- $3.08 \cdot 10^{-5}$ mol/kg AO7 as reference, (7) $5.0 \cdot 10^{-1}$ mol/kg- $3.00 \cdot 10^{-5}$ mol/kg AO7 as reference.

In the case where the potentiometric measurements were done in the solutions, which contain all three components DTA, AR88 or AO7 and TX100, it was considered that DTA cations form complexes with the both species, dye anions and TX100 micelles. Therefore, the concentration of bound DTA cations, which can be obtained from the potentiometric measurements, consists of two contributions- the first due to binding of DTA to the dye and the second due to binding of DTA to TX100 micelles. Since the measurements of E versus m_S of DTA were done in the TX100 solution in the presence as well as in the absence of AR88 and AO7, the difference between the deviations of the potentiometric curves from the calibration curve at any stoichiometric concentration was a measure for the concentration of DTA cations bound to dye anions in the TX100 solution. According to this the degree of binding of DTA cations to dye anions, β_D, in the presence of TX100 micelles can be calculated as follows:

$$\beta_D = \frac{m_s - m_{S,F} - \beta_M m_M}{m_D} \tag{9}$$

The complex formation process can also be presented graphically in the form of binding isotherms, where β_D and β_M are plotted against the concentration of free DTA cations, log $m_{S,F}$. Some of the typical curves are shown in Figs. 7 and 8.

It can be seen from the Fig. 7 that the degree of DTA cation binding to AR88 anions is much higher than that of DTA cations to AO7 anions in binary mixtures in the early stage of binding. The shapes of DTA–AR88 binding isotherms which increase progressively with the increased DTA concentration are significant for the stepwise binding process. In contrast to DTA–AR88 system the degree of binding of DTA to AO7 is zero at low surfactant concentrations. Above the $m_{S,\text{crit.}}$ the shapes of binding isotherms show a very steep initial rise which indicates that the binding process of DTA to AO7 is cooperative in its early stage. The cooperative binding can be explained by means of theoretical treatment of nearest-neighbour interactions [33], and binding is cooperative when the bound surfactant ions interact with one another, resulting in the aggregation process between the bound surfactant due to strong hydrophobic interactions between them. The result of such interactions is the formation of the complexes containing more than one surfactant ion per dye ion. It is also observed that the stronger the binding the lower the cooperativity. The results are in good agreement with the results obtained for the interactions of AO7 to dodecyl- and cetylpyridinium chloride (CPC) [8]. Similar results have been also obtained for the surfactant-polyelectrolite interactions [25].

