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A Study of Dye-Surfactant Interactions. Part 1. Effect of Chemical Structure of Acid Dyes and Surfactants on the Complex Formation

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ABSTRACT

The study of the interactions between anionic azo dyes C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88), with different surfactants, i.e., the cationic surfactants dodecylpyridinium chloride (DPC) and cetylpyridinium chloride (CPC) and the anionic surfactant sodium dodecylsulphate (SDS), in submicellar concentration ranges has been researched by a potentiometric technique using a surfactant-cation-sensitive membrane electrode. The e.m.f. measurements versus surfactant concentration have been performed for the systems CPC-AO7, DPC-AO7, DPC-AR88 and SDS-AO7 in pure water at 25°C. Experimental measurements give the option to determine the concentration of free and of bound surfactant cations at a given stoichiometric concentration and calculation of the dye-surfactant complex formation constant, K, and the standard free enthalpy change, ΔG°. The results show that under the same experimental conditions the complex formation between CPC and AO7 takes place at much lower surfactant concentration than between DPC and AO7, accompanied by much higher values of K. It can be seen from the shapes of the binding isotherms that the binding of DPC to AO7 is most likely cooperative. The results indicate that in the DPC-AR88 system, where more hydrophobic dye AR88 is used, the dye-surfactant interactions are stronger compared to DPC-AO7 system. Such observations enable the conclusion, to be made that, beside the electrostatic attractive interactions, the noncoulonic interactions are also very important for the formation of the complex between the oppositely-charged dyes and surfactants. The study of the interactions between the same-charged dye AO7 and surfactant SDS shows that they do not interact with one another in the whole measured *concentration range. The most logical explanation for this is that the repulsive electrostatic interactions prevent the formation of the complex between the same charged AO7 and SDS.* *© 1997 Elsevier Science Ltd*

Keywords: acid dyes, ionic surfactants, interactions, complex formation, potentiometry.

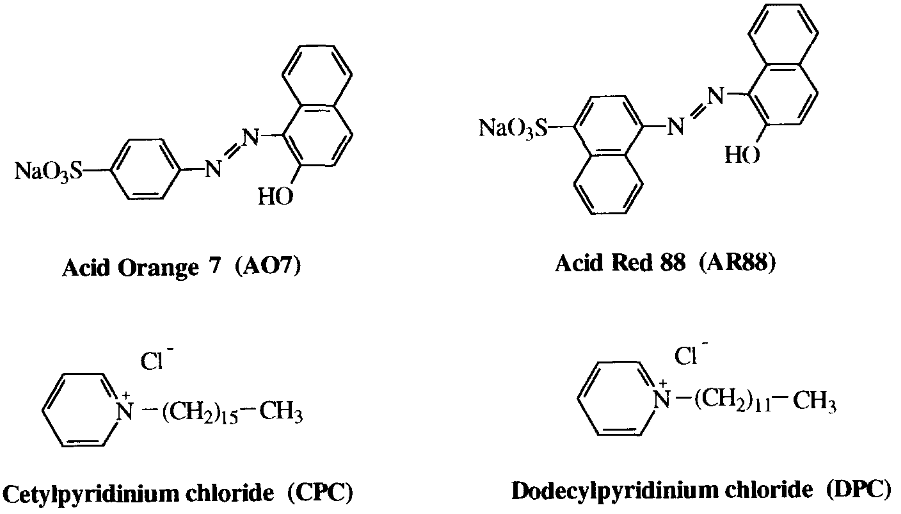
INTRODUCTION

Interactions between dyes and surfactants in aqueous solutions are of great importance in the theory and technology of dyeing [1–5]. Surfactants, which are used as levelling, dispersing and wetting agents in the dyeing process, mostly act in two ways. The first possibility is the complex formation between ionic dye and oppositely-charged surfactant or nonionic surfactant, and the second possibility is the competitive adsorption of equally-charged dye and surfactant into the fibre. In recent years, interactions between dyes and surfactants have been studied, mostly spectroscopically [6–12]. These researches 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 colour of the dye can be explained as a result of dye-surfactant interactions.

