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Conductometric investigation of dye–surfactant ion pair formation in aqueous solution

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Abstract

The formation of a dye–surfactant ion pair was studied using a conductometric method in which the conductance of aqueous solutions of C.I. Acid Orange 7 was measured in the presence of the cationic surfactants dodecylpyridinium chloride or hexadecylpyridinium chloride at four different temperatures. Two theoretical models to calculate the relevant equilibrium constants were derived. Both methods of calculation led to similar results that were in good agreement with other methods of investigation of dye–surfactant association. The results have shown that an increase in temperature lowers the tendency for ion pair formation as the equilibrium constants decrease with increasing temperature. A comparison of the behaviour of both surfactants revealed that the surfactant which contained the longer hydrophobic chain had a stronger tendency to associate with the dye and the corresponding equilibrium constants were considerably higher than those recorded for the surfactant with the shorter aliphatic chain. Such findings indicate that not only long range electrostatic forces but also short range, non-electrostatic interactions have a significant influence on dye–surfactant ion pair formation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conductometry; Anionic dye; Cationic surfactant; Ion pair; Equilibrium constant

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1. Introduction

Surfactants have been widely used as auxiliaries in many areas of textile finishing. Study of the interactions between dyes and surfactants in aqueous solution is necessary to fully understand the mechanism of finishing procedures and to select the correct auxiliary for dyeing and finishing. Fundamental to this is an understanding of the interactions that can occur between the dye and the surfactant and the influence of the dye and the surfactant structure [1].

In this paper, a conductometric method was used to study the formation of an ion pair between an anionic dye and a cationic surfactant because, while this method has been widely used in investigations of the association of simple ions, rarely has it been employed to investigate dye–surfactant systems [2]. The specific conductivity of dye–surfactant mixtures in aqueous solution was measured as a function of surfactant concentration. The anionic dye, C.I. Acid Orange 7 and the cationic surfactants dodecylpyridinium chloride and hexadecylpyridinium chloride were chosen for the study. In this paper are described two methods of calculation of equilibrium constants, each having been derived on the basis of corresponding theoretical models. The results of these calculations

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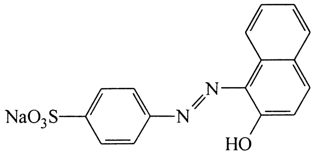
enabled the influence of both temperature and surfactant structure on ion pair formation to be evaluated.

2. Experimental

C.I. Acid Orange 7 (I) was synthesized and purified using the method previously described [3]. Dodecylpyridinium chloride (DPC) was obtained from Aldrich and hexadecylpyridinium chloride (CPC) was obtained from Merck. Each surfactant was recrystallized from acetone three times and dried at 50°C in vacuum.



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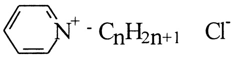
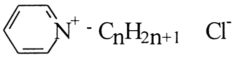


DPC, n = 12



CPC, n = 16

Stock solutions of dye and surfactants were prepared by mass. The exact concentration of the AO7 stock solution was determinated potentiometrically with the surfactant CPC. All solutions were prepared using doubly distilled water. Conductance measurements were performed using a laboratory microprocessor conductometer, model MA 5964 (Iskra) and a cell equipped with black platinum electrodes, type HEK 1213 (Iskra). Before each series of measurements, the cell constant was determinated using aqueous 0.01 M KCl solution [4]; their values ranged from 1.0330 to 1.0581 cm^{-1}.

Measurements were made in a thermostated glass cell. To perform each series of measurements, an exact volume of doubly distilled water was introduced into the cell and the specific conductivity of water measured. Afterwards, an exact volume of the dye stock solution was added to measure the specific conductivity of the dye at a given concentration, c_D° (DPC: $c_D^\circ = 9.271\times10^{-5}$ M; CPC: $c_D^\circ = 3.826\times10^{-5}$ M). The dye solution was then titrated with surfactant and the specific conductivity measured after each addition. Measurements were made at 15, 25, 35 and 45°C; the temperature of the solutions being maintained within ±0.02°C.

3. Results and discussion

In Fig. 1, the measured conductivity of the dye solution is presented as a function of the surfactant DPC concentration at 15, 25, 35 and 45°C. Fig. 2 shows the specific conductivity of the dye solution as a function of the surfactant CPC concentration at 15, 25 and 35°C.

If no interactions occurred between the dye and the surfactants in solution, the measured conductance would be expected to be the sum of the conductivities of the individual species in the solution; in turn, this would increase linearly with increasing concentration of the added surfactant. However, as is evident from Figs. 1 and 2, this was not the case for both dye–surfactant systems studied.

