A study of dye–surfactant interactions. Part 3. Thermodynamics of the association of C.I. Acid Orange 7 and cetylpyridinium chloride in aqueous solutions

Barbara Simončič *, Jože Špan

Department of Textiles, Faculty of Natural Sciences and Engineering, University of Ljubljana, Snežniška 5, 1000 Ljubljana, Slovenia

Abstract

The association of C.I. Acid Orange 7 (D) and the surfactant cetylpyridinium chloride (S) was studied at 15, 25, 35 and 45°C in the presence of 0, 0.05 and 0.1 mol/kg NaCl, by potentiometric titration, using a surfactant cation sensitive membrane electrode. By using the association constant (K_1) for the first step of the association $[D^- + S^+ \leftrightarrow (DS)^\circ]$, the standard free energy change, standard enthalpy change, and standard entropy change of the association were calculated at low surfactant concentrations. The unitary entropy of association was negative, suggesting that hydrophobic interactions do not play a major role in the initial interaction between dye and surfactant. On the other hand, in the second step $[S^+ + (DS)^\circ \leftrightarrow (DS_2)^+]$, the unitary entropy change in the medium-level surfactant concentration domain was highly positive, indicating that water-structure contributions are appreciable in the stabilisation of the $(DS_2)^+$ species. It was shown that a further stepwise association is not very likely in the third domain, and that a neutral quadruple species of type $(SD)_2^\circ$ may be present in the solution. Further increases in surfactant concentration led to a very steep increase in bound surfactant as the concentration of free surfactant ions approached the c.m.c. point. It was also shown that the addition of a simple electrolyte (e.g. NaCl) decreased K_1, mainly due to interference with the interaction of dye and surfactant ions. Since long range Coulombic interactions are absent in the second association step, the increase in K_2 with increasing NaCl concentration can be mainly attributed to short range hydrophobic interactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: C.I. Acid Orange 7; Dye–surfactant interactions; Thermodynamics; Potentiometry

1. Introduction

In our previous paper [1], the influence of the chemical structure of some cationic and anionic surfactants on their interactions with C.I. Acid Orange 7 and C.I. Acid Red 88 was studied.

Potentiometric titrations of these dyes with surfactant solutions were performed, and the results were used to calculate the association constants for various dye–surfactant systems.

In the present paper, potentiometric titration was used to assess the thermodynamic aspects of the association between C.I. Acid Orange 7 (AO7; Fig. 1) and cetylpyridinium chloride (CPC; Fig 1). The standard free energy, enthalpy and entropy changes for the two first association steps were

* Corresponding author: Fax: +386-61-125-31-75.
E-mail address: barbara.simoncic@ntftex.uni-lj.si (B. Simončič).

determined, and their role in dye–surfactant interactions is discussed.

2. Experimental

Dye AO7 was synthesised and purified by the method previously described [2], and the surfactant
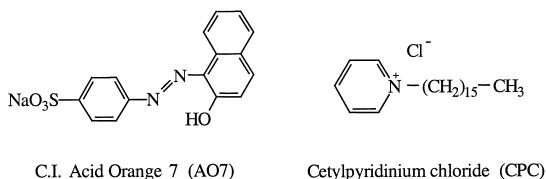

C.I. Acid Orange 7 (AO7)   Cetylpyridinium chloride (CPC)

