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Interactions between some anionic dyes and cationic surfactants with different alkyl chain length studied by the method of continuous variations

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Abstract

The method of continuous variations was used to investigate the interactions of anionic dyes C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88) with cationic surfactants: *N*-cetylpyridinium chloride (CPCl), *N*-dodecylpyridinium chloride (DPCl), *N*-decylpyridinium chloride (DecPCl) and octadecyltrimethylammonium bromide (OTMABr) in aqueous submicellar solutions. With the increasing alkyl chain length of surfactants and with increasing number of benzene rings of dyes, the interactions become stronger, which shows the importance of hydrophobic forces. Electrostatic interactions also play an important role, as shown by the effect of KCl on the binding process. Two methods for determining the formation constants, Schaeppi–Treadwell's and Schwarzenbach's methods, are described in this paper. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Interactions between dyes and surfactants are subjects of numerous investigations. Surfactants are used as auxiliaries in most textile finishing processes such as washing, wetting, dispersing, dyeing and finishing. It is important to understand how surfactants and dyes interact in aqueous solutions to clarify the mechanisms of dyeing and other finishing procedures. The interactions between dyes and surfactants were also studied to provide insight into

small molecule–macromolecule interactions, which are of major importance in biochemistry [1]. Although most research was done with nonionic surfactants [2–4], the association of oppositely charged dyes and surfactants was also investigated [1,5–18].

Investigations were done with different methods: potentiometry [11,12], conductometry [13,14], voltammetry [2], tensiometry [15] and other methods, but the most widely used are spectroscopical methods [6,16–18]. Surfactants are able to affect the electronic absorption spectra of many dyes. Below the critical micelle concentration (CMC) a spectral change indicates a formation of complex between dye and surfactants and above

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the CMC the spectral change is a result of incorporation of dye to micelle [5,18,19].

In this paper, spectrophotometry was used to investigate the ion pair formation between anionic dyes and cationic surfactants in submicellar concentration ranges. We used the method of continuous variations to obtain the stoichiometry and the stability of the associate. Other researchers applied this method only to establish the ratio of surfactant to dye in the complex [6,20,21]. The possibilities to obtain the equilibrium association constants (K) by this method are described in the following paper.

Several authors [3,4,7] who studied interactions between micelles of nonionic surfactants and dyes of different ionic structure found that non-coulombic interactions, mainly hydrophobic, play a major role in binding. It was also established that for association between ionic surfactants and ionic dyes both electrostatic and hydrophobic forces are important [9–14]. In the present paper we have investigated the interactions of a series of cationic surfactants with different alkyl chain length; *N*-cetylpyridinium chloride (CPCl), *N*-dodecylpyridinium chloride (DPCl), *N*-decylpyridinium chloride (DecPCl) and octadecyltrimethylammonium bromide (OTMABr) with anionic dyes C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88) in aqueous submicellar solutions at different temperatures and with the addition of a simple electrolyte KCl. We can confirm the supplementing action of coulombic and non-coulombic forces.

1.1. The method of continuous variations

The method of continuous variations or Job's method is one of the most common techniques used for complex ion studies. Where a measured experimental property is a linear function of the concentration and where only one complex is important, Job's method is capable of yielding both the stoichiometric composition and the association constant of the complex [22].

Continuous variation plots are the diagrams of a physical property, which is related to the concentration of an equilibrium two component complex against volume or mole fraction of one of the two constituents [23]. Spectrophotometric measurements are very suitable for the application of this method. Plots are prepared by mixing the solutions of individual components in varying volume ratios in such a way that the total volume of each mixture is the same. The absorbance of each mixed solution is measured and plotted against the volume fraction of one of the reactants. The resulting curve has a maximum or a minimum, the position of which shows the composition of the associate on the abscise.

According to Job [24] the stoichiometry of the complex is determined from equimolar diagrams, which are obtained from solutions of identical initial concentration, while to determine the equilibrium constant, a nonequimolar diagram, obtained of solutions of different initial concentration, must be plotted. This means that two series of measurements are needed. In this paper we report on the determination of the equilibrium association constants (K) by two methods, Schaeppi–Treadwell's and Schwarzenbach's, which are derived from Job's method. The stoichiometry and the stability of the associate can be determined by equimolar solutions by these modified methods, so the additional measuring of nonequimolar solutions is not necessary.