Fig. 1 shows that above a certain concentration of DPC at 15, 25 and 35°C, the measured conductance ceased to increase linearly and became lower than expected. These deviations can be explained as a consequence of the formation of a non-conducting or a less-conducting species in solution. It is very likely that the dye anion and the surfactant cation formed a practically non-conducting, soluble ion pair. Similarly, the measured conductance of the dye–CPC mixture did not increase linearly with increasing CPC concentration over the concentration range observed. This can, again, be explained as a consequence of the formation of a non-conducting, slightly dissociated ion pair.

As the measured conductance is the sum of the contributions of all free ions in the solution, it is not possible to determine the concentration of free or bound dye and surfactant ions and, thereby the equilibrium constant, solely on the basis of the measured conductivity. Thus, a theoretical model which describes the conditions within the solution

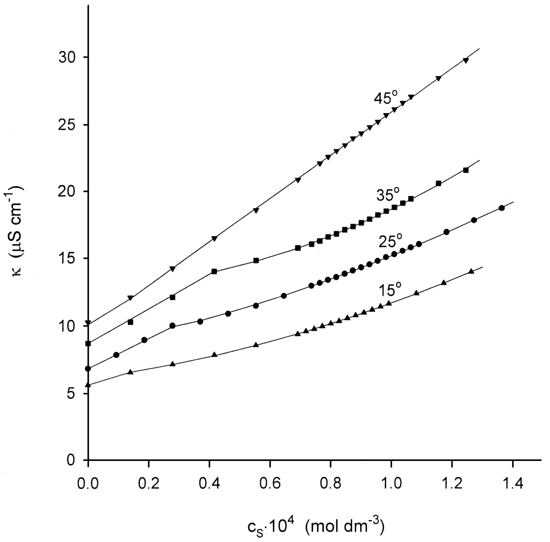


Fig. 1. Specific conductivity of the dye–DPC mixture in aqueous solution as a function of the DPC concentration at 15°C (▲), 25°C (●), 35°C (■) and 45°C (▼).

must be applied; two methods of calculating the equilibrium constants were used.

3.1. Method 1

This is based on a comparison between the measured conductivity of the dye–surfactant mixture and a theoretical straight line which represents the sum of the specific conductivities of the dye and the surfactant.

If it is assumed that the dye anion and the surfactant cation form a non-conducting, slightly dissociated ion pair (DS) in solution, the reaction between the dye, NaD, and the surfactant, SCl, can be described as an equilibrium reaction:

$$D^- + S^+ \rightleftharpoons DS \tag{1}$$

If there was no interaction between the surfactant and dye in the solution, the measured conductance would be given by Eq. (2):

$$10^3\kappa = c_D\lambda_{Na^+} + c_D\lambda_{D^-} + c_S\lambda_{S^+} + c_S\lambda_{Cl^-} \tag{2}$$

where c_D and c_S are the molar concentrations of the dye and surfactant, respectively and λ_{Na^+}, λ_{D^-}, λ_{S^+} and λ_{Cl^-} are the equivalent conductances of the ions Na^+, D^-, S^+ and Cl^-.

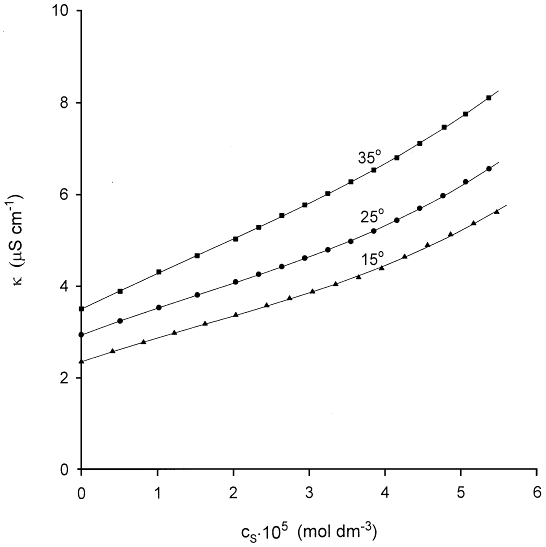


Fig. 2. Specific conductivity of the dye–CPC mixture in aqueous solution as a function of the CPC concentration at 15°C (▲), 25°C (●) and 35°C (■).

