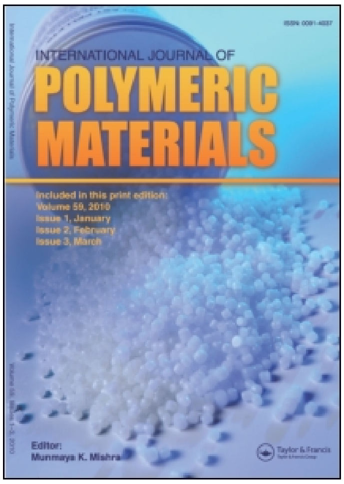

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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P. Forte Tavčer[a]
[a] Department of Textiles, University of Ljubljana, Ljubljana, Slovenia

To cite this Article Tavčer, P. Forte(2000) 'The Influence of a Simple Electrolyte KCI on Surfactant - Dye Interactions in Water Solution', International Journal of Polymeric Materials, 47: 4, 727 — 733
To link to this Article: DOI: 10.1080/00914030008031328
URL: http://dx.doi.org/10.1080/00914030008031328

Intern. J. Polymeric Mater., 2000, Vol. 47, pp. 727–733
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The Influence of a Simple Electrolyte KCl on Surfactant – Dye Interactions in Water Solution

P. FORTE TAVČER

University of Ljubljana, Department of Textiles, Snežniška 5,
SI-1000 Ljubljana, Slovenia

(Received 15 December 1998)

The influence of a simple electrolyte KCl on the interactions between the anionic dyes C. I. Acid Orange 7 (AO7) and the cationic surfactant N-cetylpyridinium chloride (CPCl) in water solutions was studied.

To determine the equilibrium association constants, which enabled us to make the conclusions about the strength of interactions the Method of Continuous Variations was used.

The light absorption of mixed dye and surfactant solutions in the visible absorption range at 25°C was measured. The concentration of the dye in the measured solutions was up to $6 \cdot 10^{-5}$ $\mathrm{mol \cdot l^{-1}}$ and the concentration of the surfactant was up to $1.2 \cdot 10^{-4}$ $\mathrm{mol \cdot l^{-1}}$, which is below the critical micelle concentration of surfactant in pure water. The molal concentrations of KCl in the measured solutions were 0, 0.1, 0.5 and 1 mol/kg.

It was found that the addition of KCl reduces the tendency of the dye AO7 and the surfactant CPCl to associate.

Keywords: Surfactant – dye interactions; electrolyte; spectrophotometry; associates; Job's method

INTRODUCTION

In the dyeing process many surfactants have been used as levelling or dispersing agents. Understanding of how surfactant and dye interact in aqueous solution is of importance to clarify the mechanisms of the dyeing process.

The influence of different surfactants on the dyeing of wool, polyamide, cellulose, acrylic and other fibers has been the subject of a number of publications [1 – 4]. Very suitable measuring technique for such investigations is spectrophotometry, which was also used in our study.

The nature of the interactions between dyes and surfactants depends mostly on their chemical structure [5 – 7]. Oppositely charged ionic dyes and surfactants often form stable associates. Beside the ionic constitution of dyes and surfactants, the interaction also depends on the alkyl chain length of surfactant [8], the molecular structure of dye [9], temperature and the addition of different compounds. The dyeing processes often require the addition of electrolytes, to improve the exhaustion of dyes from the dyeing bath.

In the present study the influence of a simple electrolyte KCl on the interactions between the anionic azo dye C.I. Acid Orange 7 (AO7) and the cationic surfactant N-cetylpyridinium chloride (CPCl) was investigated.

To calculate the equilibrium association constants the method of continuous variations or the Job's method was used [10, 11].

EXPERIMENTAL

Materials

C.I. Acid Orange 7 is a monoazo monosulfonated anionic dye ($M = 350.3\,\mathrm{g \cdot mol^{-1}}$). It was synthesised [12] and purified by repeated recrystallization from water – acetone solution and from the N,N-dimethylformamide – benzene solution.

N-cetylpyridinium chloride ($M = 358.01\,\mathrm{g \cdot mol^{-1}}$); Merck, was purified by repeated recrystallization from acetone.

Measurements

Mother solutions of the dye and surfactant with concentration c_D^0 and c_S^0, respectively, were prepared. The ratio between the dye and the surfactant concentration was $c_S^0 = p \cdot c_D^0$, where p was 2. Two different dye concentrations ($3 \cdot 10^{-5}$ and $6 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$) and two different surfactant concentrations ($6 \cdot 10^{-5}$ and $1.2 \cdot 10^{-4}\,\mathrm{mol \cdot l}$) were used. The concentration of KCl in parallel mother solutions was 0, 0.1, 0.5 and $1\,\mathrm{mol \cdot kg^{-1}}$.

