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Anionic dye–cationic surfactant interactions in water–ethanol mixed solvent

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Abstract

The interactions between an anionic dye and two cationic surfactants were studied by conductometry. The specific conductance of dye–surfactant mixtures was measured at three different temperatures in water–ethanol mixed solvent, containing 5, 10, 15 or 20 wt.% of ethanol. The equilibrium constants and other thermodynamic functions for the process of dye–surfactant ion pair formation were calculated on the basis of two theoretical models. The results showed that the presence of ethanol decreases the tendency for ion pair formation. According to the results, long range as well as short range interactions are responsible for the formation of the ion pair. The importance of long range electrical forces is basically to bring the dye anion and the surfactant cation close enough to enable the action of short range interactions whose contribution represents the major part of the standard free enthalpy change for the formation of the anionic dye–cationic surfactant ion pair. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic dye; Cationic surfactant; Ion pair; Conductometry; Water–ethanol mixture; Thermodynamics

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1. Introduction

The nature of the interactions between dyes and surfactants is one of the basic pieces of information for understanding the process of dyeing and finishing of textile material. To study this phenomenon, numerous investigations have been made and various investigation techniques have been used to establish which interactions are decisive for the process of dye–surfactant complex formation and for the size and shape of the complex [1–6].

In this paper, a conductometric study of the interactions between the anionic dye C.I. Acid Orange 7 and two cationic surfactants, hexadecylpyridinium chloride and dodecylpyridinium chloride, is described. To investigate the importance of different types of interactions for the formation of a dye–surfactant ion pair, a series of conductance measurements was performed at three different temperatures in water–ethanol mixtures containing various amounts of ethanol. Two methods of calculation were applied to obtain the equilibrium constants and other thermodynamic functions for the formation of the dye–surfactant ion pair. The results enabled the influence of ethanol on the dye–surfactant ion pair formation and the significance of long range and

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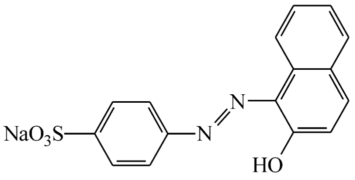
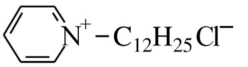
short range interactions for the process to be evaluated.

2. Experimental

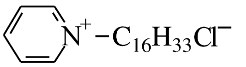
C.I. Acid Orange 7 (AO7) was synthesized and purified using a method already described [7]. Dodecylpyridinium chloride (DPC) was obtained from Aldrich and hexadecylpyridinium chloride (CPC) was obtained from Merck. They were each recrystallized from acetone three times and dried at 50 °C in vacuum.



AO7



DPC



CPC

Stock solutions of dye and surfactants were prepared by mass as previously described [8]. As solvent, doubly distilled water or water–ethanol mixtures containing 5, 10, 15 or 20 wt.% of ethanol (absolute ethanol, Riedel de Haën) were used. Conductance measurements were made at 15, 25 and 35 °C using the apparatus and method already described [8].

3. Results and discussion

In Fig. 1, the specific conductivity of the dye AO7–surfactant DPC mixture in 5% ethanol is presented at 15, 25 and 35 °C as a function of surfactant DPC concentration. As is evident, the measured conductivity does not always increase linearly with the surfactant concentration. This can be explained as a consequence of the presence of a non-conducting species in the solution [8]. However, the deviations of measured values from linearity decrease with increasing temperature. At 35 °C the measured conductance of the AO7–DPC mixture in 5% ethanol increases linearly, indicating that there are no non-conducting species in the solution.