The method of Schaeppi and Treadwell [25] is suitable when only one stable associate is formed and the equilibrium constant value is high [26]. The plot then approaches two straight line segments with a curved peak. Schwarzenbach [27] introduced a method, which is also valid for less stable associates, where Job's plots have no linear parts and an exact relation between a slope of the curve and the equilibrium constant must be determined. The smaller the K, the more curved the plot obtained is [23,26].

2. Experimental

2.1. Composition of the associate

The reaction between the dye (D) and the surfactant (S) can be described as an equilibrium reaction:

$$x\mathrm{D} + y\mathrm{S} \rightleftharpoons \mathrm{D}_x\mathrm{S}_y.$$
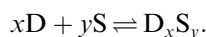
The mother solutions of the dye and the surfactant with concentrations c_D^0 and c_S^0, respectively, must be prepared. At the present work, where the concentrations are equal, we can write $c_D^0 = c_S^0 = c^0$. The mother solutions are mixed in varying volume ratios, but in such a way that the total volume of each mixture remains the same. x volume units of the dye solution are added to $(1 - x)$ volume units of the surfactant solution $(x < 1)$. A series of mixed solutions is prepared and the absorbance (E) of each solution is measured.

A Job's plot is made by plotting the corrected absorbance of particular mixture ΔE versus the volume fraction of dye x. The maximum or minimum occurs at volume ratio x, corresponding to the combining ratio of surfactant and dye in the associate.

The corrected absorbance ΔE represents the difference between the measured E_{exp} and the theoretical absorbance E_{teor}. E_{teor} is the absorbance of the mixture if no reaction has occurred in solution and E_{exp} is the sum of absorbances of all compounds existing in solution:

$$E_{teor} = \varepsilon_D c_D^0 x + \varepsilon_S c_S^0 (1 - x), \tag{1}$$

$$E_{exp} = \varepsilon_D c_D + \varepsilon_S c_S + \varepsilon_{DS} c_{DS}, \tag{2}$$

where ε_D and ε_S are the molar decadic absorption coefficients of dye and surfactant, c_D and c_S are the concentrations of dye and surfactant in a measured mixture, ε_{DS} is the molar decadic absorption coefficient of the associate formed, and c_{DS} is its concentration.

We measured the absorption of mixtures in the visible absorption range, where the surfactants we used show no absorbance. Thus, we could use the following equation to calculate ΔE:

$$\Delta E = E_{exp} - \varepsilon_D c_D^0 x. \tag{3}$$

2.2. Equilibrium association constants

2.2.1. Schaeppi–Treadwell's method

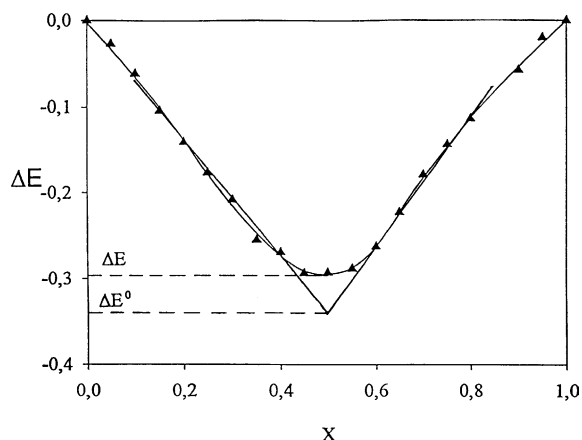The principle of determination of equilibrium constants by this method is shown in Fig. 1 for the

Fig. 1. Determination of ΔE and ΔE^0 to calculate K with Schaeppi–Treadwell's method.

example of AO7 and CPCl solutions. The ascending and the descending of the curve on both sides of the minimum are almost linear with a parabolic shape at the end point. This curvature is a result of an incomplete association. The minimum at $x = 0.5$ means that 1:1 associates are formed, and the dye and the surfactant ions interact in the equilibrium reaction:

$$D^- + S^+ \rightleftharpoons DS. \tag{4}$$

The measured ΔE at $x = 0.5$ is compared to theoretical ΔE_0, derived by extrapolation of linear parts of the curve to their intersection. The quotient of these values represents the degree of association $(1 - \alpha)$:

$$\frac{\Delta E}{\Delta E_0} = 1 - \alpha, \tag{5}$$

where α represents the degree of unassociated ions.