As the method of continuous variations [10] requires, the mother solutions were 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 surfactant solution were added to $(1-x)$ volume units of the dye solution. A series of mixed solutions were prepared and the light absorbance of each solution was measured.

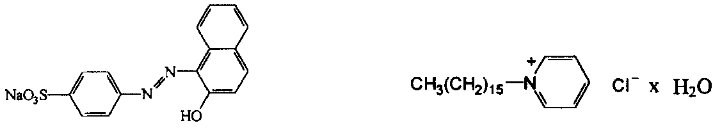
The absorbances were measured on a double beam absorbance spectrophotometer Cary 1E, Varian, in the absorption range from 400 to 600 nm. The measurements were made at $25 \pm 0.1°C$ in 1 cm cells.

RESULTS AND DISCUSSION

The equilibrium constants can be obtained from Job's plots [10]. They are prepared by plotting the corrected absorbances of particular mixtures ΔE *versus* the volume fraction of surfactant x. The corrected absorbance ΔE is the difference between the measured and the theoretical absorbance, which represents the absorbance of mixture if no reaction occurred in solution. When the mother solutions are equimolar $(c_S^0 = c_D^0)$ the diagrams are also called equimolar, and when $c_S^0 \neq c_D^0$ they are called nonequimolar. The stoichiometry of the associate is generally determined from equimolar diagrams. If the equilibrium constant K is required, a nonequimolar diagram must be plotted in which the position of the peak (X_m) provides information on K.

Nonequimolar Job's plots for AO7 – CPCl mixtures at different concentration of KCl at 485 nm, where the AO7 spectrum has a maximum, are shown on Figures 2 and 3.

From such plots the equilibrium association constants (K) can be determined if the composition of associates is known. It was confirmed



C. I. Acid Orange 7 (AO7)

N-cetylpyridinium chloride (CPC)

FIGURE 1 The structural formulae of dye and surfactant used.

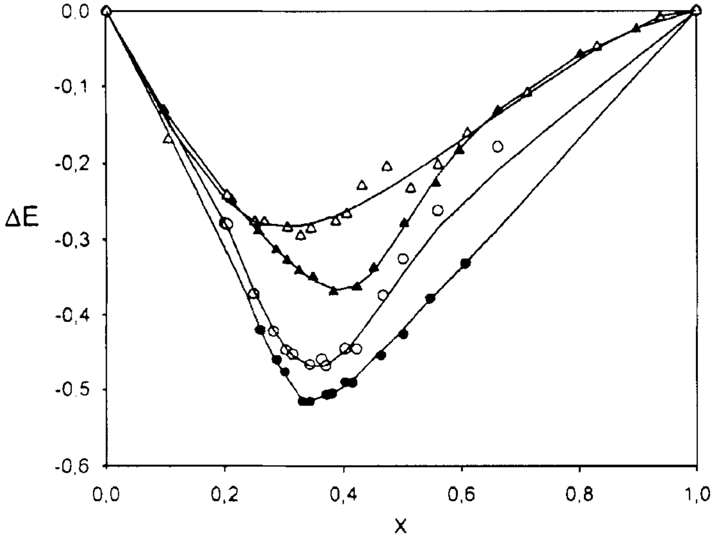


FIGURE 2 Job's plot for nonequimolar solutions of CPCl and AO7 at 485 nm. $T = 25°C$. $c_D^0 = 6 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$, $c_S^0 = 1,2 \cdot 10^{-4}\,\mathrm{mol \cdot l^{-1}}$. c_{KCl}: 0 : ●-●, 0.1 m : ○-○, 0.5 m : ▲-▲, 1 m: Δ-Δ.

