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Title: Effects of micelle nature and concentration on the acid dissociation constants of the metal extractor PADA

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Abstract: The pyridine-2-azo-p-dimethylaniline (PADA) ligand presents two acid dissociation constants, being pKa1 related to the pyridinium and pKa2 related to the anilinium residue. These have been measured by spectrophotometric titrations in aqueous solutions containing either the anionic (SDS), or the non-ionic (Triton X-100) or the cationic (DTAC) surfactants. The pKai shifts of the charged systems from that of the PADA/Triton X-100 reference (ΔpKai0) are compared. For PADA/DTAC ΔpKa10 = 0.05 and ΔpKa20 = 0.6. For PADA/SDS ΔpKa10 = 2.1 and ΔpKa20 = 2.1 both yielding the value of -126 mV for the surface potential (ψ) of SDS. The ψ value, lying between the calculated Stern potential and the zeta potential, indicates that the dye is located on the SDS micelles between the fixed and the shear layer. In contrast, the behaviour of PADA/DTAC is explained assuming that the positively charged deprotonation sites of PADA are forced to protrude towards the bulk solvent by the positive charges of DTAC micelles. The shifts of the apparent pKai from the aqueous values (ΔpKaiw) have also been analysed. Concerning PADA/Triton X-100, the shifts ΔpKa1w = -0.1 and ΔpKa2w = -0.9 are rationalized in terms of dielectric constant reduction at the reaction sites. Concerning PADA/DTAC, ΔpKa1w= -0.05 and ΔpKa2w= -0.3 whereas, for PADA/SDS, ΔpKa1w = 2.0 and ΔpKa2w = 1.2. The pKa2w values decrease on raising the surfactant concentrations for all the investigated systems. This behaviour is explained assuming that the increase of the overall micellar surface and, by consequence, of the reaction sites number, results in a site dilution effect which disfavours proton association. The addition of NaCl induces changes of pKa1 and pKa2 which are explained in terms of (large) reduction of ψ for PADA/SDS and of (small) reduction of the dielectric constant for the other systems.

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Pisa, July 10th 2014

Dear Editor,
we submit to your attention the article entitled:

Effects of micelle nature and concentration on the acid dissociation constants of the metal extractor PADA

by Sabriye Aydinoglu, Tarita Biver, Fernando Secco and Marcella Venturini

to be considered for publication in Colloids and Surfaces A.

This paper reports on a detailed analysis of the influence of anionic (SDS), non–ionic (Triton X-100) or cationic (DTAC) micellar media on the acid-base characteristics of a metal extracting ligand (pyridine-2-azo-p-dimethylaniline, PADA). The in depth analysis here presented for PADA could represent a guideline to be employed to predict the behaviour of similar systems, and therefore, of interest for a wide readership.

The interest on the effects of surfactants on drug properties is continuously increasing and micellar systems have attracted attention also as potential extracting media, in particular for precious/toxic metal ions. The H^+ concentration in the bulk solution generally differs from the value on the micelle surface and this can have dramatic repercussions on the acid characteristic of a weak acid (as many ligands are) and, therefore, on the speciation of the ligand on the micelle surface.

Despite the increasing interest on surfactants and micellar phases and the work of different authors, some details of the reactivity changes of ligands on the micellar phase still need to be analysed and/or are often underestimated.