Fig. 1. Structures of the dye and surfactant used in this study.
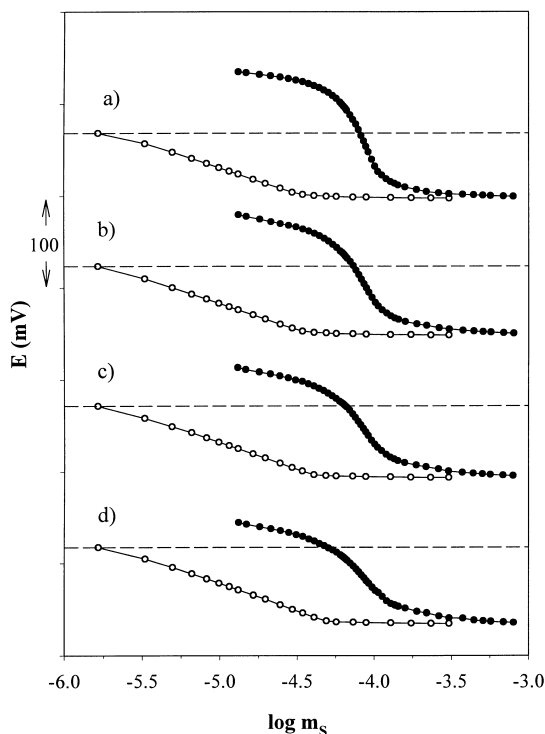

Fig. 2. Electrode response to CPC concentration m_S in 0.1 m NaCl and 7.5×10^{-5} m AO7 at different temperatures: (a) 15°C, (b) 25°C, (c) 35°C, (d) 45°C. -○-○- = 0 mol/kg AO7 (calibration curve), -●-●- = 7.5×10^{-5} m AO7 (titration curve). Broken horizontal lines represent the highest measured E values of the calibration curves. In further calculations only these values of E in the titration curves which lie below these lines were taken into consideration.

CPC (Kemika, Zagreb) was purified by repeated recrystallizations from acetone. Aqueous solutions were prepared in triple distilled water, and are expressed in molal (m) concentrations.

The CPC-selective membrane electrode was prepared according to a well-known method [3]. The potentiometric measurements and the corresponding galvanic cell have also been described in detail elsewhere [1].

3. Results and discussion

Fig. 2 shows a typical electrode responses (E) to the addition of CPC to solutions of 0.1 m NaCl and 7.5×10^{-5} m AO7 at 15, 25, 35 and 45°C. Fig. 3 is a plot of E vs m_S for 7.5×10^{-5} m AO7 solutions containing different electrolyte concentrations. It is evident from both figures that the curves deviate considerably from Nernstian behaviour, due to dye-surfactant association. The titration and calibration curves can be used to determine the average
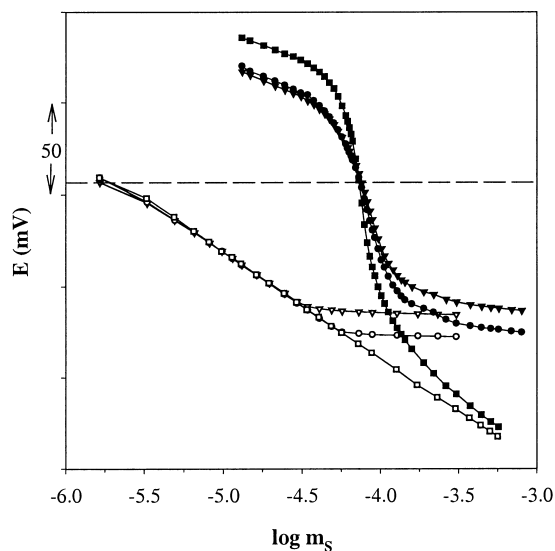

Fig. 3. Electrode response to CPC interactions with 7.5×10^{-5} m AO7 at different NaCl concentrations at 25°C. Calibration curves: -□-□- = 0 mol/kg NaCl, -○-○- = 0.05 mol/kg NaCl, -▽-▽- = 0.1 mol/kg NaCl; titration curves: -■-■- = 0 mol/kg NaCl, -●-●- = 0.05 mol/kg NaCl, -▼-▼- = 0.1 mol/kg NaCl. Broken line represents the highest measured E values of the calibration curves.

number of surfactant cations bound to each dye anion, with the aid of Eq. (1) [4,5]:

$$\beta = \frac{m_S - m_{S,F}}{m_D} \tag{1}$$

where $m_{S,F}$ is the free surfactant concentration and m_D is the total concentration of added dye. In the calculation of β, only those experimental points that lie below the highest measured E value of the calibration curve (Figs. 2 and 3) were used.