This paper presents a potentiometric study of the interactions of two anionic azo dyes, i.e., C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88), with the cationic surfactants dodecylpyridinium chloride (DPC) and cetylpyridinium chloride (CPC), and with the anionic surfactant sodium dodecylsulphate (SDS), in submicellar concentration ranges. The study of such systems can give more information about the influence of hydrophobic and electrostatic effects (closely connected with the chemical structure of the surfactant and the dye) on the formation of the dye-surfactant complex in aqueous solution at surfactant concentrations below their critical micellar concentration (cmc).

EXPERIMENTAL

The dyes AO7 and AR88 were synthesised and purified by the method described previously [13, 14]. The surfactants CPC, DPC and SDS (Kemika, Zagreb, products) were purified by repeated recrystallization from acetone. The structural formula of the dyes and surfactants are shown in Fig. 1. All solutions were prepared in triple distilled water.



Acid Orange 7 (AO7)

Acid Red 88 (AR88)

Cetylpyridinium chloride (CPC)

Dodecylpyridinium chloride (DPC)

$H_3C-(CH_2)_{11}-OSO_3^- \ Na^+$

Sodium dodecylsulphate (SDS)

Fig. 1. The structural formulae of dyes and surfactants investigated.

The formation of the dye-surfactant complex was studied potentiometrically using a surfactant-selective polymeric membrane electrode. The electrode membrane consisted of 0.35 g PVC, 1.15 g dioctylphthalate and 0.005 g surfactant-surfactant carrier complex (in our case DPC-SDS or CPC-SDS) [15].

Potentiometric measurements take place in the membrane electrode cell which was constructed as follows:

Ag I AgCl I reference solution; $1\cdot10^{-4}$ m surfactant in 0.1 m NaCl I polymer membrane + surfactant-surfactant complex I test solution; $\times$ m m_S without and with m_D II KCl (satd.) I Hg_2Cl_2 I Hg, where m_S represents the molal concentration of studied surfactant, and m_D the molal concentration of dye added to the test solution. Measurements of the dependence of the electromotive force, e.m.f. (E) of the cell versus the surfactant concentration m_S were carried out in the concentration range $1\cdot10^{-7}$ to $1\cdot10^{-3}$ mol kg^{-1} at 25°C.

A typical experiment is carried out in three stages [16]. Firstly, a calibration plot E versus log m_S for studied surfactant is determined in pure water, without dye. This experiment is repeated in the presence of constant dye concentrations ($1\cdot10^{-5}$, $2.5\cdot10^{-5}$, $5\cdot10^{-5}$, $7.5\cdot10^{-5}$ and $1\cdot10^{-4}$ mol kg^{-1}). Finally, the calibration curve is repeated and compared to the first one as a check.

Because the surfactant-selective electrode is sensitive to free surfactant ions, the experimental results allow the direct determination of the concentration of free surfactant ions as well as the concentration of surfactant ions bound in the dye-surfactant complex at a given stoichiometric concentration, m_S.

RESULTS AND DISCUSSION

Interactions between dyes and surfactants were studied for the systems, CPC-AO7, DPC-AO7, DPC-AR88 and SDS-AO7.

Figure 2 shows plots of measured E versus log m_S of the surfactant CPC in aqueous solution at 25°C when the dye AO7 of different concentrations, m_D, is added to the solution.

It is evident from the figure that the calibration curve (curve a; in the absence of AO7) is linear over the concentration range $1 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$ m CPC with a slope from 58.9 to 59.2 mV per decade, which indicates excellent agreement with the Nernstian response (59.1 mV at 25°C). In the presence of