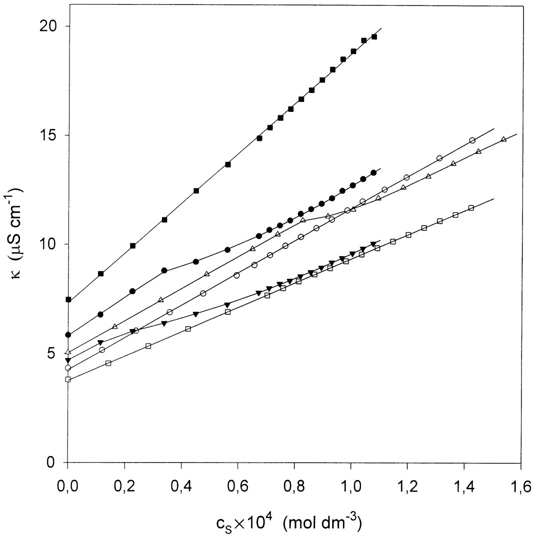


Fig. 1. Specific conductivity of the AO7–DPC mixture as a function of surfactant DPC concentration in water–ethanol mixtures. ▼ 5% ethanol, $T = 15\,°C$; ● 5% ethanol, $T = 25\,°C$; ■ 5% ethanol, $T = 35\,°C$; △ 10% ethanol, $T = 25\,°C$; ○ 15% ethanol, $T = 25\,°C$; □ 20% ethanol, $T = 25\,°C$.

Also in Fig. 1, the specific conductivity of the system AO7–DPC in solvents containing different amounts of ethanol is presented as a function of surfactant DPC concentration. Fig. 1 shows that the deviations of measured values from linearity decrease with increasing amount of ethanol in the solvent. In the presence of 15 or 20% of ethanol, the measured conductivity increases linearly with surfactant DPC concentration, indicating that there are no non-conducting or less-conducting species in the solution.

In Fig. 2, the specific conductivity of AO7–CPC mixtures in solvents containing different amounts of ethanol is presented as a function of surfactant CPC concentration. Although significant differences in behaviour of the AO7–CPC mixture in solutions containing different amounts of ethanol can be detected, a direct comparison of the results on Fig. 2 is difficult because the increasing amount of ethanol in the solvent causes a decrease in the