The equilibrium constant for Eq. (5) could be written as:

$$K = \frac{[DS]}{[D][S]} = \frac{1 - \alpha}{(c^0/2)\alpha^2} = \frac{2(1 - \alpha)}{c^0 \alpha^2}. \tag{6}$$

The concentration of D and S in the minimum of Job's plot is $c^0/2$. Namely, at $x = 0.5$ the initial concentration is diluted in 1:1 ratio.

2.2.2. Schwarzenbach's method

For Eq. (4) Schwarzenbach [27] derived Eq. (7) for Job's diagram:

$$\Delta E = \varepsilon_m \left[\frac{c^0 + 1/K}{2} - \sqrt{\left(\frac{c^0 + 1/K}{2} \right)^2 - c^{02}x(1-x)} \right]. \tag{7}$$

He defined

$$\varepsilon_m = \varepsilon_{DS} - \varepsilon_D - \varepsilon_S \tag{8}$$

and obtained the slope of Eq. (7) by derivation of $d\Delta E/dx$

$$\frac{d\Delta E}{dx} = \frac{\varepsilon_m K c^{02}(1-2x)}{[(Kc^0+1)^2 - 4K^2 c^{02}x(1-x)]^{1/2}}. \tag{9}$$

At $x = 0.5$, where the curve has the minimum, the result of Eq. (10) is zero. At $x = 0$ and $x = 1$ we obtain:

$$\left(\frac{d\Delta E}{dx} \right)_{x=0} = - \left(\frac{d\Delta E}{dx} \right)_{x=1} = \frac{\varepsilon_m K c^{02}}{Kc^0 + 1}. \tag{10}$$

K and ε_m are calculated from Eqs. (11) and (12), which are obtained by expressing ε_m from Eqs. (9) and (10)

$$(\varepsilon_m)_1 = \frac{\Delta E}{\frac{c^0+1/K}{2} - \left(\left(\frac{c^0+1/K}{2} \right)^2 - xc^{02}(1-x) \right)^{1/2}} \tag{11}$$

and

$$(\varepsilon_m)_2 = \frac{\frac{d\Delta E}{dx}c^0 K + \frac{d\Delta E}{dx}}{Kc^{02}}. \tag{12}$$

Different values of K are put into Eqs. (11) and (12). The true K is the value where the calculated absorption coefficients are equal $[(\varepsilon_m)_1 = (\varepsilon_m)_2]$ or most similar $[(\varepsilon_m)_1 - (\varepsilon_m)_2 = \text{min}]$.
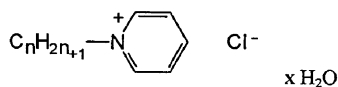
2.3. Materials

Fig. 2 presents the structural formulas of the dyes and surfactants. N-cetylpyridinium chloride (CPCl) by Merck and N-dodecylpyridinium chloride (DPCl) by Aldrich were purified by three recrystallizations from acetone. N-decylpyridinium bromide (DecPBr) was synthesized by the previously described method [28] and purified by three recrystallizations from acetone. Cooling with the CO_2–acetone mixture was needed for crystallization. Octadecyltrimethylammonium bromide (OTMB) by Fluka was used without purification. Each surfactant was dried at 50 °C in vacuum. C.I.
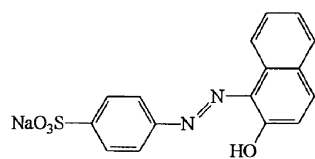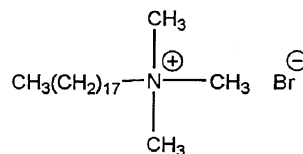

C. I. Acid Orange 7 (AO7)
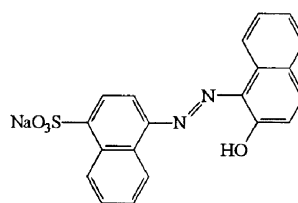
C. I. Acid Red 88 (AR88)

n=16: *N-cetylpyridinium chloride (CPCl)*
n=12: *N-dodecylpyridinium chloride (DPCl)*
n=10: *N-decylpyridinium chloride (DecPCl)*

octadecyltrimethylammonium bromide
(OTMABr)

Fig. 2. The structural formulas of the dyes and surfactants used.

Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88) were synthesized [29] and purified by repeated recrystallization from the aqueous acetone solution and from the *N,N*-dimethylformamide-benzene.