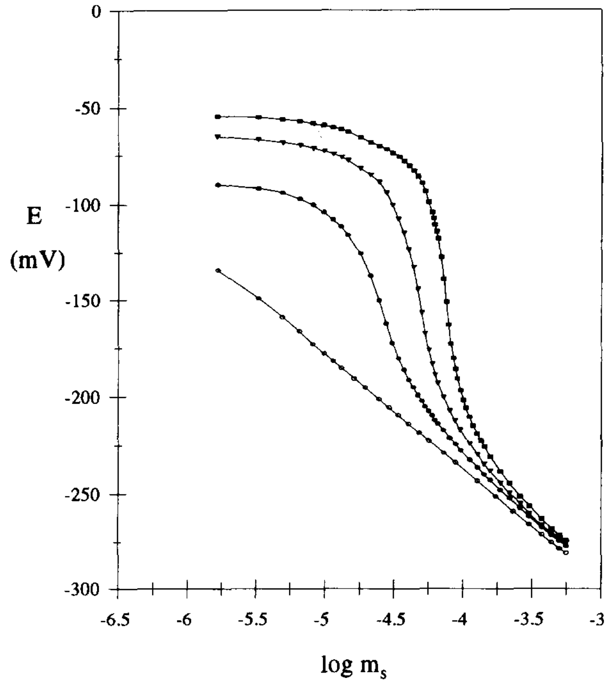


Fig. 2. Plots of e.m.f. (E) of the cell vs log of CPC surfactant concentration (log m_S) in the presence of different concentrations of dye AO7 at 25°C. — ○ — ○ — : 0 mol kg^{-1} AO7 (calibration curve), — ● — ● — : $2.501 \cdot 10^{-5}$ mol kg^{-1} AO7, — ▼ — ▼ — : $4.957 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7.

the dye AO7 in the test solution, deviation from the linear response is noticeable over the whole measured concentration range (curves b, c and d), indicating that the formation of the dye-surfactant complex takes place. At any m_S, the concentration of free surfactant, $m_{S,F}$, was determined from the calibration curve at the same e.m.f. value. The concentration of bound surfactant cations, $m_{S,B}$, which is equal to $m_S - m_{S,F}$, was calculated and plotted together with $m_{S,F}$ against m_S at different m_D of the dye AO7 (Fig. 3).

Figure 3 clearly shows that in the presence of dye AO7 the concentration of free surfactant, $m_{S,F}$, is zero at low surfactant concentration, m_S. It can also be seen that at m_S higher than m_D, $m_{S,F}$ starts to increase almost linearly with the increase of m_S. On the other hand, the concentration of bound surfactant, $m_{S,B}$, increases strongly with increase of m_S at very low surfactant concentration, until the value of m_S reaches the concentration equal to m_D. After that concentration level, $m_{S,B}$ only slightly increases with the increase of m_S. It is also seen from the Figure that $m_{S,F}$ decreases, while $m_{S,B}$ increases, with increase of m_D. The shapes of the experimental curves b, c and d in Fig. 2 also show that even at very low m_S values the electrode response is far from the region of the limit of detection with E values much higher above the calibration curve 1, indicating that CPC strongly interacts with AO7 within the measured concentration range. These results correspond to a nearly quantitative binding of CPC to AO7 at low m_S ($m_{S,F}$ / $m_S \cong 0$) [16] and

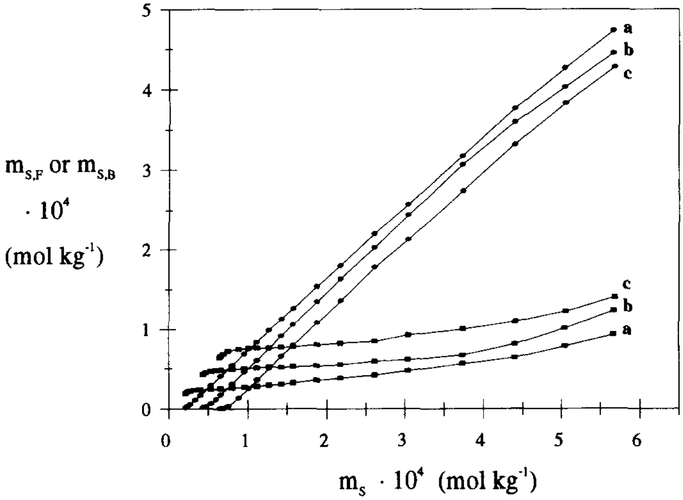


Fig. 3. Dependence of concentrations of free surfactant, $m_{S,F}$, and of bound surfactant, $m_{S,B}$, on the stoichiometric concentration, m_S, of CPC in the presence of different concentrations of dye AO7 at 25°C. (a) $2.501 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$; (b) $4.957 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$; (c) $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$.

suggest the formation of 1:1 molecular complex between CPC and AO7 characterised by a poor solubility in water. The experimental data also permits the calculation of the degree of binding of CPC to AO7, β, defined as the concentration of bound CPC divided by the dye AO7 concentration ($\beta = m_{S,B}/m_D$). Figure 4 shows the binding isotherms of CPC to AO7, where the degree of binding, β, is plotted against log $m_{S,F}$ at different dye concentrations.