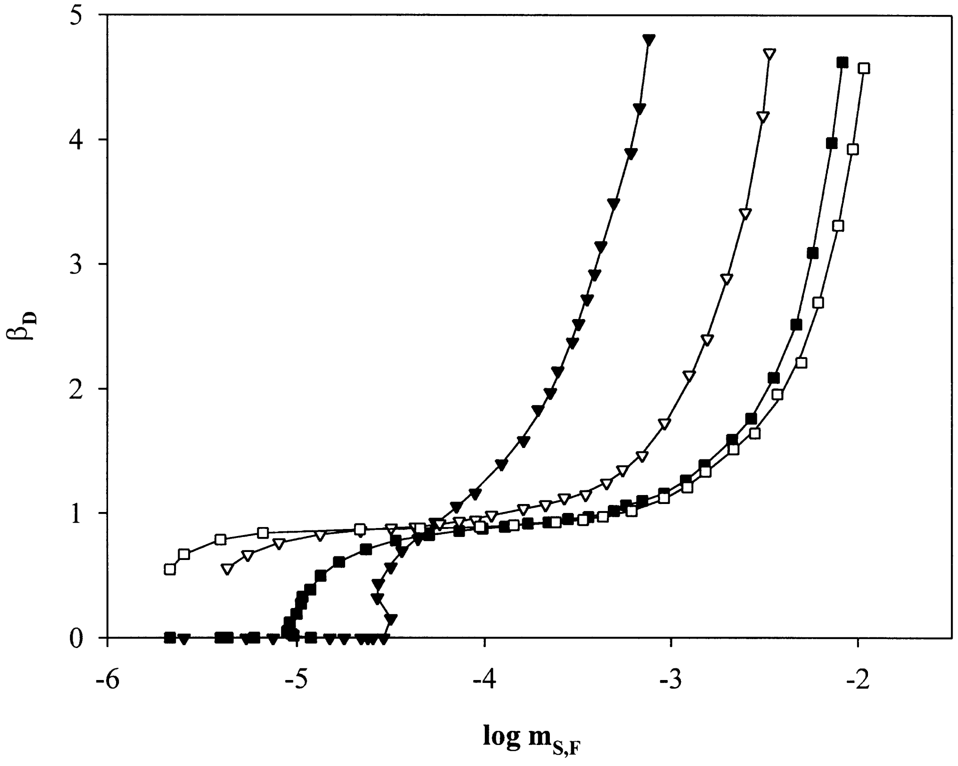

Fig. 7. Binding isotherms of DTA cations to AR88 and AO7 anions in binary mixtures of different dye concentrations at 25 °C. -▽-▽-: 1.0·10^{-4} mol/kg AR88,-□-□-: 5.0·10^{-4} mol/kg AR88,-▼-▼-: 1.0·10^{-4} mol/kg AO7,-■-■-: 5.0·10^{-4} mol/kg AO7.

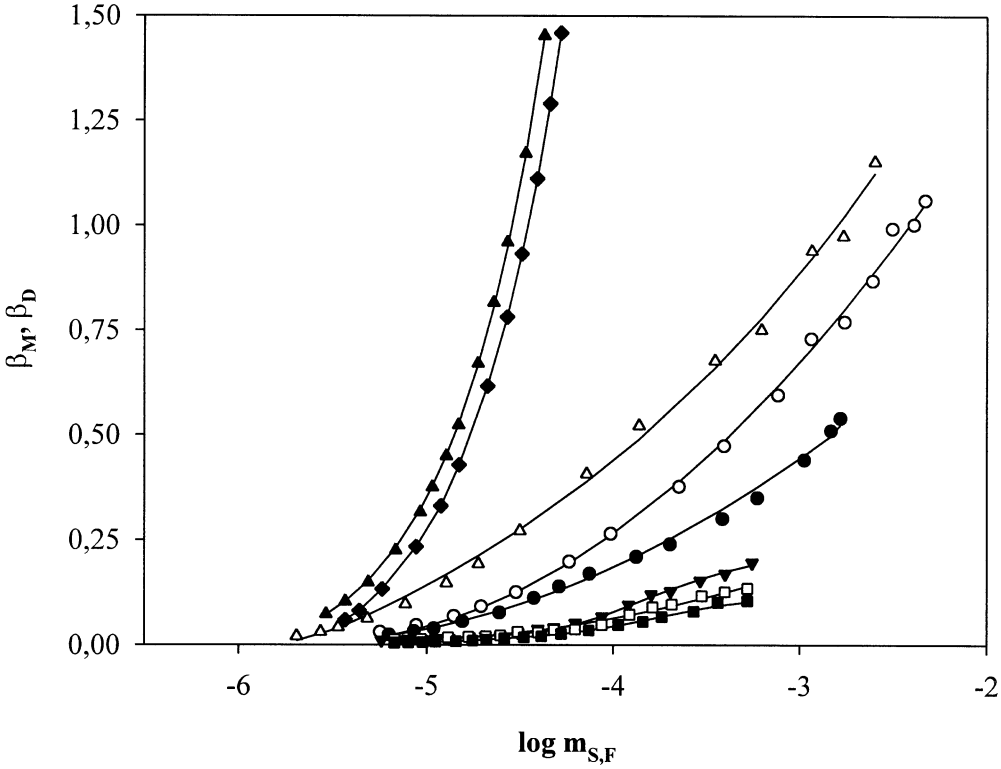

Fig. 8. Binding isotherms of DTA cations to TX100 micelles in binary mixtures, and to AR88 or AO7 anions in TX100 solutions of different dye and surfactant concentrations at 25 °C. -▲-▲-: 5.0·10^{-2} mol/kg TX100, -◆-◆-: 1.0·10^{-2} mol/kg TX100, -△-△-: mixture of 5.0·10^{-3} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88, -○-○-: mixture of 1.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88, -●-●-: mixture of 1.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AR88, -▼-▼-: mixture of 5.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AO7, -□-□-: mixture of 5.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88, -■-■-: mixture of 5.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AO7.