The solutions were prepared in double distilled water, and expressed in molar concentrations. The initial concentration of the dye and surfactant solutions, c^0, was 6×10^{-5} mol l^{-1}. At this concentration, the dyes used do not spontaneously aggregate [29] and the surfactants used do not form micelles. Submicellar concentrations were preserved also at the addition of 0.05 M KCl [30]. The absorbances were measured on the double beam absorbance spectrophotometer Cary 1E, Varian with thermostated cells. The measurements were taken at 15, 25 and 35 °C. The mixed solutions were prepared instantly and the absorbances were measured after thermostation. The absorbances were read at the absorption maximum at 485 nm and 503 nm for AO7 and AR88, respectively.

3. Results and discussion

Figs. 3 and 4 show the equimolar Job's plots for binding of the dye AO7 and the surfactant CPCl at 15, 25 and 35 °C in water solutions and with addition of 0.05 mol l^{-1} KCl, respectively. The minimum is at $x = 0.5$ on all plots. At this point the concentration of the dye and the surfactant ions is
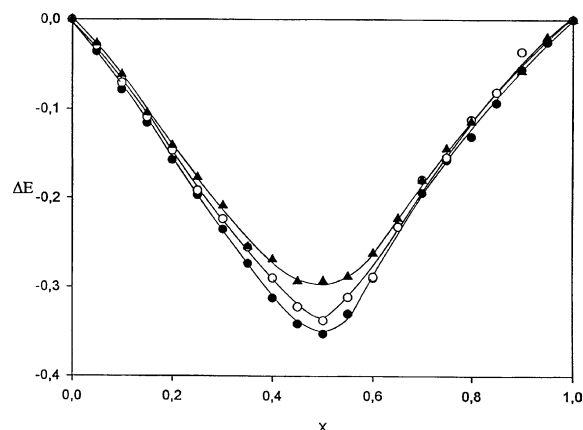

Fig. 3. Job's plots of CPCl and AO7 in water solutions at 15 °C (●), 25 °C (○) and 35 °C (▲). $c^0 = 6 \times 10^{-5}$ mol l^{-1}.
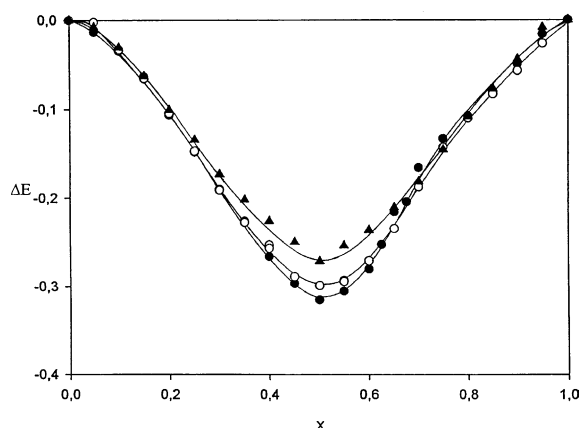

Fig. 4. Job's plots of CPCl and AO7 in 0.05 mol l^{-1} KCl solutions at 15 °C (●), 25 °C (○) and 35 °C (▲). $c^0 = 6 \times 10^{-5}$ mol l^{-1}.

equal and in such a mixed solution the highest amount of the associate is formed. This means that 1:1 associates are formed between the dye AO7 and the surfactant CPCl ions. The binding ratio remains the same at different temperatures and at addition of a simple electrolyte, too.

It is also evident that Job's plots differ one from another in the height of the minimum. A higher $-\Delta E$ means that the concentration of the associate is higher, too. We can conclude that the amount of bound particles is smaller at higher temperature and that the addition of electrolyte slightly diminishes the association.

Figs. 5 and 6 show the equimolar Job's plots for binding of the dye AO7 and the surfactant OTMABr at 15, 25 and 35 °C in water and in electrolyte solutions. 1:1 associates are also formed at all conditions. With increasing temperature and with the addition of KCl the $-\Delta E$ becomes smaller, like at AO7–CPCl mixtures.