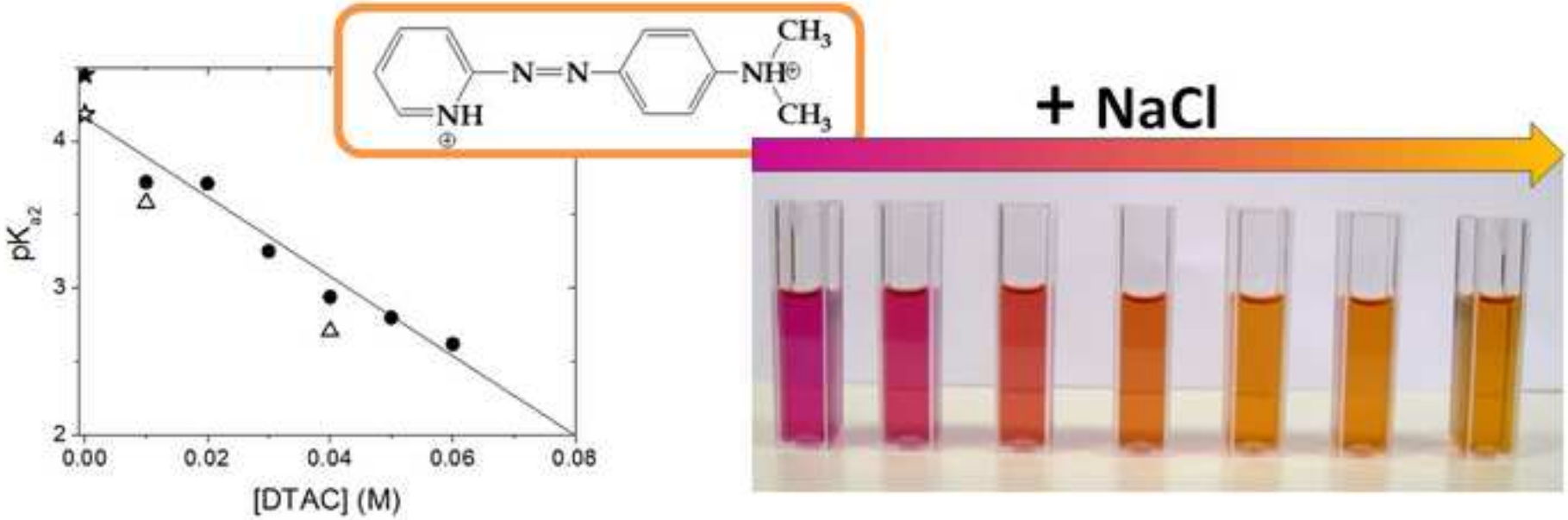
The results of this work clearly indicate that for the analysed ligand both the pK_{a1} and pK_{a2} shifts induced by the presence of micelles strongly depend on the protolytic equilibrium involved, on the charge of the micelles, on the dye components absorbed and on the ionic medium (absence or presence of NaCl). These shifts are discussed on the basis of surface potential (ψ) of SDS, ligand position on the micelle, dielectric constant reduction at the reaction sites and site dilution effects.

With kindest regards

Fernando Secco
Tarita Biver

*Graphical Abstract (for review)

The pKs of PADA ligand shift in the presence of micelles, depending on equilibrium involved, charge of the micelles, dye components absorbed and ionic medium



Highlights

- SDS (-), DTAC (+) or TritonX (non-ionic) micelles differently affect PADA's pKs
- In the SDS negative micelle, PADA is located between the fixed and the shear layer
- In the DTAC positive micelle, PADA protrudes towards the bulk solvent
- In Triton X, dielectric constant reduction at the reaction sites occurs
- NaCl induces reduction of surf. potential (SDS) or of dielectric constant (others)

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Effects of micelle nature and concentration on the acid dissociation constants of the metal extractor PADA

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Abstract

The pyridine-2-azo-p-dimethylaniline (PADA) ligand presents two acid dissociation constants, being pK_{a1} related to the pyridinium and pK_{a2} related to the anilinium residue. These have been measured by spectrophotometric titrations in aqueous solutions containing either the anionic (SDS), or the non–ionic (Triton X-100) or the cationic (DTAC) surfactants. The pK_{ai} shifts of the charged systems from that of the PADA/Triton X-100 reference (ΔpK_{ai}^0) are compared. For PADA/DTAC $\Delta pK_{a1}^0 = 0.05$ and $\Delta pK_{a2}^0 = 0.6$. For PADA/SDS $\Delta pK_{a1}^0 = 2.1$ and $\Delta pK_{a2}^0 = 2.1$ both yielding the value of -126 mV for the surface potential (ψ) of SDS. The ψ value, lying between the calculated Stern potential and the zeta potential, indicates that the dye is located on the SDS micelles between the fixed and the shear layer. In contrast, the behaviour of PADA/DTAC is explained assuming that the positively charged deprotonation sites of PADA are forced to protrude towards the bulk solvent by the positive charges of DTAC micelles. The shifts of the apparent pK_{ai} from the aqueous values (ΔpK_{ai}^w) have also been analysed. Concerning PADA/Triton X-100, the shifts $\Delta pK_{a1}^w = -0.1$ and $\Delta pK_{a2}^w = -0.9$ are rationalized in terms of dielectric constant reduction at the reaction sites. Concerning PADA/DTAC, $\Delta pK_{a1}^w = -0.05$ and $\Delta pK_{a2}^w = -0.3$ whereas, for PADA/SDS, $\Delta pK_{a1}^w =$

2.0 and ΔpK_{a2}^{w} = 1.2. The pK_{a2}^{w} values decrease on raising the surfactant concentrations for all the investigated systems. This behaviour is explained assuming that the increase of the overall micellar surface and, by consequence, of the reaction sites number, results in a site dilution effect which disfavours proton association. The addition of NaCl induces changes of pK_{a1} and pK_{a2} which are explained in terms of (large) reduction of ψ for PADA/SDS and of (small) reduction of the dielectric constant for the other systems.