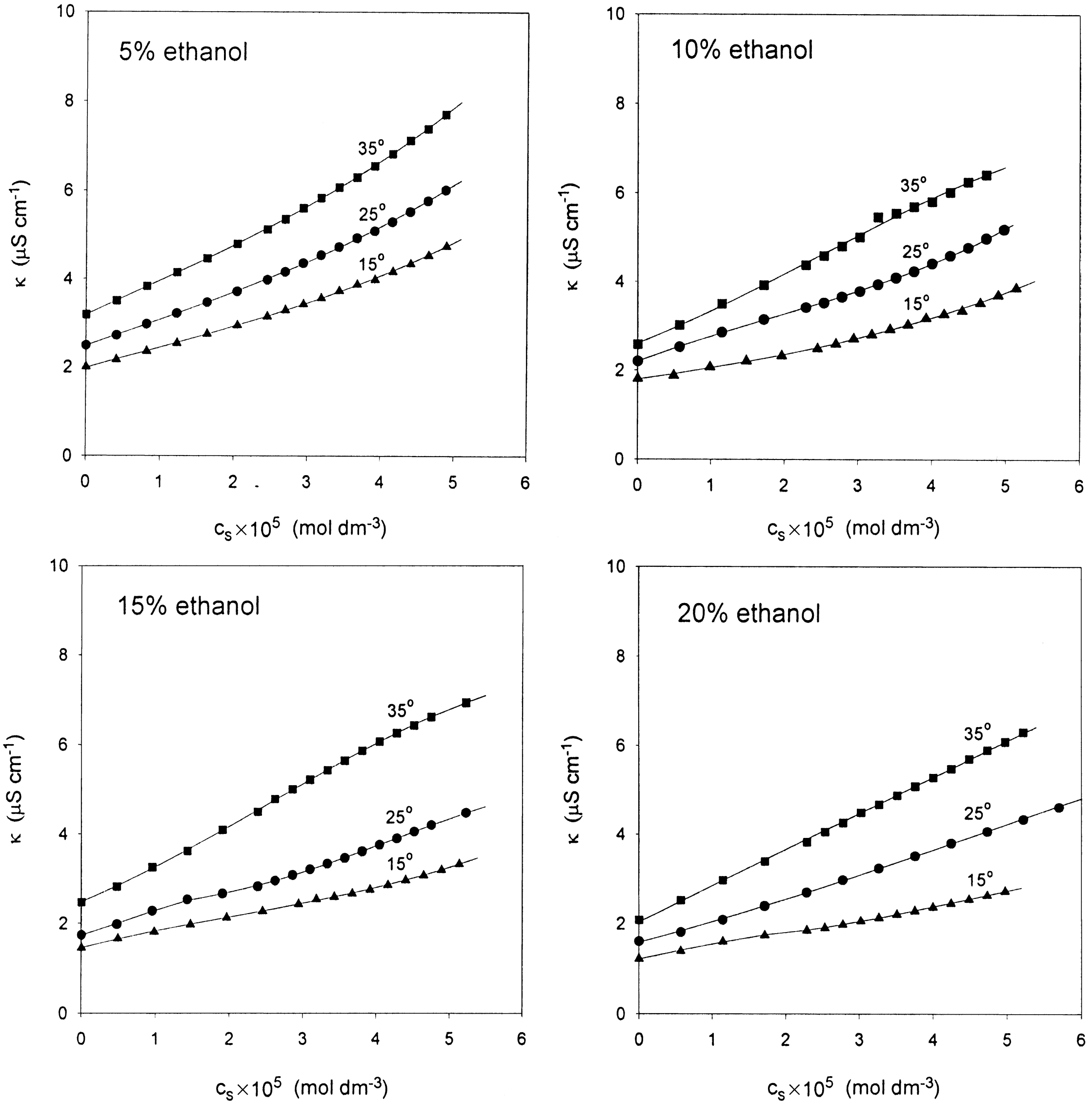


Fig. 2. Specific conductivity of the AO7–CPC mixture at 15 °C (▲), 25 °C (●) and 35 °C (■) as a function of surfactant CPC concentration in water–ethanol mixtures containing 5, 10, 15 or 20 wt.% ethanol.

measured specific conductivity due to the changed dielectric constant of the solvent. Therefore, to calculate the thermodynamic functions of dye–surfactant complex formation, a theoretical model is necessary.

The equilibrium constants for dye–surfactant complex formation were calculated using two theoretical methods. The first method [8] is based on the presumption that the dye anion and the surfactant cation form a non-conducting ion pair in the solution:

$$D^- + S^+ \rightleftharpoons DS \qquad (1)$$

The equilibrium constant is for this case given by Eq. (2):

$$K = \frac{c_{\mathrm{DS}}}{(c_{\mathrm{D}} - c_{\mathrm{DS}})(c_{\mathrm{S}} - c_{\mathrm{DS}})} \tag{2}$$

The results of calculations using Method 1 are given in Table 1; the numbers represent the average values of several repeats for a given dye–surfactant system.

The values ΔG^{o}, ΔH^{o} and ΔS^{o} for the reaction of ion pair formation were calculated using the usual thermodynamic equations (Eqs. (3)–(5)) and are shown in Fig. 3.

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

$$\Delta H^{\mathrm{o}} = \left[\frac{\partial(\Delta G^{\mathrm{o}}/T)}{\partial(1/T)}\right]_P \tag{4}$$

$$\Delta S^{\mathrm{o}} = \frac{\Delta H^{\mathrm{o}} - \Delta G^{\mathrm{o}}}{T} \tag{5}$$

The second method of calculation of the equilibrium constants is also limited to the formation of a dye–surfactant ion pair. It is based on the presumption that at the equivalent point the dye–surfactant ion pair can be treated as a partly associated electrolyte [8]. For this case, the equilibrium constant is given by Eq. (6):

$$K = \frac{1 - \alpha}{\alpha^2 c} \tag{6}$$

where α is the degree of ionization [9]. The calculated equilibrium constants obtained with Method 2 are given in Table 2. The values ΔG^{o}, ΔH^{o} and $T\Delta S^{\mathrm{o}}$ are shown in Fig. 4.

The results of calculations were used to evaluate the importance of long range and short range interactions in the process of ion pair formation. Although the numerical values obtained by Method 1 slightly differ from those obtained by Method 2, the general trends are in good agreement and they provide the same conclusions.