From the data presented in Figs. 2 and 3 and from Eq. (1), binding isotherms, i.e. plots of β vs log $m_{S,F}$, were constructed. Fig. 4 depicts the binding isotherm obtained for the AO7–CPC mixture containing 7.5×10^{-5} m dye and 0.1 m NaCl at 25°C. It can be seen that the binding process took place in three main steps (concentration domains A, B and C). Domain A was observed at $\beta \leqslant 1.0$, the second domain at $1.0 < \beta < 1.2$, and the third domain, which was characterised by a very steep slope at $\beta > 1.2$, was observed as the free surfactant concentration approached the c.m.c. value (denoted by an arrow).

Having analysed the experimental results obtained, we turned our attention to the thermo-
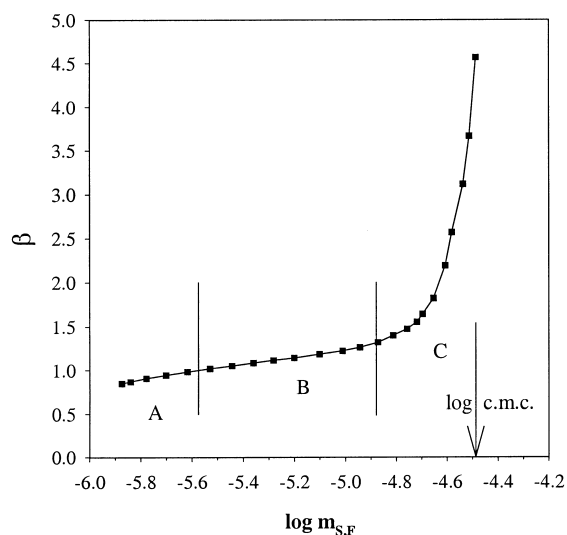

Fig. 4. Degree of binding, β, as a function of the logarithm of the free CPC concentration, log $m_{S,F}$. A, B and C represent three distinct concentration domains at 25°C, $m_D = 7.5 \times 10^{-5}$ mol/kg, $m_{NaCl} = 0.1$ mol/kg; the c.m.c. of CPC is denoted by the arrow.

dynamics of the AO7–CPC association process. The dye and surfactant concentrations (m_S and m_D) are given by Eqs. (2) and (3):

$$m_S = m_{S,F} + m_{DS} + 2m_{SD_2} + 3m_{DS_3} + ... + nm_{DS_n} \tag{2}$$

and

$$m_D = m_{D,F} + m_{DS} + m_{DS_2} + m_{DS_3} + ... + m_{DS_n} \tag{3}$$

Introducing Eqs. (2) and (3) into Eq. (1) one obtains:

$$\beta = \frac{m_{DS} + 2m_{DS_2} + 3m_{DS_3} + ... + nm_{DS_n}}{m_{D,F} + m_{DS} + m_{DS_2} + m_{DS_3} + ... + m_{DS_n}} \tag{4}$$

The multiple equilibria between surfactant ions bound to a dye ion and free surfactant ions in bulk solution have been defined using two approaches [6]. One approach is based on the stepwise binding of surfactant to dye, as shown in Eq. (5):

$$S + DS_{i-1} \overset{K_i}{\longleftrightarrow} DS_i; \; K_i = \frac{m_{DS_i}}{m_{DS_{i-1}} m_{S,F}} \tag{5}$$
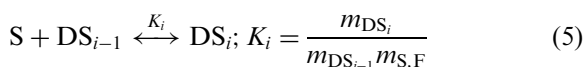
where K_i is the equilibrium constant. Applying (5) to Eq. (4) gives (6):

$$\beta = \frac{\begin{array}{c} K_1 m_{S,F} + 2K_1 K_2 m_{S,F}^2 + 3K_1 K_2 K_3 m_{S,F}^3 + ... \\ + n(K_1 K_2 ... K_n) m_{S,F}^n \end{array}}{\begin{array}{c} 1 + K_1 m_{S,F} + K_1 K_2 m_{S,F}^2 + K_1 K_2 K_3 m_{S,F}^3 + ... \\ + (K_1 K_2 ... K_n) m_{S,F}^n \end{array}} \tag{6}$$

where K_1, K_2, K_3, ... K_n are the stepwise equilibrium constants. In this approach, a maximum of n surfactant ions can interact with a single dye anion.