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 [17]:

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

with the equilibrium constant, K, equal to:

$$K = \frac{[S^+D^-]}{[S^+][D^-]} = \frac{m_{S,B}}{m_{S,F}(m_D - m_{S,B})} \tag{1}$$

By applying the expression of the degree of binding, β, to eqn (1), it can be written as:

$$\frac{1}{\beta} = \frac{1}{K}\frac{1}{m_{S,F}} + 1 \tag{2}$$

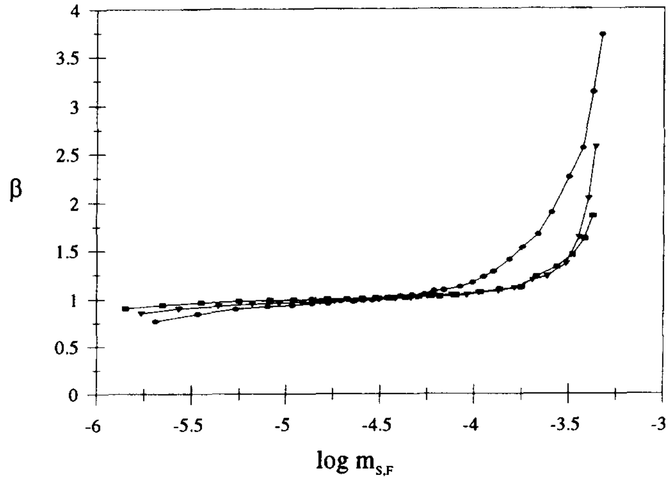


Fig. 4. Binding isotherms of CPC to AO7 at different dye concentrations at 25°C. — ● — ● — : $2.501 \cdot 10^{-5}$ mol kg^{-1} AO7, — ▼ — ▼ — : $4.957 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7.

and the complex formation constant, *K*, can be graphically obtained from the slope of the line when $1/\beta$ is plotted against $1/m_{S,F}$ at low surfactant concentrations ($\beta \leq 1$) (Fig. 5). Constants, *K*, at different concentrations of added AO7 are collected in Table 1. The standard free enthalpy, ΔG°, for the dye-surfactant complex formation can be calculated from the values obtained for *K*, as follows:

$$\Delta G^\circ = -RT \ln K \tag{3}$$

The results shown in Table 1 indicate that the formation of the complex between CPC and AO7 is characterised by high values of *K*. It is also evident that the value of *K* slightly increases by increasing the dye concentration. The results are similar to those obtained in spectrophotometrical studies of interactions between anionic dyes and cationic surfactants [18].

The E versus log m_S plots for DPC at increased AO7 concentrations are shown in Fig. 6. The DPC-selective electrode shows the Nernstian response with a slope from 58.5 to 58.7 mV.

Figure 6 shows that at very low surfactant concentrations the potentiometric curves are linear, in agreement with the calibration plot. 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 concentration,

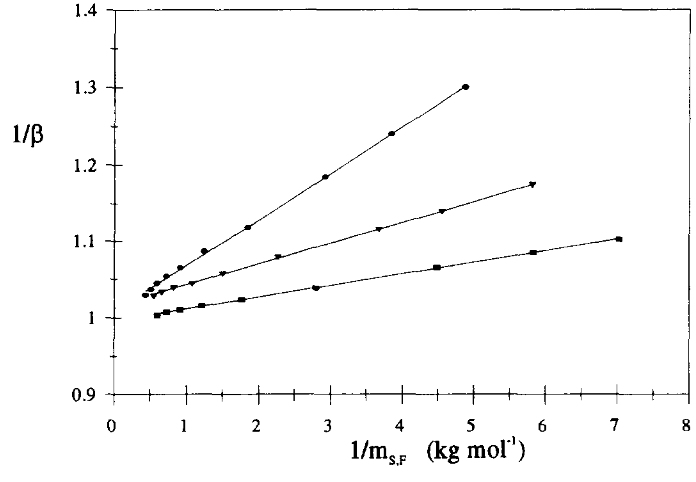


Fig. 5. Plots of reciprocal values of degree of binding, $1/\beta$, vs reciprocal values of concentration of free surfactant, $1/m_{S,F}$, at different AO7 dye concentrations at 25°C. — ● — ● — : $2.501 \cdot 10^{-5}$ mol kg^{-1} AO7, — ▼ — ▼ — : $4.957 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7.