When inspecting the binding of DTA to TX100 micelles in binary mixtures in Fig. 8, we found out that it increases progressively with the increased DTA concentration. Since the degree of binding increases with the increase of the TX100 concentration, it suggests that the increase of the binding sites adds to the increase of the complex formation. It is also evident that the addition of TX100 into the DTA–AR88 mixture strongly affects the extent of DTA–AR88 complex formation which results in the decrease of the binding degree. Furthermore, the important difference between the DTA–AO7 binding process with and without added TX100 micelles is also obtained. It is evident from Fig. 8 that the binding of DTA to AO7 in TX100 solution takes place over the whole measured concentration range, and that it does not exhibit the steep initial rise in β at a given free surfactant concentration as in cooperative binding of DTA to AO7 in binary mixtures. Since the degree of DTA binding in the presence of AO7 and TX100 increases progressively with increased DTA concentration, which is very similar to that obtained in DTA–TX100 mixtures, it can be concluded that the addition of TX100 micelles into the DTA–AO7 mixtures strongly affects the nature of the binding process.

For the systems where the DTA binding process increases progressively with increased DTA concentration the stability of DTA–AR88, DTA–AO7 and DTA–TX100 complexes formed in the first association step in the multiple equilibria (1) and (2) can be calculated from the Eqs. (7)–(9) as follows [32,34]:

$$\lim_{m_{S,F}\to 0} \frac{\beta_D}{m_{S,F}} = K_1; \quad \lim_{m_{S,F}\to 0} \frac{\beta_M}{m_{S,F}} = \kappa_1 \tag{10}$$

In Eq. (10) the association constant K_1 accompanies the DTA–AR88 complex formation with and without added TX100 as well as the DTA–AO7 complex formation in the TX100 solutions, and the association constant κ_1 represents the stability of DTA–TX100 complexes.

If the values of $\beta_D/m_{S,F}$ and $\beta_M/m_{S,F}$ are plotted against $m_{S,F}$ the values K_1 and κ_1 are obtained by the extrapolation to zero free DTA concentration. In Figs. 9 and 10 the determination of association constants for some typical studied systems are shown. The values of K_1 and κ_1 for DTA–AR88–TX100 systems are collected in Table 1.

In inspection of the association constants in Table 1 shows that regardless of the TX100 and AR88 concentrations, the values of K_1 for the DTA cation-AR88 anion complex formation in binary mixtures are about ten times higher than the values of κ_1, accompanying the DTA cation–TX100 micelle complex formation in the absence of AR88. Since the value of association constant indicates the stability of the complex, it means that DTA cation interacts strongly and easier with the AR88 anion than with the TX100 micelle. As argued in our previous studies [10,27] the formation of DS complex is governed by attractive long- and short-range interactions, such as electrostatic interactions between ions, dispersive interactions, charge transfer interactions between the quaternary ammonium cation of DTA and the π-electron system of the AR88 and hydrophobic interactions. In the MS^+ complex formation short-range hydrophobic interactions as well as charge transfer interactions between the quaternary ammonium cation of DTA and TX100 micelle play an important role.