The formation of the dye–surfactant ion pair is a consequence of mutual influences of long range and short range interactions. The surfactants DPC and CPC as well as dye AO7 possess a strong polar group. In aqueous solution they dissociate into ions and therefore electrostatic attractive interactions can appear between the dye anion and the surfactant cation. The non-polar part of the surfactant is a long aliphatic chain so it is very likely that hydrophobic interactions will appear in the process. As both surfactants and dye AO7 possess one or more aromatic rings, $\pi{-}\pi$ electronic interactions and Van der Waals interactions can also be expected.

The contribution of electrostatic interactions can be estimated from Eq. (7) which describes the

Table 1
Equilibrium constants *K* for dye–surfactant ion pair formation in water–ethanol mixtures calculated using Method 1[a]

% Ethanol	*T*	*K*	
		AO7–DPC	AO7–CPC
5	15	7.20×10^4	5.17×10^5
	25	4.02×10^4	3.43×10^5
	35	0	1.44×10^5
10	15	–	5.96×10^5
	25	1.34×10^4	1.73×10^5
	35	–	3.75×10^4
15	15	–	2.05×10^5
	25	0	9.70×10^4
	35	–	4.80×10^3
20	15	–	6.65×10^5
	25	0	1.71×10^4
	35	–	0

[a] Units: *T* (°C); *K* ($\mathrm{dm^3\ mol^{-1}}$).

Table 2
Equilibrium constants *K* for dye–surfactant ion pair formation in water–ethanol mixtures calculated using Method 2[a]

% Ethanol	*T*	*K*	
		AO7–DPC	AO7–CPC
5	15	1.30×10^5	2.41×10^5
	25	3.96×10^4	1.97×10^5
	35	0	9.06×10^4
10	15	–	3.62×10^5
	25	6.08×10^4	1.09×10^5
	35	–	2.64×10^4
15	15	–	5.29×10^4
	25	0	1.20×10^5
	35	–	8.14×10^3
20	15	–	2.88×10^4
	25	0	5.03×10^3
	35	–	0

[a] Units: *T* (°C); *K* ($\mathrm{dm^3\ mol^{-1}}$).