$m_{S,crit.}$, which is much lower than the cmc ($1.7 \cdot 10^{-2}$ mol kg^{-1}) of DPC, the development of complex formation between DPC and AO7 causes that the experimental curves to deviate from linearity. It is also evident that $m_{S,crit.}$ decreases with increase of m_D, suggesting that the increase of the dye concentration promotes the formation of the dye-surfactant complex. In

TABLE 1

Complex Formation Constant, K, Cooperative Binding Constant, Ku, Cooperative Parameter, u, and the Standard Free Enthalpy, ΔG°, for the Binding of CPC and DPC to AO7 and AR88 at 25°C

Surfactant	*dye*	m_D *(mol kg^{-1})*	*K* *(kg mol^{-1})*	*Ku* *(kg mol^{-1})*	*u*	*ΔG°* *(kJ mol^{-1})*
CPC	AO7	$2.501 \cdot 10^{-5}$	$1.7 \cdot 10^{6}$			−33
		$4.957 \cdot 10^{-5}$	$3.6 \cdot 10^{6}$			−35
		$7.523 \cdot 10^{-5}$	$6.5 \cdot 10^{6}$			−36
DPC	AO7	$5.002 \cdot 10^{-5}$	$1.7 \cdot 10^{3}$	$3.1 \cdot 10^{4}$	18	−17
		$7.523 \cdot 10^{-5}$	$3.2 \cdot 10^{3}$	$4.5 \cdot 10^{4}$	14	−19
		$1.001 \cdot 10^{-4}$	$4.8 \cdot 10^{3}$	$5.8 \cdot 10^{4}$	12	−20
DPC	AR88	$1.011 \cdot 10^{-5}$	$1.3 \cdot 10^{4}$	$2.5 \cdot 10^{5}$	20	−22

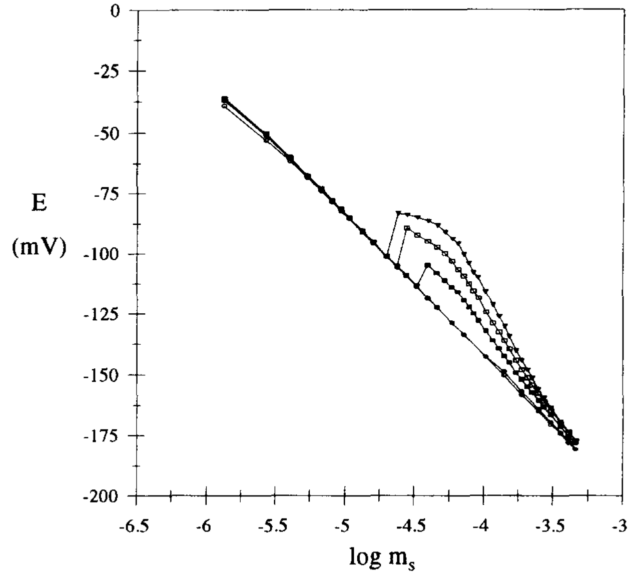


Fig. 6. Plots of e.m.f. (E) of the cell vs the log of DPC surfactant concentration (log m_S) in the presence of different concentrations of the dye AO7 at 25°C. — ○ — ○ — : 0 mol kg^{-1} AO7 (calibration curve), — ● — ● — : $2.563 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $5.002 \cdot 10^{-5}$ mol kg^{-1} AO7, — □ — □ — : $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7, — ▼ — ▼ — : $1.001 \cdot 10^{-4}$ mol kg^{-1} AO7.

Fig. 7 the concentration of free, $m_{S,F}$, and bound, $m_{S,B}$, surfactant, obtained from the observed deviations, is plotted against the surfactant concentration, m_S.

It can be seen from the figure that $m_{S,B}$ is zero at low surfactant concentrations, before it increases at the critical concentration, $m_{S,crit.}$. Then $m_{S,B}$ gradually increases with the increase of m_S at concentrations greater than $m_{S,crit}$, until it becomes almost constant at high surfactant concentrations. Such response of $m_{S,B}$ to m_S for DPC-AO7 system is completely different compared to the CPC-AO7 system. The same differences between the two studied systems are obtained when the binding isotherms are inspected. Figure 8 shows plots of β vs. log $m_{S,F}$ for DPC at different m_D of AO7.