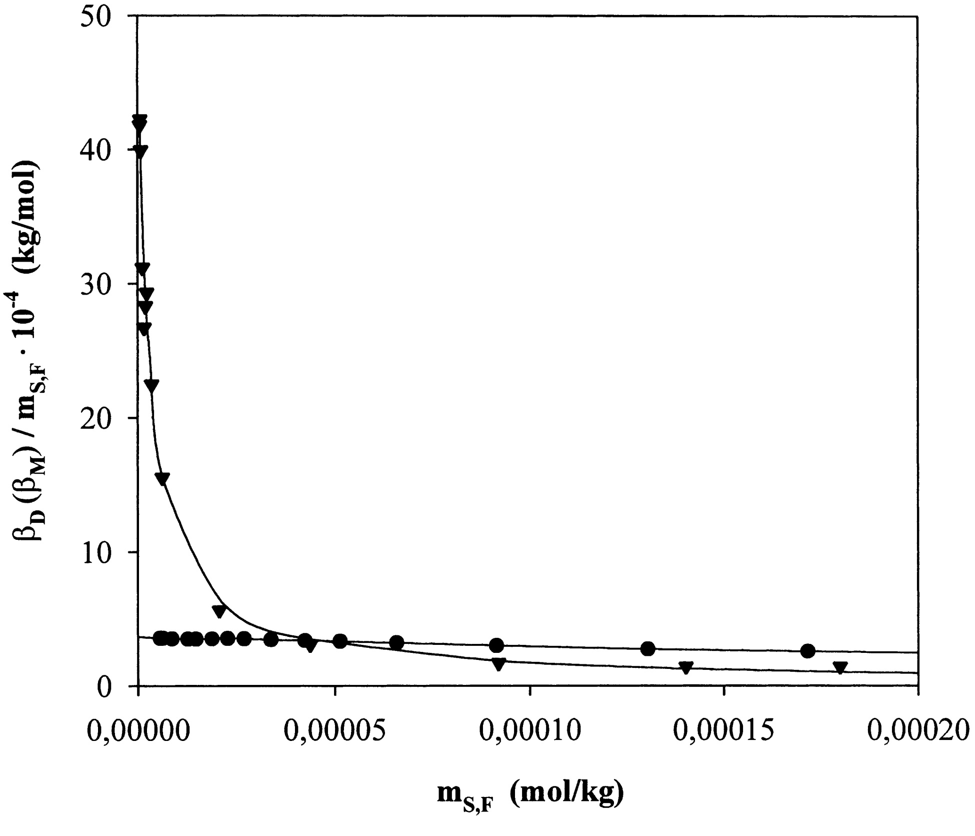

Fig. 9. Plots of values of $\beta_D/m_{S,F}$ and $\beta_M/m_{S,F}$ versus the DTA free cation concentration $m_{S,F}$ at low concentrations of DTA, obtained in AR88 and TX100 solutions at 25 °C. -▼-▼-: 5.0·10^{-4} mol/kg AR88, -●-●: 5.0·10^{-2} mol/kg TX100.