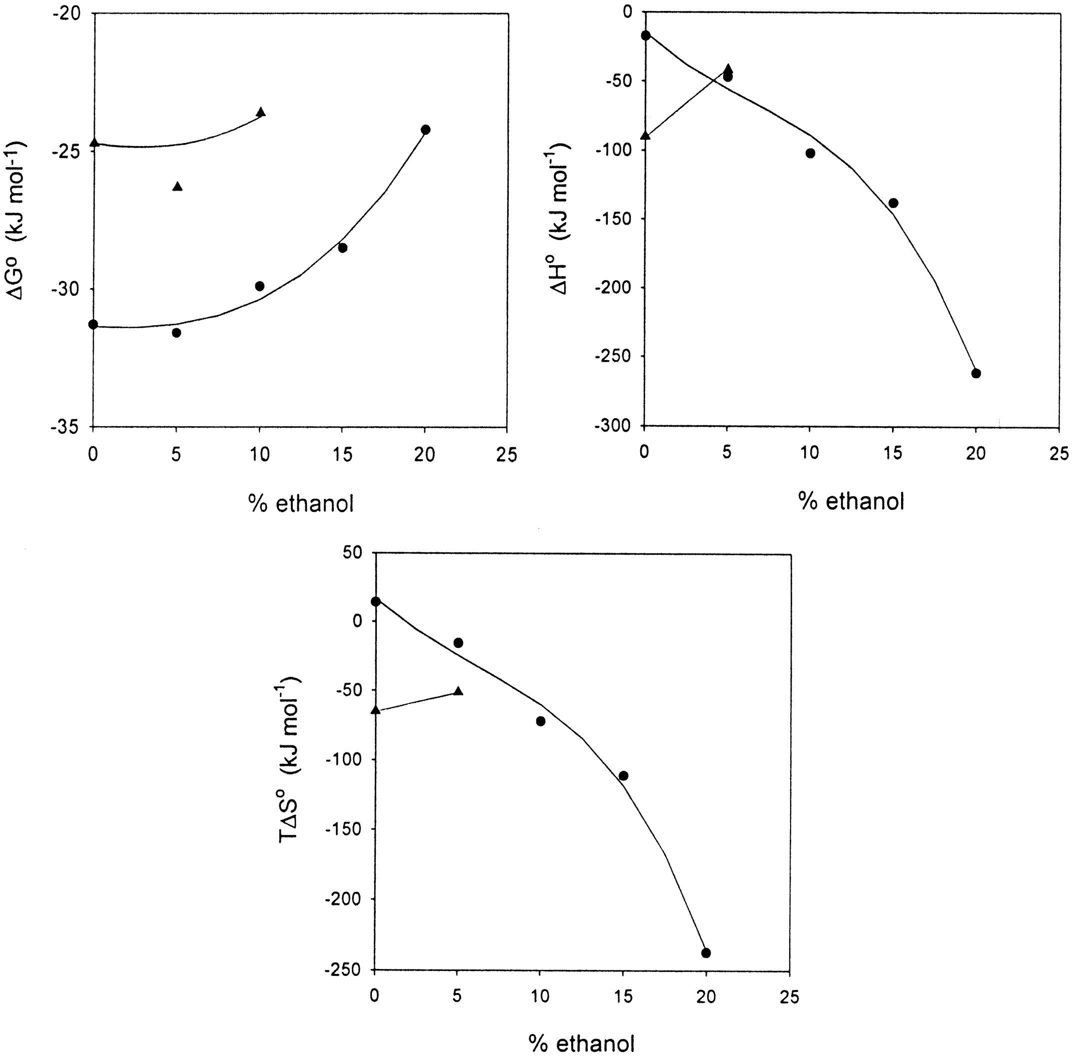


Fig. 3. ΔG^{o}, ΔH^{o} and $T\Delta S^{\text{o}}$ calculated using Method 1 for the mixtures AO7–DPC (▲) and AO7–CPC (●) at 25 °C as a function of ethanol wt.% in the solvent.

electrical work required for the process of transferring two charges on the distance a [10–12].

$$\Delta G^{\text{o}}_{\text{el}} = -\frac{|z_1 z_2| e_0^2 N_{\text{A}}}{\varepsilon a} \tag{7}$$

where z_1 and z_2 are the valencies of cation and anion, respectively, e_0 is the unit charge, N_{A} the Avogadro number and ϵ the dielectric constant of the solvent. a represents the contact distance, i.e. the sum of the radii of the two ions. On the basis of the Bjerrum equation [9], this was estimated to be approximately 4×10^{-10} m. Using Eq. (7), the contribution of attractive electric interactions was estimated to be approximately −5 kJ/mol.

With an increase in the proportion of ethanol in the water–ethanol mixed solvent, the values of $\Delta G^{\text{o}}_{\text{el}}$ decrease because of the reduction in dielectric constant of the solvent. If $\Delta G^{\text{o}}_{\text{el}}$ would represent the crucial contribution in the standard free enthalpy change of the reaction, an increase of the proportion of ethanol in the solvent would also