The results presented above showed that the measured conductance did not increase linearly with surfactant concentration and it was lower than expected. If this were to be explained by the formation of non-conducting ion pairs, which caused a decrease in the concentration of free ions, Eq. (2) becomes:

$$\begin{aligned}10^3\kappa &= (c_D - c_{DS})\lambda_{D^-} + c_D\lambda_{Na^+}\\ &\quad + (c_S - c_{DS})\lambda_{S^+} + c_S\lambda_{Cl^-}\end{aligned} \tag{3}$$

where c_{DS} is the concentration of the non-conducting dye–surfactant ion pairs. After deduction of Eq. (3) from Eq. (2) we obtain:

$$10^3\Delta\kappa = c_{DS}\left(\lambda_{D^-} + \lambda_{S^+}\right) \tag{4}$$

where $\Delta\kappa$ is the difference between the theoretical and measured conductances at a given surfactant concentration.

As measurements were made in dilute solution of the dye and surfactant, Eq. (4) can be written as:

$$10^3\Delta\kappa \approx c_{DS}\left(\lambda^{\circ}_{D^-} + \lambda^{\circ}_{S^+}\right) = c_{DS}\Lambda^{\circ}_{DS} \tag{5}$$

where Λ^o_{DS} is the equivalent conductance of the dye–surfactant ion pair at infinite dilution. The Λ^o_{DS} values were determined experimentally by measuring the specific conductivities of the surfactants DPC and CPC and the dye; these values are shown in Table 1.

The equilibrium constant for the reaction of ion pair formation is given by Eq. (6).

$$K = \frac{c_{DS}}{(c_D - c_{DS})(c_S - c_{DS})} \tag{6}$$

The equilibrium constants K, obtained in this way, varied slightly with surfactant concentration. However, the deviations were too large to be caused merely by the influence of the activity coefficients. As the values K or ln K showed no tendency to increase or decrease with surfactant concentration, c_S, it was not possible to obtain the thermodynamic equilibrium constant by means of extrapolation to the concentration $c_S = 0$ [5,6]. This problem was solved by defining the maximum value of the equilibrium constant for a given system, i.e. the maximum of the function ln K versus c_S over the observed concentration range. This procedure gave results of very good repeatability and, in addition, it did not include extrapolation to $c_S = 0$ which would be less reliable for those measurements taken at low surfactant concentrations because of temperature oscillations, the influence of CO_2 from the air and adsorption of any less-soluble complex on the glass surface of the conductivity cell.

Table 2 displays the results of the calculation made using Method 1; the numbers represent the average values of several repeats for a given dye–surfactant system.

3.2. Method 2

At the equivalent point, the concentration of dye, c_D, is the same as the concentration of added surfactant, c_S, and so, $c_D = c_S = c$. At this point, the concentration of ions D^- is equal to the concentration of ions S^+ and the ion pair, DS, can be treated as a partly associated electrolyte. In this case, the degree of ionization, α, can be defined as [5]:

$$\alpha = \frac{\Lambda}{\Lambda_\varepsilon} \tag{7}$$

where Λ is the measured equivalent conductance of the dye–surfactant mixture, diminished for the conductance of NaCl, which is also present as a product of reaction between dye NaD and surfactant SCl Λ_ε. is the equivalent conductance of the hypothetic, completely ionized electrolyte at the concentration $c_i = \alpha c$. The evaluation of Λ_ε is based on the assumption that at low ion concentrations the conductivities are additive (8):

$$\Lambda_{\varepsilon DS} = \Lambda_{NaD} + \Lambda_{SCl} - \Lambda_{NaCl} \tag{8}$$

The concentration c_i can be determinated by a series of successive approximations; the first of these is obtained as:

$$c'_i = \frac{c\Lambda}{\Lambda^\circ_{DS}}$$

$$\Lambda'_\varepsilon = \Lambda_{NaD} + \Lambda_{SCl} - \Lambda_{NaCl}$$

$$c''_i = \frac{c\Lambda}{\Lambda'_\varepsilon}$$

Table 1
Equivalent conductances at infinite dilution in water for dye, DPC, CPC, ion pair *DS* and ion S^+ [units: T (°C); Λ°, λ° (Ω^{-1} cm^2 mol^{-1})]

T	Λ°_{AO7}	Λ°_{DPC}	$\Lambda^\circ_{DS,DPC}$	$\lambda^\circ_{S^+,DPC}$	Λ°_{CPC}	$\Lambda^\circ_{DS,CPC}$	$\lambda^\circ_{S^+,CPC}$
15	58.5	89.1	46.42	27.69	78.9	36.22	17.49
25	74.4	112.8	60.75	36.45	98.4	46.35	22.05
35	92.3	138.4	76.95	46.19	118.9	57.45	26.69
45	110.3	161.0	88.65	52.08	–	–	–

The procedure is complete when c_i and Λ_ε are constant within the experimental error. The equilibrium constant is then given by (9):

$$K = \frac{1-\alpha}{\alpha^2 c} \quad (9)$$

The results of calculations using Method 2 are given in Table 3.