The binding isotherms show a very steep initial rise above the $m_{S,crit}$ and tend to level off at β lower than 0.8. Such a shape of the binding isotherms suggests that the binding of DPC to AO7 is cooperative and that the cooperativity appears only in the early stage of the binding process [16, 19–21].

The cooperative binding can be explained by means of the theoretical treatment of nearest-neighbour interactions [22, 23], which has been developed to explain the binding of surfactants to polyions, which is cooperative when the bound surfactant ions interact with one another, resulting in strong hydrophobic interactions among them. This means that the cooperative binding leads to the aggregation process between the bound surfactants.

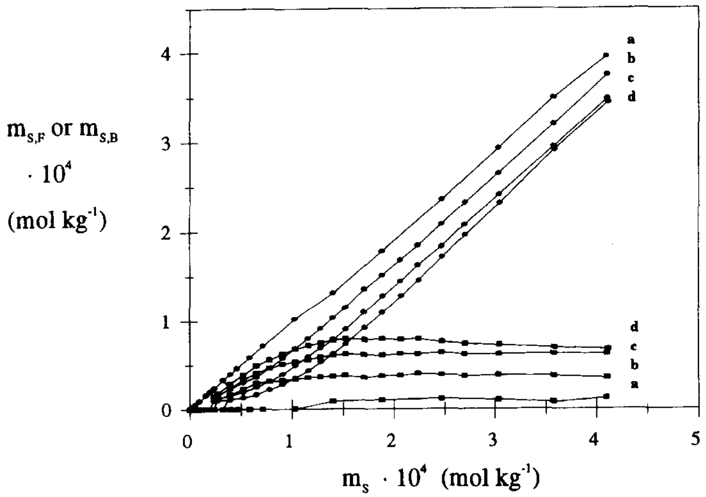


Fig. 7. Dependence of concentrations of free surfactant, $m_{S,F}$, and of bound surfactant, $m_{S,B}$, on the stoichiometric concentration, m_S, of DPC in the presence of different concentrations of the dye AO7 at 25°C. (a) $2.563 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$; (b) $5.002 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$; (c) $7.523 \cdot 10^{-5}$ mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$; (d) 1.001 . 10^{-4} mol kg^{-1} AO7, — ● — ● — $m_{S,F}$, — ■ — ■ — $m_{S,B}$.

According to this observation we can conclude that, because of the cooperative binding of DPC to AO7, the binding takes place not only because of the electrostatic and noncoulombic interactions between the dye and the surfactant, but also because of hydrophobic interactions between the bound surfactant ions. The result of such interactions is the formation of mixed micelles, containing more than one surfactant ion per dye ion. In order to interpret the binding equilibrium, Schwarz [22], and later Satake and Yang [23] , derived the following expressions:

$$2\beta - 1 = (Kum_{S,F} - 1)/[(1 - Kum_{S,F})^2 + 4Km_{S,F}]^{1/2} \tag{3}$$

$$Ku(m_{S,F})_{\beta=0.5} = 1 \tag{4}$$

$$(d\beta/d\,ln\ m_{S,F})_{\beta=0.5} = u^{1/2}/4 \tag{5}$$

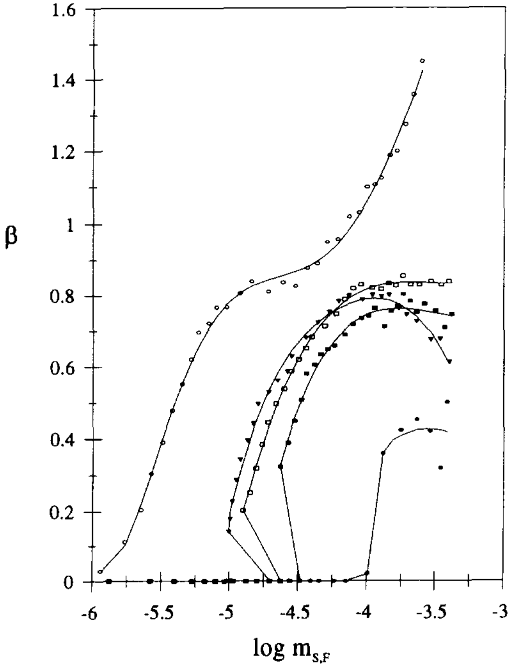


Fig. 8. Binding isotherms of DPC to AO7 and to AR88 at different dye concentrations at 25°C. — ● — ● — : $2.563\cdot10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $5.002\cdot10^{-5}$ mol kg^{-1} AO7, — □ — □ — : $7.523\cdot10^{-5}$ mol kg^{-1} AO7, — ▼ — ▼ — : $1.001\cdot10^{-4}$ mol kg^{-1} AO7, — ○ — ○ — : $1.011\cdot10^{-5}$ mol kg^{-1} AR88.

where K is the binding constant and u is the cooperativity parameter determined by the hydrophobic interactions between the two bound surfactants. The value of Ku, which equals the reciprocal of the free surfactant concentration $m_{S,F}$ at $\beta = 0.5$ eqn (4) has been obtained from the binding isotherm at half-bound point, and u from the maximum slope of the β versus $m_{S,F}$ plot (eqn (5)). It has to be emphasized, that because the values of β in the binding isotherms do not reach the value 1, it is very difficult to obtain the correct values of Ku and u from the plots, and therefore the errors can be rather large. Values of Ku, u and K are given in Table 1. It is evident that the value of Ku slightly increases with the increase of the concentration of the added dye.

Comparison of the systems CPC-AO7 and DPC-AO7 shows that under the same experimental conditions the formation of the complex between CPC and AO7 takes place at much lower m_S value than between DPC and AO7, and that the values of the complex formation constants K are much higher for the CPC-AO7 system than for the DPC-AO7 system. Study of the values for the standard free enthalpy change, ΔG°, which is an indication of the tendency of the formation of the dye-surfactant complex, shows that AO7 interacts with CPC more easily and strongly ($\Delta G^\circ = -33$ to -36 kJ/mol) than with DPC ($\Delta G^\circ = -17$ to -20 kJ/mol) at the same conditions. Because the only difference between the systems is the length of the alkyl chain of both studied surfactants (CPC has 16 carbon atoms in the alkyl chain and DPC has 12 carbon atoms), it implies that the hydrophobicity of the alkyl chain, which is responsible for hydrophobic interactions, plays an important role in the dye-surfactant interactions. This is confirmed by the fact that CPC, which has the longer hydrophobic chain, interacts with AO7 much stronger than DPC. In other words, the binding energy increases with increase of the hydrophobicity of the alkyl chain. This conclusion can be confirmed by the system DPC-AR88 (where the dye AR88 which has two naphthalene rings in the molecular structure was used, instead of the dye AO7 with one benzene and one naphthalene ring). The appearance of the planar aromatic naphthalene ring in the structure of the dye AR88 increases the partial hydrophobicity of the dye, which reflects in stronger noncoulombic interactions (including hydrophobic interactions) between the dye and the surfactant. It is clearly seen from Fig. 9 that in $1 \cdot 10^{-5}$ m dye solution DPC does not interact with dye AO7 over the whole measured concentration range (the titration curve is equivalent to the calibration curve), but interacts with the dye AR88 (the titration curve is deviated from the calibration curve). This means that the formation of the DPC-AR88 complex takes place at lower concentration compared to the DPC-AO7 system, accompanied by higher values of Ku, K and ΔG° (Table 1, Fig. 8). The results can not precisely determine to what extent hydrophobic interactions are present, and to what extent other noncoulombic interactions are present.