In the second approach, the equilibrium constants for the formation of individual species can be defined by Eq. (7):

$$iS + D \overset{k_i}{\leftrightarrow} DS_i; \; k_i = \frac{m_{DS_i}}{m_{D,F} m_{S,F}^i} \tag{7}$$
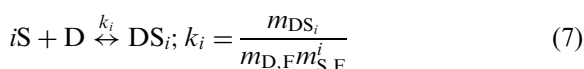
where k_i is the equilibrium constant. Combining Eqs. (4) and (7) produces (8):

$$\beta = \frac{k_1 m_{S,F} + 2k_2 m_{S,F}^2 + 3k_3 m_{S,F}^3 + ... + nk_n m_{S,F}^n}{1 + k_1 m_{S,F} + k_2 m_{S,F}^2 + k_3 m_{S,F}^3 + ... + k_n m_{S,F}^n} \quad (8)$$

By comparing (6) and (8), it follows directly that:

$$k_n = K_1 K_2 K_3 ... K_n = \prod_{i=1}^{n} K_n \quad (9)$$

A least-squares treatment of the data obtained in this study was conducted, and calculations were carried out using Eq. (8). Dye and surfactant molecules and associates $(DS)^\circ$, $(DS_2)^+$ and $(DS_3)^{2+}$ were assumed to be the only species present in solution. These calculations afforded reasonable k_1 and k_2 values, while the k_3 values corresponding to the formation of $(DS_3)^{2+}$ were unreasonable, for reasons presented later.

To determine the highest concentration of free surfactant ions at which there were no $(DS_2)^+$ species present in the solution, Eq. (8) was rearranged to (10):

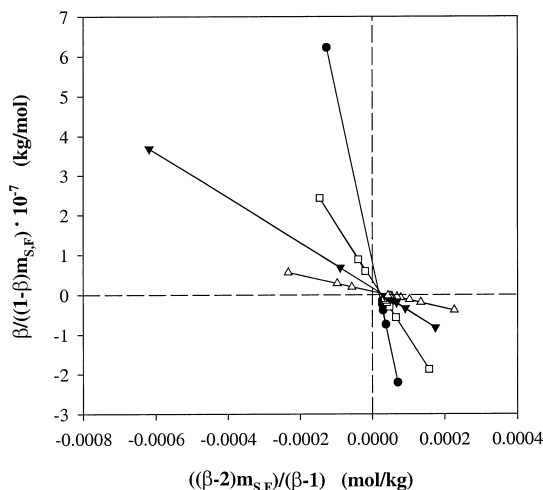$$\frac{\beta}{(1-\beta)m_{S,F}} = k_1 - \frac{(\beta-2)m_{S,F}}{(1-\beta)}k_2 \quad (10)$$

Fig. 5. Determination of k_1 and k_2 for the AO7–CPC association using Eq. (10): -●-●- = 15°C, -□-□- = 25°C, -▼-▼- = 35°C, -△-△- = 45°C.

When $\beta/(1-\beta)m_{S,F}$ was plotted against $(\beta-2)m_{S,F}/(1-\beta)$ the intercept of the ordinate afforded k_1 and the slope gave k_2. It is evident from Fig. 5 that such plots are linear over a relatively large range. Beyond certain $m_{S,F}$ values, however, the curves deviated from linearity. These points correspond to the upper limit of domain B, where only the species $(DS)^\circ$ and $(DS_2)^+$ exist in solution. The $(m_{S,F})_{lim}$ and β_{lim} values obtained are listed in Table 1, and reflect an increase in $(m_{S,F})_{lim}$ with increasing temperature, while β_{lim} was essentially constant. It should also be noted that the range of β values in domain B is relatively narrow (0.2).