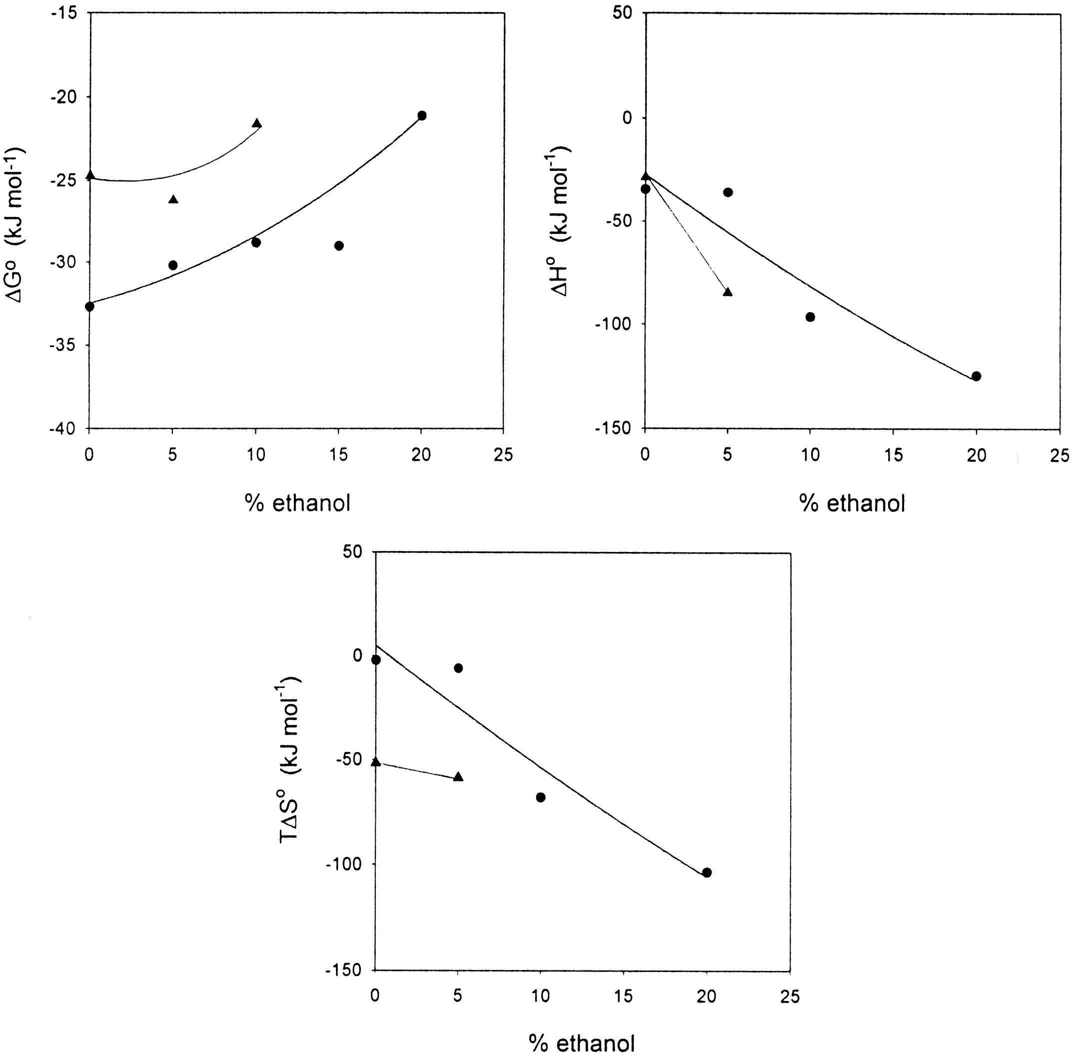


Fig. 4. ΔG^{o}, ΔH^{o} and $T\Delta S^{o}$ calculated using Method 2 for the mixtures AO7–DPC (▲) and AO7–CPC (●) at 25 °C as a function of ethanol wt.% in the solvent.

cause an increased tendency for dye–surfactant ion pair formation. The calculated values K and ΔG^{o}, however, showed exactly the opposite.

According to the results, the long range electrostatic interactions contribute only a minor part to the standard free enthalpy change of the reaction, ΔG^{o}, which increases with increasing ethanol content in the solution and was calculated to range from −40 to −20 kJ/mol for both methods of calculation. Therefore, it can be presumed that the electrical interactions and their negative contribution ΔG^{o}_{el} support the formation of an ion pair, but their contribution is too small to be regarded as the only driving force of the reaction. Apparently, their major function is to attract the dye anion and the surfactant cation at the beginning of the process close enough to enable the action of short range interactions which are finally responsible for the formation of the ion pair.

Evidently, the behaviour of the dye–surfactant system in different solvents is not influenced only by the dielectric constant of the solvent but also by its other characteristics. The results showed that the changes of standard entropy for the AO7–DPC system are negative in all solvents studied. For the AO7–CPC system in water [8] the values ΔS^o are positive (calculated by Method 1) or slightly negative (calculated by Method 2). The positive values of ΔS^o calculated for the surfactant with the longer aliphatic chain indicate the presence of hydrophobic interactions. The importance of these interactions for the formation of the AO7–CPC ion pair in water is also confirmed by the fact that the change of standard enthalpy for this reaction is considerably higher than for the formation of the AO7–DPC ion pair in water [8]. Nevertheless, the equilibrium constants calculated for the AO7–CPC system in water are higher than those calculated for AO7–DPC in water; indicating the decisive contribution of the $T\Delta S^o$ part.