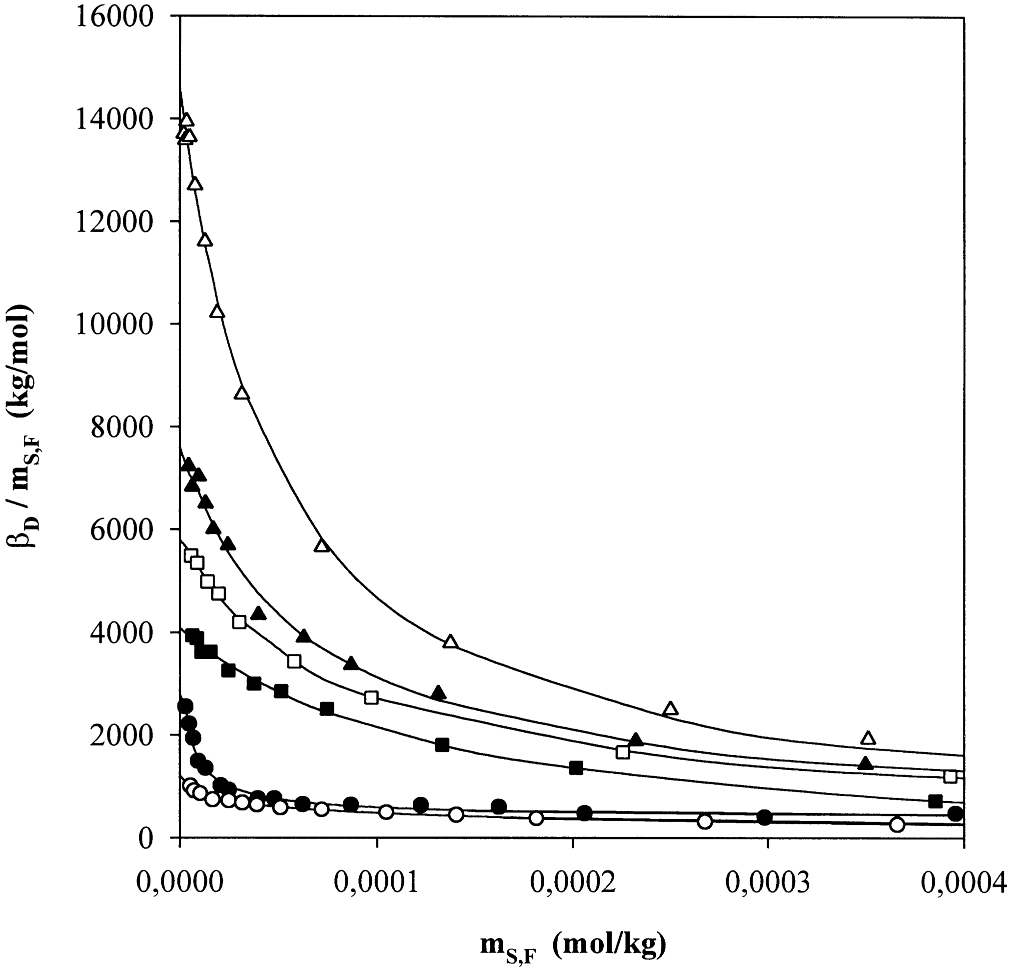

Fig. 10. Plots of values of $\beta_D/m_{S,F}$ versus the DTA free cation concentration $m_{S,F}$ at low concentrations of DTA, obtained in mixtures of AR88 and TX100 of different concentrations at 25 °C. -▲-▲-: 5.0·10^{-3} mol/kg TX100 and 1.0·10^{-4} mol/kg AR88, -△-△-: 5.0·10^{-3} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88, -■-■-: 1.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AR88, -□-□-: 1.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88, -●-●-: 5.0·10^{-2} mol/kg TX100 and 1.0·10^{-4} mol/kg AR88, -○-○-: 5.0·10^{-2} mol/kg TX100 and 5.0·10^{-4} mol/kg AR88.

Since an association constant is a quality composed of contributions of all attractive forces which act between species in the solution, the higher value of K_1 comparing to κ_1 indicates that long-range electrostatic and short-range non-Coulombic attractive interactions act co-operatively.

The addition of TX100 in the mixture of DTA and AR88 causes the decrease of values of K_1 accompanying the formation of DS complexes. At the same time it must be emphasised that in spite of the fact that the presence of TX100 micelles in the studied solutions resulted in the increase of the concentration of binding sites, there was a decrease in the concentration of the bound DTA cations at low total DTA concentration. This suggests that the tendency of DTA–AR88 complex formation as well as the stability of this complex decrease in the presence of TX100 micelles. It has been observed that the value of K_1 decreases as the TX100 concentration increases, but to a larger extent at higher than at lower AR88 concentration (Table 1). This also indicates that the concentration

Table 1
Association constants K_1 and κ_1 for the formation of DTA–AR88 and DTA–TX100 complexes at 25 °C

m_N (mol/kg)	m_D (mol/kg)	K_1, κ_1 (kg/mol)
0	$1.0{\cdot}10^{-4}$	$2.6{\cdot}10^{5}$
	$5.0{\cdot}10^{-4}$	$4.2{\cdot}10^{5}$
$5.0{\cdot}10^{-3}$	0	$2.3{\cdot}10^{4}$[a]
	$1.0{\cdot}10^{-4}$	$7.6{\cdot}10^{3}$
	$5.0{\cdot}10^{-4}$	$1.5{\cdot}10^{4}$
$1.0{\cdot}10^{-2}$	0	$3.0{\cdot}10^{4}$ [a]
	$1.0{\cdot}10^{-4}$	$4.1{\cdot}10^{3}$
	$5.0{\cdot}10^{-4}$	$5.8{\cdot}10^{3}$
$5.0{\cdot}10^{-2}$	0	$3.7{\cdot}10^{4}$[a]
	$1.0{\cdot}10^{-4}$	$2.8{\cdot}10^{3}$
	$5.0{\cdot}10^{-4}$	$1.2{\cdot}10^{3}$

[a] Association constant κ_1.