Eq. (9) gave K_1 and K_2 values from k_1 and k_2 (see Table 2). From the K_1 and K_2 values obtained at different temperatures, standard free energy changes (ΔG_1° and ΔG_2°), standard enthalpy change (ΔH_1° and ΔH_2°), and standard entropy changes (ΔS_1° and ΔS_2°) for the formation of $(DS)^\circ$ and $(DS_2)^+$ species were calculated. Upon plotting $\Delta G^\circ/T$ vs $1/T$, the slope of the curve gave ΔH°_1 and ΔH°_2. It can be seen from Fig. 6 that $\Delta G^\circ/T$ vs $1/T$, for both species, is practically linear over the temperature range employed. The ΔG°, ΔH°, and ΔS° values for the first and second association steps are given in Tables 2 and 3.

For the first step of the AO7–CPC association process (11), the free energy change can be expressed by Eq. (12):

$$D^- + S^+ \overset{K_1}{\Leftrightarrow} (DS)^o \quad (11)$$
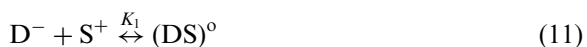
$$\Delta G_1 = \mu_{DS}^o - \mu_D^o - \mu_S^o + RT \ln \frac{\gamma_{DS}}{\gamma_D \gamma_S} + RT \ln \frac{m_{DS}}{m_D m_S} \quad (12)$$

where μ_{DS}^o, μ_D^o and μ_S^o are standard chemical potentials, and γ_{DS}, γ_D and γ_S are molal activity

Table 1
Concentration limits for $m_{S,F}$ and β

T (°C)	$(m_{S,F})_{lim} \times 10^5$ (mol/kg)	β_{lim}
15	0.49	1.2
25	1.09	1.3
35	1.24	1.2
45	1.37	1.2

Table 2
Thermodynamic data for the first AO7–CPC association step in the presence of 0.1 m NaCl

T (°C)	$K_1 \times 10^{-6}$	ΔG_1^o (kJ/mol)	ΔH_1^o (kJ/mol)	ΔS_1^o (J/mol K)	ΔG_{mix}^o (kJ/mol)	ΔG_{el}^o (kJ/mol)	ΔG_{sr}^o (kJ/mol)	ΔH_{sr}^o (kJ/mol)	ΔS_{sr}^o (J/mol K)
15	9.92	−38.6		−78.4	9.6	−4.8	−43.4	−62.8	−67.3
25	3.80	−37.6	−61.2	−79.2	10.0	−5.0	−42.6	−63.1	−68.8
35	1.91	−37.0		−78.5	10.3	−5.3	−42.0	−63.4	−69.4
45	0.86	−36.1		−78.9	10.6	−5.5	−41.2	−63.7	−70.0

coefficients. Since the solutions are very dilute, the term containing activity coefficients may be neglected, leaving:

$$\Delta G_1 = \Delta G_1^o + RT \ln \frac{m_{DS}}{m_D m_S} \tag{13}$$

where ΔG_1^o is the standard free energy change for the AO7–CPC association.
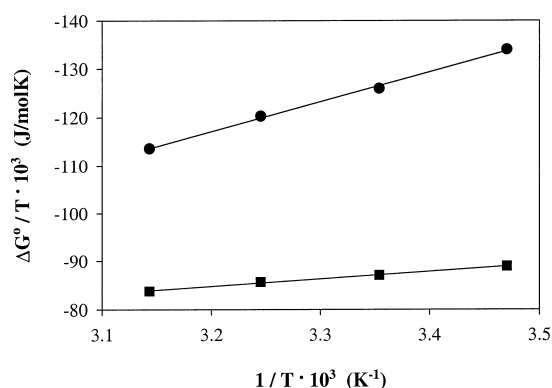
Fig. 6. Plots of $\Delta G^o / T$ vs $1/T$ for the first (-●-●-) and the second (-■-■-) association step.