The equilibrium constants for the interactions of AO7 with CPCl and OTMABr obtained by Schaeppi–Treadwell's and Schwarzenbach's methods are given in Tables 1 and 2, respectively. In Schaeppi–Treadwell's method linear regression was used to determine the slope of the initial and the final part of the curve. The cross-section x_0 and the ΔE_0 were calculated from the slopes. At Schwarzenbach's method, the linear regression was used to determine the slope of the curve
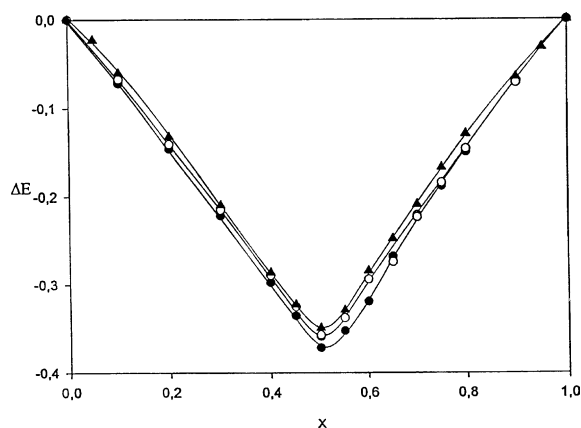
Fig. 5. Job's plots of OTMABr and AO7 in water solutions at 15 °C (●), 25 °C (○) and 35 °C (▲). $c^0 = 6 \times 10^{-5}$ mol l^{-1}.

$(\mathrm{d}\Delta E/\mathrm{d}x)$ at $x = 0$. The left slope of Job's plots, where the surfactant is in excess, was used to calculate K. Only at AO7–OTMABr in KCl solutions the right slope of Job's plot was used to calculate K. Namely, at $x = 0$ the curves are inflected, presumably because of weaker solubility of OTMABr at this concentration in KCl solution.

The calculated equilibrium constants are very high which indicates on strong interactions. The constants at Schwarzenbach's method are in general lower but the results of both methods are in accordance and we can make common conclusions. An increase in temperature causes a decrease in the
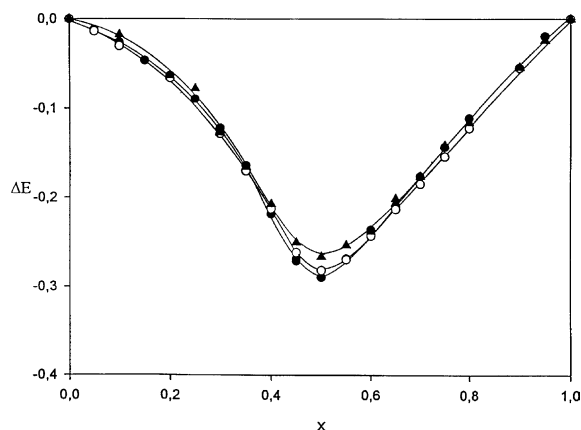

Fig. 6. Job's plots of OTMABr and AO7 in 0.05 mol l^{-1} KCl solutions at 15 °C (●), 25 °C (○) and 35 °C (▲). $c^0 = 6 \times 10^{-5}$ mol l^{-1}.

equilibrium constants, K, as well as an increase in the standard free enthalpy changes, ΔG°, for both surfactants in water solutions without electrolyte. It is evident that at higher temperature the tendency to form dye/surfactant ion pair lessens.

In electrolyte solutions the equilibrium constants are lower than in pure water solutions and in most cases they slightly decrease with increasing temperature. The lower K values could be ascribed to the screening of charges on dye and surfactant ions by electrolyte ions, which decreases the contribution of attractive long-range electrostatic forces. The standard free enthalpy changes do not increase with increasing temperature in KCl solutions. This is in accordance with previous investigations [16], where it was found that association in KCl solutions is an entropy directed-process, and the lack of electrostatic attraction is compensated by hydrophobic interactions.

Equilibrium constants and standard free enthalpy change also show that AO7 interacts with OTMABr more easily and strongly than with CPCl at the same conditions. Because the only difference between the systems is in the length of the alkyl chain of both surfactants, it implies that the hydrophobicity of the alkyl chain, which is responsible for hydrophobic interactions, plays an important role in dye–surfactant interactions. The binding energy increases with increase of the hydrophobicity of the alkyl chain.