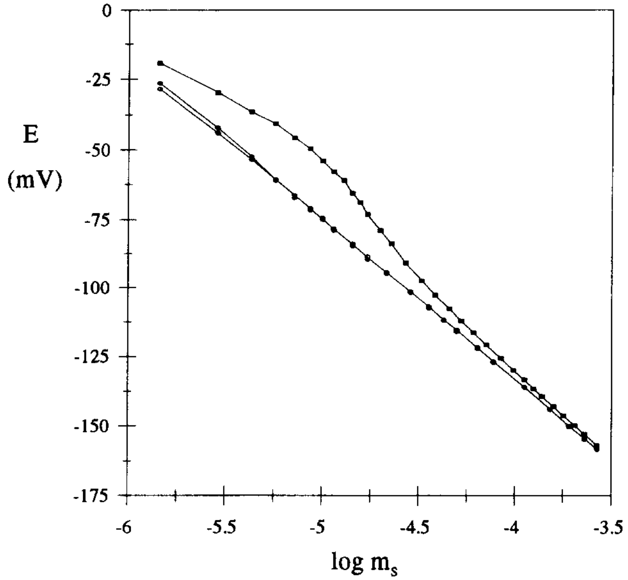


Fig. 9. Plots of e.m.f. (E) of the cell vs the log of DPC surfactant concentration (log m_S) in the presence of the dyes AO7 or AR88 at 25°C. — ○ — ○ — : calibration curve, — ● — ● — : $1.085 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $1.011 \cdot 10^{-5}$ mol kg^{-1} AR88.

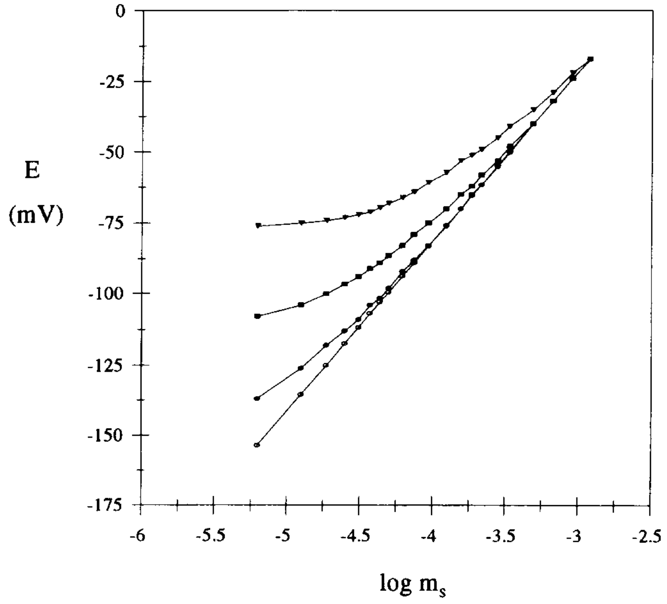


Fig. 10. Plots of e.m.f. (E) of the cell vs the log of SDS surfactant concentration (log m_S) in the presence of different concentrations of dye AO7 at 25°C. — ○ — ○ — : 0 mol kg^{-1} AO7 (calibration curve), — ● — ● — : $5.106 \cdot 10^{-5}$ mol kg^{-1} AO7, — ■ — ■ — : $5.076 \cdot 10^{-4}$ mol kg^{-1} AO7, — ▼ — ▼ — : $5.144 \cdot 10^{-3}$ mol kg^{-1} AO7.

Finally, interactions between the same-charged surfactant SDS and dye AO7 were studied. It is evident from the experimental curves in Fig. 10, that the anionic surfactant SDS does not form the complex with the anionic dye AO7 in aqueous solution within the whole concentration range, irrespective of the dye concentration. Based on our previous work [24] we can say that the behaviour of the dye anion AO7 is equal to that of the interfering ion, which affects the normal electrode response to the primary ion SDS in mixed solution, containing both the primary and interfering ions. Therefore, the deviation from linear behaviour at low SDS concentration is observed due to the detection limit of the ion-selective electrode, which depends upon the concentration of interfering ion in the sample. The higher the concentration of the interfering ion AO7, the higher the deviation from linearity. These results are in good agreement with the theory of ion-selective electrodes [25,26].

CONCLUSION

The potentiometric method using the surfactant-cation-sensitive membrane electrode is very suitable for studying dye-surfactant interactions in aqueous solution.

Our results show that the interactions between the oppositely-charged dyes and surfactants in the systems CPC-AO7, DPC-AO7 and DPC-AR88 are strongly dependent on noncoulombic interactions, and that increase of the hydrophobicity, either of the surfactant or the dye, increases the binding energy, resulting in a higher value of the dye-surfactant complex formation constant, *K*. In the case when the same-charged dye AO7 and surfactant SDS were used, it was found that the noncoulombic interactions are not strong enough to dominate over the electrostatic repulsion between the same-charged ions.

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