Keywords: SDS, DTAC, Triton X-100, surface potential, surfactant

Abbreviations

PADA	Pyridine-2-azo-p-dimethylaniline
SDS	Sodium dodecyl sulphate
DTAC	Dodecyl trimethyl ammonium chloride
Triton X-100	Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether
ΔpK_{ai}^{0}	pK_{ai} shift of the charged systems from that of the PADA/Triton X-100 reference system
ΔpK_{ai}^{w}	apparent pK_{ai} shift from the value in water

1. Introduction

The molecular structure of surfactants and their unusual properties leads to both widespread and highly specialized applications [1-5]. Surfactant micellar media can increase the solubility of the substances poorly soluble in water. This is of a special significance in the field of drug action, since aqueous micellar systems can simulate far more complex biological systems. Because of that, the interest on the effects of surfactants on drug properties is continuously increasing [6]. Moreover, micellar systems have attracted attention also as potential extracting media, in particular for precious/toxic metal ions [7]. The replacement of the organic phase by pseudo-phases built up with surfactants offers an attractive alternative to classical, environmental unfriendly water/organic solvent extraction. Extracting agents (or ligands), have often limited solubility in water, but this is considerably enhanced in micellar solutions. Moreover, the hydrogen ion concentration in the bulk solution generally differs from the value on the micelle surface. For instance, in the presence of SDS micelles, the negatively charged surface will attract protons, resulting in an increase of proton concentration at the micelle surface with a consequent decrease of pH. This effect can have dramatic repercussions on the acid characteristic of a weak acid (as many ligands are) and, therefore, on the speciation of the ligand on the micelle surface. Based on the Boltzmann's law of charged particle distribution in the presence of an electrically charged surface, Hartley and Roe [8] assumed that the proton activity (a_{H^+S}) on a surface at the potential ψ (that they identify as the ζ potential) differs from that in the bulk water (a_{H^+W}) according to the relationship (a_{H^+S})/ (a_{H^+W}) = exp(-*F* ψ/*RT*) which, at 25 °C, can be rewritten as equation (1)

$$pH_s - pH_w = \psi / 59.2 \qquad (1)$$

where ψ is expressed in mV and has the same sign as that of the micelle charge. Hence, addition of an anionic surfactant (as SDS) to an aqueous solution results in a decrease of pH at the interface

whereas addition of a cationic surfactant (as DTAC) makes the pH on the micelle surface higher with respect to the bulk solution pH.

The pK_a of a weak acid, located on the micelle surface, is also shifted and the above authors attributed the pK_a shift to the change of proton concentration close to the micelle surface, disregarding any possible intrinsic effect arising from changes in the environment [9]. According to this assumption, the surface pK_a (pK_a^s), is related to the bulk pK_a (pK_a^w), by equation (2) valid at 25°C [8, 10].

$$pK_a^s - pK_a^w = - \psi / 59.2 \qquad (2)$$

However, the equilibrium of a weak acid bound to a surface may be affected not only by the electrostatic potential but, in addition, by the local characteristics of the environment. In effect it was observed that the pK_a values of umbrelliferone, bromthymol bue and methyl red were shifted by neutral micelles [11]. Such an observation makes equation (2) unsuitable to evaluate the surface potential of a micelle or, alternatively, to evaluate (pK_a^s) from the known values of (pK_a^w) and ψ. In order to derive the value of the electrostatic contribution to the free energy of a protolytic equilibrium in the presence of charged micelles, the reference system, devised as (pK_a^w) by Hartley and Roe, should be replaced by the "intrinsic" parameter (pK_a^i) corresponding to the surface pK_A of the probe in the absence of surface potential [12]. Under the hypothesis that the contribution of the local environment remains the same, independently of the surface charge, (pK_a^i) can be replaced by (pK_a^0), the probe pK_a measured in the presence of uncharged micelles [13] (equation (3)).

$$pK_a^s - pK_a^0 = - \psi / 2.3RT \qquad (3)$$

Pyridine-2-azo-p-dimethylaniline (PADA) is a diprotic acid that dissociates as shown in Figure 1 [14]. It is widely used as a metal extractor in micellar enhanced extraction processes [15, 16] owing

to the property of being almost totally adsorbed in many micelles including SDS, DTAC and Triton X-100, the surfactants employed in the present work.