The results obtained by other methods are in agreement with our results. The K values for AO7 and CPCl at 25 °C in water solution obtained by potentiometric titration [11] are in the range from 1.7×10^6 to 6.5×10^6, depending on the initial dye concentration. The values of K obtained by conductometric titration [13] are 5.6×10^5, 5.4×10^5 and 2.2×10^5 at 15, 25 and 35 °C, respectively. In 0.1 M solution of NaCl Simončič and Špan [12] obtained K values of 9.92×10^6, 3.8×10^6 and 1.9×10^6 at 15, 25 and 35 °C, respectively. Spectrophotometrically [16] we got K values between 5×10^6 and 3.78×10^5 in water and between 4×10^6 and 6×10^5 in KCl solutions. For AO7–OTMABr interactions the comparable results were not found in the literature. We may conclude that our methods are suitable for calculating the equilibrium association constants.

Table 1
Equilibrium association constants (K) calculated by the method of Schaeppi–Treadwell and the degrees of association ($1 - \alpha$) in the minimum of Job's plots

Dye–surfactant	KCl (mol l^{-1})	T (°C)	$1 - \alpha$	K (dm^3 mol^{-1})	$\Delta G°$ (kJ mol^{-1})
AO7–CPCl	0	15	0.928	6.01×10^6	−37.3
		25	0.912	2.88×10^6	−36.8
		35	0.841	1.11×10^6	−35.6
	0.05	15	0.864	1.56×10^6	−34.1
		25	0.849	1.24×10^6	−34.7
		35	0.846	1.19×10^6	−35.8
AO7–OTMABr	0	15	0.972	3.96×10^7	−41.8
		25	0.962	2.09×10^7	−41.7
		35	0.950	1.20×10^7	−41.7
	0.05	15	0.936	7.68×10^6	−37.9
		25	0.926	5.65×10^6	−38.5
		35	0.906	3.42×10^6	−38.5

Fig. 7 shows the Job's plot for mixtures of the dye AO7 and the surfactant DPCl at 25 °C in water solutions. At concentration $c^0 = 6 \times 10^{-5}$ mol l^{-1} the deviation of zero line is very small. At higher concentration, $c^0 = 1.8 \times 10^{-4}$ mol l^{-1}, regular Job's plot is obtained. Minimum occurs at $x = 0.5$, meaning that the dye and the surfactant ions are bound in 1:1 ratio. The equilibrium constant value obtained by Schaeppi–Treadwell's method is 3.7×10^5 dm^3 mol^{-1} and by Schwarzenbach's method 6.2×10^5 dm^3 mol^{-1}. Both values are much lower than at interactions of AO7 with CPCl and OTMABr. DPCl has shorter alkyl chain

and the contribution of hydrophobic interactions to the association is therefore smaller. The measurements with other methods also reveal that complexes between AO7 and DPCl are formed at higher dye and/or surfactant concentrations as between AO7 and CPCl [11,13,31].

At DecPCl, with the shortest alkyl chain, the absorbencies of mixtures do not differ from the absorbencies of pure dye solutions and $-\Delta E$ equals zero, which means that interactions do not occur. Much higher concentrations are needed to notice the appearance of interactions [1]. We can conclude that the tendency to form dye–surfactant complex

Table 2
Equilibrium association constants (K) calculated by the method of Schwarzenbach and the absorption coefficients of the associate (ε_m)

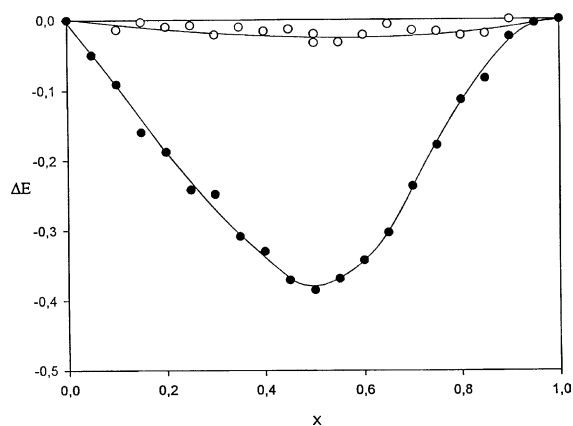| Dye–surfactant	KCl (mol l^{-1})	T (°C)	ε_m (l mol^{-1} cm^{-1})	K (dm^3 mol^{-1})	$\Delta G°$ (kJ mol^{-1})
AO7–CPCl	0	15	12 981	3.45×10^6	−36.0
		25	12 585	2.01×10^6	−35.9
		35	12 938	4.53×10^5	−33.3
	0.05	15	13 750	4.59×10^5	−31.2
		25	14 717	3.07×10^5	−31.3
		35	11 812	4.87×10^5	−33.5
AO7–OTMABr	0	15	12 634	9.50×10^7	−43.9
		25	12 395	2.00×10^7	−41.6
		35	12 942	2.94×10^6	−38.1
	0.05	15	10 602	3.91×10^6	−36.3
		25	10 430	3.09×10^6	−37.0
		35	10 680	1.02×10^6	−35.3