It is well known that the presence of ethanol has a negative influence on hydrophobic interactions due to its destructive action on structured water molecules around the hydrophobic parts of the surfactant and dye molecules [13,14]. This is also evident from the results of the measurements: ΔS^o of the AO7–CPC system decreases with increasing amount of ethanol in the solvent. It is interesting that an increasing amount of ethanol in the solvent also causes a rapid decrease of the standard enthalpy change (Figs. 3 and 4), but nevertheless the equilibrium constants decrease and standard free enthalpy changes increase. Obviously, the contribution of ΔH^o is dominated by the $T\Delta S^o$ part, proving again the importance of the hydrophobic interactions.

These findings demonstrate the significant influence of hydrophobic interactions on the formation of the anionic dye–cationic surfactant ion pair. However, with the exception of one system examined, the calculated values of ΔS^o were negative and, therefore, it is not possible to regard the hydrophobic interactions as the main force in this process.

4. Conclusions

The addition of ethanol to the solvent reduces dye–surfactant ion pair formation. Its influence can be interpreted in two ways: firstly, the increase of the ethanol content in the water–ethanol mixed solvent causes a decrease of the dielectric constant of the solvent and thereby causes an increase of attractive electrical interactions; secondly, ethanol is known for its negative influence on hydrophobic interactions because of its ability to break down the structured water molecules around the hydrophobic parts of the solute. According to the results, the first influence is dominated by the second one as the equilibrium constants of the dye–surfactant systems examined decrease with increasing amount of ethanol in the solvent.

The results presented lead to the conclusion that long range electrical forces as well as short range attractive forces are responsible for the dye–surfactant ion pair formation. The importance of electrical forces is basically to bring the dye anion and the surfactant cation close enough to enable the action of short range interactions whose contribution represents the major part of the standard free enthalpy change of the reaction.

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Appendix

Equivalent conductances at infinite dilution for NaCl, AO7, DPC, CPC, ion pair DS and ion S^+ in water–ethanol mixtures containing 5, 10, 15 and 20 wt.% ethanol[a]

	T	$\Lambda^\circ_{\mathrm{NaCl}}$	$\Lambda^\circ_{\mathrm{AO7}}$	$\Lambda^\circ_{\mathrm{DPCl}}$	$\Lambda^\circ_{\mathrm{DS,DPCl}}$	$\lambda^\circ_{\mathrm{S^+,DPCl}}$	$\Lambda^\circ_{\mathrm{CPCl}}$	$\Lambda^\circ_{\mathrm{DS,CPCl}}$	$\lambda^\circ_{\mathrm{S^+,CPCl}}$
5% Ethanol	15	91.1	52.8	73.7	35.4	21.1	73.4	35.1	16.9
	25	117.4	63.9	91.5	38.0	22.8	93.0	39.5	18.8
	35	143.0	80.3	107.5	44.8	26.9	115.4	52.7	24.5
10% Ethanol	15	77.1	43.9	–	–	–	56.2	23.0	11.1
	25	98.3	55.7	77.8	35.2	21.12	80.3	37.7	17.9
	35	125.9	67.3	–	–	–	97.8	39.2	18.2
15% Ethanol	15	61.6	34.8	–	–	–	48.1	21.3	10.3
	25	87.1	47.9	64.7	25.5	15.3	62.3	23.1	11.0
	35	112.5	63.5	–	–	–	85.5	36.5	17.0
20% Ethanol	15	52.3	26.0	–	–	–	40.1	13.8	6.7
	25	72.5	41.2	–	–	–	57.6	26.3	12.5
	35	99.1	54.7	–	–	–	70.9	26.5	12.3

[a] Units: T (°C); Λ°, λ° (Ω^{-1} cm^2 mol^{-1}).