As the results of calculations obtained using Method 2 are in accordance with those obtained using Method 1, both methods produce the same conclusions. The equilibrium constants obtained for the system dye–CPC in water at 25°C are in good agreement with the results of both the potentiometric [7] and spectrophotometric examinations [8]. The equilibrium constants obtained for dye–DPC system in water at 25°C, however, are 10 times larger than the values obtained using the potentiometric study [7]. These discrepancies are the consequence of the different theoretical models that were used in the calculations; by considering only one surfactant cation to be bound to the dye anion, the results of the potentiometric study would be in very good agreement with the results secured using conductometric method of investigation.

The results obtained conductometrically using Methods 1 and 2 revealed that an increase in temperature caused a decrease in the equilibrium constants as well as an increase in the standard free enthalpy changes for both surfactants. It is therefore evident that at higher temperatures, the tendency to form dye–surfactant ion pairs lessens. As evident from Fig. 1 and Table 2, the measured conductance of the dye–DPC system in water at 45°C increased linearly with increasing concentration of surfactant. There were no deviations of the measured values from the theoretical straight line and so the formation of ion pairs does not occur, therefore $K = 0$.

According to the results, the equilibrium constants for the dye–CPC system are considerably higher than those for dye–DPC system, indicating a stronger tendency to ion pair formation. Such behaviour is in accordance with Traube's rule [9] and is clearly a consequence of the structural characteristics of CPC. Compared to DPC, the surfactant CPC has a longer aliphatic chain due to four additional methylene groups. Clearly, the formation of dye–surfactant ion pairs is the consequence of mutual influences of long range electrostatic forces and hydrophobic, dispersion and

Table 2
Equilibrium constants K and standard free enthalpy changes ΔG° for surfactant–dye ion pair formation calculated using Method 1

	DPC–dye		CPC–dye	
T (°C)	K (dm^3 mol^{-1})	ΔG° (kJ mol^{-1})	K (dm^3 mol^{-1})	ΔG° (kJ mol^{-1})
15	7.47×10^4	−26.9	3.32×10^5	−30.5
25	2.11×10^4	−24.7	3.04×10^5	−31.3
35	1.92×10^4	−25.3	2.08×10^5	−31.4
45	0	–	–	–

Table 3
Equilibrium constants K and standard free enthalpy changes ΔG° for surfactant–dye ion pair formation calculated using Method 2

	DPC–dye		CPC–dye	
T (°C)	K (dm^3 mol^{-1})	G° (kJ mol^{-1})	K (dm^3 mol^{-1})	G° (kJ mol^{-1})
15	3.90×10^4	−25.3	5.61×10^5	−31.7
25	2.12×10^4	−24.7	5.43×10^5	−32.7
35	1.81×10^4	−25.1	2.20×10^5	−31.5
45	0	–	–	–

other short-range attractive forces. Due to a longer hydrophobic chain, the surfactant CPC has a greater opportunity to interact with the dye in solution.

4. Conclusions

Conductance measurement proved to be a simple method for the detection of dye–surfactant ion pairs in an aqueous solution. As the specific conductivity of the individual species in the solution increased linearly with concentration, a gradual lowering of specific conductivity after a certain concentration of added surfactant indicates the formation of non-conducting species. The main drawback to conductometric investigations of dye–surfactant ion pair formation is that for a numerical description, namely the calculation of equilibrium constants, a suitable theoretical model is required and this can include certain simplifications.

The two methods of calculation described gave results that were in good agreement with those obtained using other techniques of investigating dye–surfactant complex formation. A comparison of the behaviour of the two surfactants of different chain length showed that surfactant structure had a significant influence on formation of ion pairs with the particular dye used. The equilibrium constants were considerably higher in the case of the surfactant with the longer aliphatic chain proving the importance of non-electrostatic forces in dye–surfactant complex formation.

An increase in temperature reduced the tendency to ion pair formation. In addition, at higher temperatures, a higher concentration of the surfactant DPC was required to initiate the process of ion pair formation.

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