Table 2
Cooperative binding constants Ku and association constants K_1 for the formation of DTA–AO7 complexes at 25 °C

m_N (mol/kg)	m_D (mol/kg)	Ku, K_1 (kg/mol)
0	$1.0{\cdot}10^{-4}$	$3.5{\cdot}10^{4}$[a]
	$5.0{\cdot}10^{-4}$	$7.5{\cdot}10^{4}$[a]
$5.0{\cdot}10^{-2}$	$1.0{\cdot}10^{-4}$	$2.7{\cdot}10^{3}$
	$5.0{\cdot}10^{-4}$	$1.1{\cdot}10^{3}$

[a] Cooperative binding constant Ku.

of TX100 strongly affects the change of K_1 with the increase of the AR88 concentration. While the significant increase of the value of K_1 is observed in $5.0{\cdot}10^{-3}$ m solution of TX100 when m_D is increased from $1.0{\cdot}10^{-4}$ to $5.0{\cdot}10^{-4}$ mol/kg, the rise of K_1 with increased m_D is much smaller in the presence of $1.0{\cdot}10^{-2}$ mol/kg of TX100 and the value of K_1 even decreases with increased m_D when the concentration of TX100 is $5.0{\cdot}10^{-2}$ mol/kg.

For the DTA–AO7 systems where the binding of DTA to AO7 is cooperative in its early stage, the cooperative binding constant, Ku, could not be calculated from the Eq. (10). According to the interpretation of the cooperative binding interactions [33], Ku can be obtained from the equation:

$$Ku\left(m_{S,F}\right)_{\beta=0.5} = 1 \tag{11}$$

where K is the binding constant of the surfactant to an isolated binding site and u is the cooperativity parameter. The value of Ku, which is equal to reciprocal value of the free surfactant concentration $m_{S,F}$ at $\beta=0.5$ [Eq. (11)] has been obtained from the binding isotherm at half-bound point (Fig. 8). Values of Ku are given in Table 2.

It can be seen from Table 2 that the value of Ku slightly increases with the increase of AO7 concentration. The comparison of the DTA–AO7 and DTA–AR88 binary systems shows that under the same experimental conditions the complex formation between DTA and AR88 takes place at much lower DTA concentration than between DTA and AO7, and consequently the values of the association constants are higher for the DTA–AR88 system than for the DTA–AO7, which means that DTA interacts with AR88 strongly than with AO7. The explanation for such behaviour may be the appearance of the planar aromatic naphthalene ring in the structure of the dye AR88 compared to the dye AO7, which increases the partial hydrophobicity of the dye, reflecting in stronger non-Coulombic interactions between the dye and the surfactant in the complex. The results are in good agreement with the results obtained for the DPC–AR88, DPC–AO7 and CPC–AO7 systems [8]. Higher value of Ku ($5.8{\cdot}10^4$ kg/mol) for DPC–AO7 complex formation [8] compared to Ku ($3.5{\cdot}10^4$ kg/mol) for DTA–AO7 complex formation in $1.0{\cdot}10^{-4}$ m solution of AO7 under the same conditions is expected and may be due to the easier packing of the planar pyridinium group of DPC into the complex with AO7 in comparison with the tetrahedral trimethylammonium group of DTA, as well as due to the possibility of the π–π electronic interactions between AO7 and the pyridinium ring of DPC. These results also comply with the ones obtained by spectrophotometric measurements in AO7 solutions when the cetylpyridinium chloride or cetaltrimehtylammonium chloride are present [9].