In the framework of our studies on metal extraction using MEUF [17-20] we have investigated the influence exerted by micelles of different concentration and charges on the acidity constants of PADA. The results of this work and the comparison with literature results clearly indicate that both the pK_{a1} and pK_{a2} shifts induced by the presence of micelles strongly depend on the protolytic equilibrium involved, on the charge of the micelles and on the dye components absorbed.

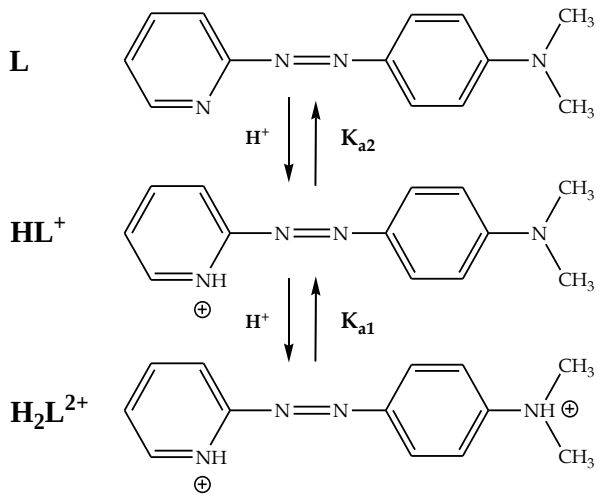

Figure 1 Pyridine-2-azo-p-dimethylaniline (PADA) in its neutral (L) and protonated forms (HL^+ and H_2L^{2+}).

2. Materials and Methods

2.1 Materials

The ligand pyridine-2-azo-p-dimethylaniline (PADA) and the surfactants sodium dodecylsulphate were purchased from Sigma–Aldrich. Dodecyltrimethylammonium chloride (DTAC), hydrochloric acid and sodium chloride were from Fluka. Triton X-100 was from Merck. All reactants were analytical grade and were used without further purification. Ultrafiltration membranes made of regenerated cellulose (YM 3, Millipore) of 4.5cm diameter, with a molecular weight cut-off of 3000

Dalton, were used in the ultrafiltration experiments. The membranes were treated and stored as recommended by Millipore. Water from a Millipore MILLI-Q water purification system was used as a reaction medium.

2.2 Methods

The pH measurements were made using a Metrohm 713 instrument. The critical micellar concentration (cmc) of SDS in water was known from electrical conductivity and light scattering measurements (7.9×10^{-3} M, [9, 16, 21]). The cmc of our DTAC sample had already been checked by electrical conductivity and surface tension measurements and was found to be $(1.0\pm0.1)\times10^{-2}$ M [15], somewhat less than the literature value (2×10^{-2} M, [22]). The TritonX-100 cmc (2.2×10^{-4} M) has been taken from the literature [23].

The amount of PADA adsorbed on the micelle surface was determined by ultrafiltration experiments: 20 ml of an aqueous solution containing the dye and the surfactant at a concentration higher than the cmc were introduced in a 50 cm^3 cell and stirred under an applied nitrogen pressure of 1 bar. The cell was equipped with an ultrafiltration membrane whose effective area was 13.4 cm^2. Acid dissociation equilibria were investigated by means of a Perkin-Elmer Lambda 35 spectrophotometer. Spectrophotometric titrations were carried out by adding increasing volumes of HCl to the cell containing the PADA solution. The additions were made by a Hamilton micro-syringe connected to a Mitutoyo micrometric screw; such system enables additions as small as 0.166 μL. The spectrophotometer cells were thermostatted to ±0.1 °C. The titration data were analysed by a non-linear least-square fitting procedure performed by the Jandel statistical package which makes use of the Marquardt algorithm [24].

3. Results

3.1 Ultrafiltration experiments

The amount of PADA adsorbed was evaluated by spectrophotometry as the difference between the initial amount and that remaining in the permeate after filtration. The dye is strongly adsorbed on

the surface of all the employed surfactants. In fact, it was found that the percent of adsorbed dye (at pH = 3.5) was 99% in SDS, 95% in Triton X-100 and 92% in DTAC.

3.2 Spectrophotometric titrations

The spectral behaviour of PADA depends on pH and nature of surfactant as shown in Figure 2. Therefore, the (apparent) extinction coefficients, used in the analysis of the titration data, were measured before each titration.