On the other hand, at low concentrations, ΔG_1 can be expressed in terms of the mole fractions of dye (X_D), surfactant (X_S), and their associate (X_{DS}):

$$\Delta G_1 = \Delta G_u^o + RT \ln \frac{X_{DS}}{X_D X_S} \tag{14}$$

where ΔG_u^o is the standard unitary free energy.

At very low dye and surfactant concentrations, the sum of n_D mols dye, n_S mols surfactant and n_{DS} mols first dye–surfactant species is much less than n_w mols of water. In this case, mol fractions X_D, X_S and X_{DS} can be written as n_D/n_w, n_S/n_w and n_{DS}/n_w, respectively. Since the molality of a component is the amount (g) of the component per kg water, the molal concentrations (m_D, m_S and m_{DS}) can be substituted for n_D, n_S and n_{DS} in Eq. (14). For the same reason, n_w is equal to $1000/M_w = 55.6$ and becomes $1/M$. Accordingly, Eq. (14) can be written as:

$$\Delta G_1 = \Delta G_u^o + RT \ln \frac{m_{DS}}{m_D m_S} - RT \ln M_o \tag{15}$$

From Eqs (13) and (15) it follows that:

$$\Delta G_1^o = \Delta G_u^o - RT \ln M_o \tag{16}$$

Table 3
Thermodynamic data for the second AO7–CPC association step in the presence of 0.1 m NaCl[a]

T (°C)	$K_2 \times 10^{-4}$	ΔG_2^o (kJ/mol)	ΔH_2^o (kJ/mol)	ΔS_2^o (J/mol K)	ΔG_{sr}^o (kJ/mol)	ΔS_{sr}^o (J/mol K)
15	4.42	−25.6		34.7	−35.2	68.0
25	3.54	−26.0	−15.6	34.9	−36.0	68.4
35	2.98	−26.4		35.0	−36.7	68.5
45	2.36	−26.6		34.6	−37.2	67.9

[a] AO7 = 7.5×10^{-5} mol/kg.

where $-RT \ln M_o = \Delta G_{\text{mix}}^o$, i.e. the standard free energy of mixing. This represents the contribution from the random mixing of dye and surfactant ions with water, when dye and surfactant ions form $(DS)^o$ species. Differentiation of ΔG_1^o with respect to temperature gives ΔS_1^o:

$$\Delta S_1^o = \Delta S_u^o + R \ln M_o \tag{17}$$

In Eq. (17), the unitary or contact entropy of the AO7–CPC species (ΔS_u^o) represents the entropy contribution due to dye and surfactant interactions with water [7,8].

Since K_1 is a quantity composed of both short and long-range contributions to the association constant, we can write:

$$\Delta G_1^o = \Delta G_{\text{mix}}^o + \Delta G_{\text{el}}^o + \Delta G_{\text{sr}}^o \tag{18}$$

where ΔG_{el}^o is the electrostatic contribution resulting from Coulombic interactions. Furthermore, ΔG_{sr}^o contains the contributions of all attractive short-range non-Coulombic interactions. In the first approximation, ΔG_{el}^o can be expressed as:

$$\Delta G_{\text{el}}^o = -\frac{N_A e_o^2}{4\pi\varepsilon_o \varepsilon a} \tag{19}$$

where N_A is Avogadro's constant, e_o is the charge, a is the average separation between charges in the first AO7–CPC species, ϵ_o is the vacuum permittivity, and ϵ is the solvent dielectric constant. For the constant we used 3.57×10^{-10} m at 25°C [9], and ΔG_{sr}^o and ΔG_{el}^o values were calculated from Eqs. (18) and (19), respectively.