It is also seen from Table 2 that the values of K_1 obtained for DTA–AO7 complex formation in TX100 solution are very similar to those obtained for the DTA–AR88 complexes in TX100 solution under the same experimental conditions. These results additionally support our previous assumption that the addition of TX100 into DTA–AO7 mixtures significantly affects the nature of the binding process, which converts from cooperative to progressive in earlier stage of binding.

To be able to analyse the results obtained in the studied dye AR88 and two surfactants DTA and TX100 mixtures (Table 1), it is necessary to consider all interactions which can occur between species in such complex system regardless of their tendency and strength. They are presented in the following equilibrium reactions:

$$S^+ + D^- \longleftrightarrow SD \tag{12}$$

$$nN \longleftrightarrow M \tag{13}$$

$$S^+ + M \longleftrightarrow MS^+ \tag{14}$$

$$D^- + M \longleftrightarrow MD^- \tag{15}$$

$$DS + M \longleftrightarrow MSD \tag{16}$$

In this description, based on our previous spectrophotometric studies in AR88–TX100 mixtures as well as the potentiometric measurements in DTA–TX100 mixtures of TX100 surfactant concentrations below the c.m.c. [27], we can assume that the binding of the studied dye AR88, or of the surfactant DTA to free molecules of the surfactant TX100 is negligible in the studied systems.

By observing the complex formation processes described above, we have come to a conclusion that one of the reasons for the decrease of K_1 accompanied the AR88-DTA complex formation [reaction (12)] in TX100 solution can be attributed to the attractive forces between DTA and TX100 [reaction (14)], which create a counter-balancing mechanism against DTA–AR88 attractive forces. Since the value of K_1 depends on the AR88 concentration that suggests that the formation of AR88–TX100 complexes [reaction (15)], also influences the tendency of DTA cation binding to dye anions. The formation of AR88–TX100 complexes governed by the short-range hydrophobic interactions, results in the decrease of free AR88 anion concentration. The higher the TX100 concentration, the lower the concentration of free AR88 anions. Very reasonable explanation for the decrease of K_1 can also be that the addition of TX100 complicates the relationship between the hydrophobic–hydrophilic balance of DTA and AR88, which are complex and, therefore, directly influences the interactions between DTA cations and AR88 anions. This can be supported by the fact that the DTA–AR88 complexes were solubilised in the TX100 micelles [reaction (16)]. Our observations are in good agreement with the interpretation of the mechanism by which the mixture of cationic and nonionic surfactants operates as levelling agent in the anionic dye solution [35].

4. Conclusion

Potentiometric method is very convenient for the study of anionic dye–cationic surfactant interactions in binary mixtures as well as in mixtures of cationic and nonionic surfactants. The difference in potentiometric curves of the cationic surfactant DTA, obtained in the anionic dye AR88 solution in the presence and in the absence of the nonionic surfactant TX100, is a measure for the extent of DTA–AR88 interactions in the TX100 solution. In the quantitative investigations into the interactions between studied species, we used the treatment of the mononuclear complex formation where DTA studied as the ligand, AR88, AO7 and TX100 as the central group. The extent of the complex formation was expressed as the degree of binding and the stability of complexes in terms of the association constants K_1 and κ_1 for the DTA–AR88 and DTA–TX100 complex formation. The results show that by adding TX100 to DTA and AR88 mixture strongly decreases the value of K_1 compared to the system where TX100 micelles are not present. The concentration of TX100 significantly influences the change of K_1 with the increased AR88 concentration. The decrease of K_1 can be attributed to the interactions between DTA and TX100 as well as between AR88 and TX100, which create counter-balancing mechanism against DTA–AR88 interactions. Since the DTA-AR88 complexes are solubilized in the TX100 solution, it can be concluded that the presence of TX100 micelles directly influences the hydrophobic–hydrophylic balance of the complex species. The comparison of the DTA–AO7 and DTA–AR88 systems shows that DTA interacts with AR88 strongly than with AO7 under the same experimental conditions. The results also show that the addition of TX100 into DTA–AO7 mixtures significantly affects the nature of the binding process, which converts from cooperative to progressive in earlier stage of binding.

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