Fig. 7. Job's plots of DPCl and AO7 in water solutions at 25 °C. $c^0 = 6 \times 10^{-5}$ mol l^{-1} ($\bigcirc$), 1.8×10^{-4} mol l^{-1} ($\bullet$).

increases with increasing alkyl chain length of surfactant. Such behavior is in accordance with Traube's rule [32].

The binding diagram for the dye AR88 with the surfactants CPCl and DPCl is presented in Fig. 8. The curves are not parabolic in their minima but have a sharp peak. This is the characteristic of the systems where the interactions are stronger and the association is complete [23,26,27]. This means that the interactions of both surfactants with the dye AR88 are very strong, stronger than the interactions with the dye AO7. Their intensity is the result of the larger hydrophobic structure of the dye AR88 comparing with the dye AO7. We
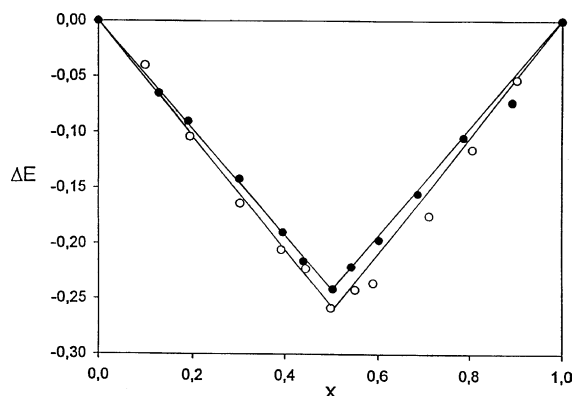

Fig. 8. Job's plots of AR88 and CPCl ($\bullet$) and of AR88 and DPCl ($\bigcirc$) in water solutions at 25 °C. $c^0 = 6 \times 10^{-5}$ mol l^{-1}.

cannot calculate the association constants from such plots, as their values are almost infinite. Furthermore, after some time the precipitation occurs in solutions containing AR88 and CPCl or DPCl. When mixing together the solutions of AR88 and DecPCl or OTMABr the precipitation occurred immediately and the absorbance could not be measured.

Absorption spectra of the mixed solutions of AR88 and AO7 with anionic surfactant sodiumdodecylsulphate (SDS) were also measured. They do not differ from theoretical absorbances and ΔE is zero. The interactions do not occur due to the repulsion between the same charged ions at all concentrations below c.m.c. of surfactant. This means that long-range electrostatic repulsion predominates the short-range non-coulombic interactions.

4. Conclusions

In this paper we introduced Schaeppi–Treadwell's and Schwarzenbach's methods for calculating the equilibrium constants of interactions between the anionic dyes and the cationic surfactants. With both methods the association constants can be determined from the equimolar Job's plots, which are also used to establish the composition of the associates. The determination of K is very simple with these methods. The calculated K values and the shape of the plots can give us basic data about the strength of the interactions between the dyes and the surfactants.

Our investigation has confirmed that interactions between the oppositely charged dyes AO7 and AR88 and surfactants DecPCl, DPCl, CPCl, OTMABr are influenced by the electrostatic attraction and the hydrophobic interactions.

The increase of the hydrophobicity, either of the surfactant or the dye, increases the tendency to associate. At DecPCl, with the smallest hydrophobic structure, the electrostatic attraction between differently charged ions is not enough to lead to the association in the measured concentration range, while the surfactants with longer chain length: DPCl, CPCl and OTMABr associate with the dye AO7. The longer the chain length the more pronounced the interactions are. Furthermore,

larger hydrophobic structure of the dye AR88 in comparison with the dye AO7 influences the stronger interactions with the surfactants DPCl and CPCl.

The importance of electrostatic interactions in the association process is reflected in the sensitivity to KCl and in the absence of interactions between AR88 and SDS with the same charged ions.

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