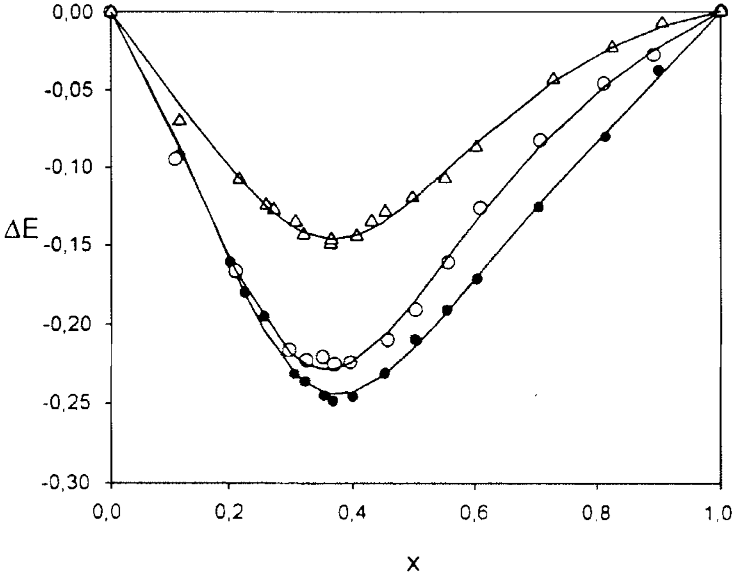


FIGURE 3 Job's plot for nonequimolar solutions of CPCl and AO7 at 485 nm. $T = 25°C$. $c_D^0 = 3 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$, $c_S^0 = 6 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$. c_{KCl}: 0 : ●-●, 0.1 m : ○-○, 1 m: Δ-Δ.

before [8, 9, 11] that the dye AO7 (D^-) and the surfactant CPCl (S^+) form simple stable 1 : 1 associates (DS), as shown by the following reaction:

$$D^- + S^+ \rightleftharpoons DS$$

For this simple reaction the following Eq. (1) derived [10, 11]:

$$K = \frac{(p-1)(1-2x_m)}{c_D^0 \cdot [(p+1)x_m - 1]^2}, \tag{1}$$

which determines the equilibrium association constant (K) as a function of the peak position X_m and the concentration of both mother solutions c_D^0 and $c_S^0 = p \cdot c_D^0$. The position of minimum X_m was defined by polynomial regression of the curves ΔE *versus* x in the Job's plots.

The equilibrium association constants calculated from the above equation from Job's plots shown on Figures 2 and 3 are listed in Tables I and II, respectively.

With increasing concentration of KCl the equilibrium constants decrease, which means that the addition of electrolyte decreases the

TABLE I Values of K for dye AO7 and surfactant CPCl interactions in solutions of 0, 0.1, 0.5 and 1 $\mathrm{mol \cdot kg^{-1}}$ KCl at 25°C. $c_D^0 = 6 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$ and $c_S^0 = 1.2 \cdot 10^{-4}\,\mathrm{mol \cdot l^{-1}}$

KCl concentration [$mol \cdot kg^{-1}$]	K [$dm^3\,mol^{-1}$]
0	$1.3 \cdot 10^6$
0.1	$7.4 \cdot 10^5$
0.5	$1.2 \cdot 10^5$
1	undefined

TABLE II Values of K for dye AO7 and surfactant CPCl interactions in solutions of 0, 0.1, 0.5 and 1 $\mathrm{mol \cdot kg^{-1}}$ KCl at 25°C. $c_D^0 = 3 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$ and $c_S^0 = 6 \cdot 10^{-5}\,\mathrm{mol \cdot l^{-1}}$

KCl concentration [$mol \cdot kg^{-1}$]	K [$dm^3\,mol^{-1}$]
0	$1.9 \cdot 10^6$
0.1	$8.4 \cdot 10^5$
1	undefined

tendency of AO7 and CPCl to associate. This can be also seen from Job's plots where the curves belonging to the solutions with less electrolyte deviate more from zero line than those with higher concentration of KCl. Or, in other words, ΔE decreases with increasing concentration of KCl. It is also evident that the curve of 1 m KCl has the smallest ΔE on both figures, which means that the interactions here are the weakest, although K couldn't be calculated for these measurements.

The very high values of K at all measurements indicate that strong interactions occur between anionic dye AO7 and cationic surfactant CPCl. It was found before [11, 13] that two kinds of attractive forces are present between oppositely charged ions of dyes and surfactants – long-range electrostatic Coulombic forces and short-range dispersion and hydrophobic forces.

It could be concluded that by the addition of KCl to the solutions of dyes and surfactants the influence of electrostatic attraction decreases because of the screening of charges on dye and surfactant ions by electrolyte ions.

Apart from screening the charges, the addition of electrolyte decreases the c.m.c of surfactants. The c.m.c of CPCl in water at 25°C is $9 \cdot 10^{-4}$ $\mathrm{mol \cdot l^{-1}}$ [14, 15]. The relevant data about the shift of c.m.c with addition of KCl for CPCl are not available from accessible literature. From the similar behaviour of mixtures, made from both different concentrated mother solutions of dye and surfactant, could be concluded that this influence is not expressed to a greater extent in our case. To confirm the influence of KCl on c.m.c and indirectly on dye-surfactant interactions. More experimental data are required.

CONCLUSIONS

The method of continuous variations or Job's method was used to study the interactions between the anionic dye AO7 and the cationic surfactant CPCl in solutions with different concentrations of a simple electrolyte KCl.

It could be seen from Job's plots and from the calculated equilibrium association constants that the addition of KCl diminishes the association of AO7 with CPCl. This 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.

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