Since $\Delta H_{\text{mix}}^o = 0$ zero in very dilute solutions, Eq. (18) becomes:

$$\Delta H_{\text{sr}}^o = \Delta H_1^o - (\Delta G_{\text{el}}^o + T\Delta S_{\text{el}}^o) \tag{20}$$

and ΔS_{el}^o is obtained from the following equation [10]:

$$\Delta S_{\text{el}}^o = -\frac{d(\Delta G_{\text{el}})}{dT} = \Delta G_{\text{el}}^o \frac{d(\ln \varepsilon)}{dT} \tag{21}$$

where $d(\ln \epsilon)/dT$ is equal to -4.6×10^{-3} K^{-1} at 25°C [10,11].

Finally, the standard entropy change for short-range interactions was determined from Eq. (22):

$$\Delta S_{\text{sr}}^o = \frac{(\Delta H_{\text{sr}}^o - \Delta G_{\text{sr}}^o)}{T} \tag{22}$$

Calculated thermodynamic data for the first association step are shown in Table 2.

For the second step of the AO7–CPC association process [Eq. (23)], we used the same thermodynamic treatment employed in the first step, except that no long-range Coulombic interactions were considered.

$$S^+ + (DS)^o \overset{K_2}{\leftrightarrow} (DS_2)^+ \tag{23}$$
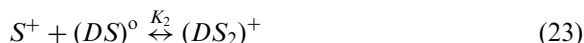
In this case, Eqs. (18) and (20) could be written in somewhat modified forms:

$$\Delta G_{\text{sr}}^o = \Delta G_2^o - \Delta G_{\text{mix}}^o \tag{24}$$

$$\Delta H_{\text{sr}}^o = \Delta H_2^o \tag{25}$$

Eq. (22) remained unchanged. The resultant thermodynamic data are shown in Table 3.

3.1. The first AO7–CPC association step

Although the number of experimental points in the first domain is limited, analysis of the data shows that the binding process in this concentration domain is governed by the Langmuir isotherm. This means that only the simplest association species $(DS)^o$ formed.

It is clear that ΔG_{sr}^o is mainly composed of dispersive, charge transfer and hydrophobic interactions, but it was not possible to completely separate the three contributions. Therefore, we will attempt to estimate the individual contributions, in only a qualitative way.

Several short range interactions, such as London type dispersive interactions, and charge transfer interactions between the pyridinium cation as acceptor and the π-electron system of the dye as donor can contribute to a negative ΔH^o. On the other hand, the contribution due to hydrophobic interactions, which results from the disruption of structured water molecules around free dye and surfactant ions when the two ions combine, is

Table 4

CPC critical micelle concentration in 0.1 m NaCl and 7.5×10^{-5} m AO7[a]

T (°C)	c.m.c. $\times 10^5$ (mol/kg)	
	A[b]	B[c]
15	3.4	3.56
25	3.8	3.64
35	4.1	4.43
45	5.1	4.89

[a] AO7, 7.5×10^{-5} mol/kg.
[b] A, Present study.
[c] B, Ref. [13].

undoubtedly endothermic. Therefore, the considerably high negative ΔH_1^o values in Table 2 indicate that hydrophobic interactions are only partly responsible for the formation of (DS)^o species.

In the solvent layer adjacent to the solute, the water molecules are more structured than those in the bulk solution are. Therefore, the entropy of aqueous medium around dye and surfactant ions is lower than in the bulk solvent. On forming (DS)^o species from free dye and surfactant ions, the structured water is converted to the less-structured bulk solvent phase. Consequently, the unitary entropy becomes higher; but, the calculated ΔS_{sr}^o is considerably negative, indicating that dispersive interactions are the main contributors to ΔS_{sr}^o and ΔG_{sr}^o.

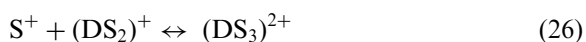### 3.2. The second AO7–CPC association step

The thermodynamic data for the second association step (Table 3) present a different picture from the corresponding data for the first step. For instance ΔH_2^o is higher than ΔH_1^o. This observation can be explained, in part, by the absence of long-range Coulombic interactions. However, the

large difference between the two values leads us to believe that hydrophobic interactions play an important role in this association step. This hypothesis is strongly supported by the relatively high positive value for ΔS_{sr}^o.

We should also mention that the structure of the $(DS_2)^+$ species depends on which side the surfactant ion (S^+) approaches (DS)^o — viz., the D-side or the S-side. While the short-range attraction between the negatively charged dye and positively charged surfactant and the charge transfer dye–surfactant interactions, produce a sandwich-like complex $(S^+D^-S^+)^+$, the hydrophobic interactions between the free surfactant ion and the already bound surfactant favour the formation of a complex of the form $(S^+S^+D^-)^+$. Potentiometric measurements did not determine unequivocally which structure exists.

3.3. The third AO7–CPC association step

Formation of complex aggregates of the stepwise association type would be expected only in solutions of lower dielectric constant, since in the reaction (26), relatively strong repulsive Coulombic interactions can play an important role in preventing the reactants from approaching each other closely.

$$S^+ + (DS_2)^+ \leftrightarrow (DS_3)^{2+} \tag{26}$$

It is more likely that quadruple type species shown in (27) are present in solution [12].

$$(DS)^o + (DS)^o \leftrightarrow (DS)_2^o \tag{27}$$

This may explain why the β vs log $m_{S,F}$ plot (Fig. 4) for the third domain does not fit Eq. (8) for the

Table 5

Additional data for the first and the second AO7–CPC association steps in 0.1 m NaCl solutions at 25°C[a]

m_{NaCl} (mol/kg)	$K_1 \times 10^{-6}$	$K_2 \times 10^{-4}$	ΔG_1^o (kJ/mol)	ΔG_2^o (kJ/mol)	$\Delta G_{u,1}^o$ (kJ/mol)	$\Delta G_{u,2}^o$ (kJ/mol)
0	6.51	1.51	−38.9	−23.9	−48.9	−33.9
0.05	4.19	2.60	−37.8	−25.2	−47.8	−35.2
0.1	3.80	3.54	−37.6	−26.0	−47.6	−36.0

[a] AO7 = 7.5×10^{-5} mol/kg.

stepwise AO7–CPC association process. With further increases in surfactant, the concentration of free surfactant ions approaches the c.m.c, and in all cases the asymptote to the β–log $m_{S,F}$ curve in this concentration range is in good agreement with the c.m.c. values for CPC (Table 4) [13].

3.4. The effect of added simple electrolyte

The effect of ionic strength on K_1 and K_2 is shown in Table 5. It was found that K_1 slowly decreases with the addition of NaCl, and becomes nearly constant at $m_{NaCl} = 0.1$ mol/kg. The K_1 decrease can be attributed to the preferred attraction between sodium ions and dye anions and between chloride ions and surfactant cations in solution, blocking the attraction between dye and surfactant ions.

In the second association step long-range electrostatic interactions are negligible. However, the addition of neutral electrolyte can cause some modifications in the water structure, contributing to a change in K_2. From Table 5, it can be seen that the K_2 value increases with NaCl concentration, suggesting that salt serves as a structure breaker, and supports the presence of short range AO7–CPC interactions.

4. Conclusion

It has been shown that the AO7–CPC association process takes place in three principal steps. In the first step, at low surfactant concentrations, the formation of $(DS)^{\circ}$ species is mainly governed by electrostatic long-range and dispersive short-range attractive forces between dye and surfactant ions. In the second step, where a free surfactant ion binds to a neutral associate forming a $(DS_2)^+$ species, hydrophobic interactions play an important role. In the third step, the formation of more complex species, such as $(DS_3)^{2+}$, may be prevented by relatively strong repulsive electrostatic interactions. It is more likely that $(DS)^{\circ}_2$ type species are present at higher surfactant concentrations.

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