The acid dissociation constants of PADA (i.e. of HL^+ and H_2L^{2+}, see Figure 1) were determined by spectrophotometric titrations at 25 °C. Calibrated amounts of HCl solution were added to the cuvette containing a known amount of PADA initially at pH 7.0.

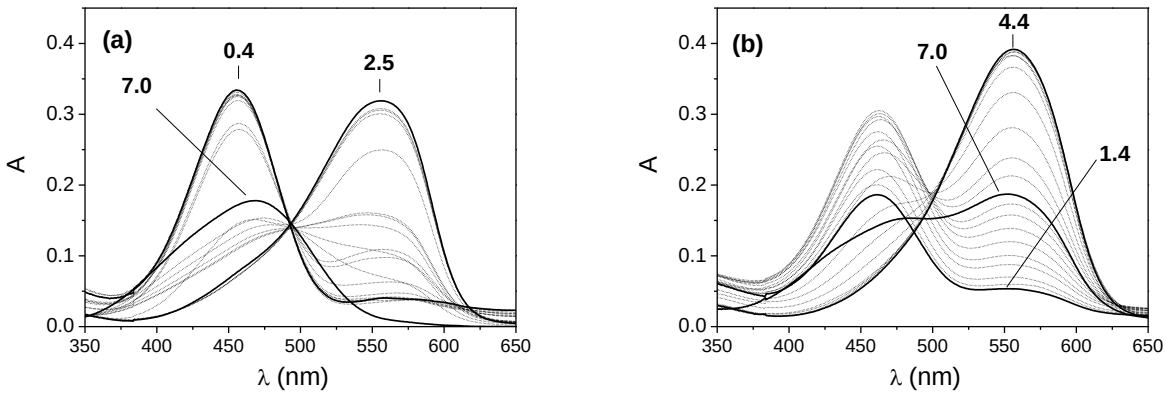

Figure 2 UV–vis spectra of PADA (1×10^{-5} M) recorded in water (a) and in SDS 0.02 M micellar solution (b) at 25°C and different pH values (the most significant are shown and labelled on the graph).

The absorbance values at 560 nm were analysed according to equation (4).

$$\frac{\Delta A}{C_L} = \frac{\Delta\varepsilon_1.K_{a1}.[H^+] + \Delta\varepsilon_2[H^+]^2}{[H^+]^2 + K_{a1}.[H^+] + K_{a1}.K_{a2}} \qquad (4)$$

where $\Delta A = A - \varepsilon_L C_L$, C_L is the total ligand concentration, $\Delta\varepsilon_1 = \varepsilon_{HL} - \varepsilon_L$, $\Delta\varepsilon_2 = \varepsilon_{H2L} - \varepsilon_L$, ε_i the extinction coefficient of the *i-th* species, and K_{a1} and K_{a2} are dissociation constants of H_2L^{2+} and HL^+ respectively (see Figure 1). The hydrogen ion concentration introduced in equation (1) corresponds to the concentration of the added HCl which is in large excess over the concentration of PADA. Figure 3 shows the experimental data points of typical titration and the curve calculated according to equation (4); the agreement with experiment is very good. Figure 4 shows the dependence of pK_{a1} and pK_{a2} values of PADA on surfactant concentration, in SDS, in DTAC and in Triton X-100. Titrations have been done also in the presence of added salt (NaCl) so that the overall ionic strength was kept constant to 0.2 M (open triangles in Figure 4).

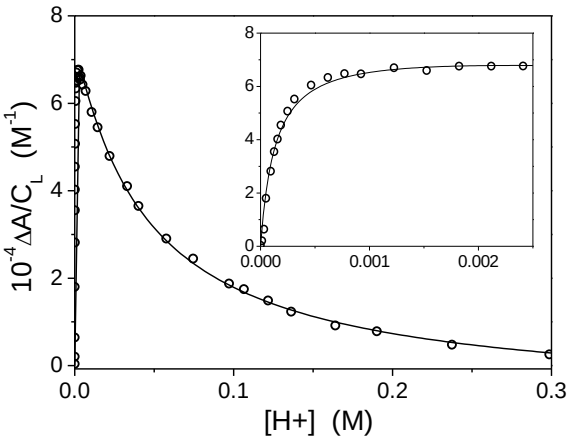

Figure 3 Biphasic binding isotherm for the titration of PADA (1×10^{-5} M) with HCl in DTAC 0.02 M micellar solution at 25°C, λ = 560nm; the continuous line represents the calculated trend according to equation (4), the inset is the enlargement of the first part of the plot.

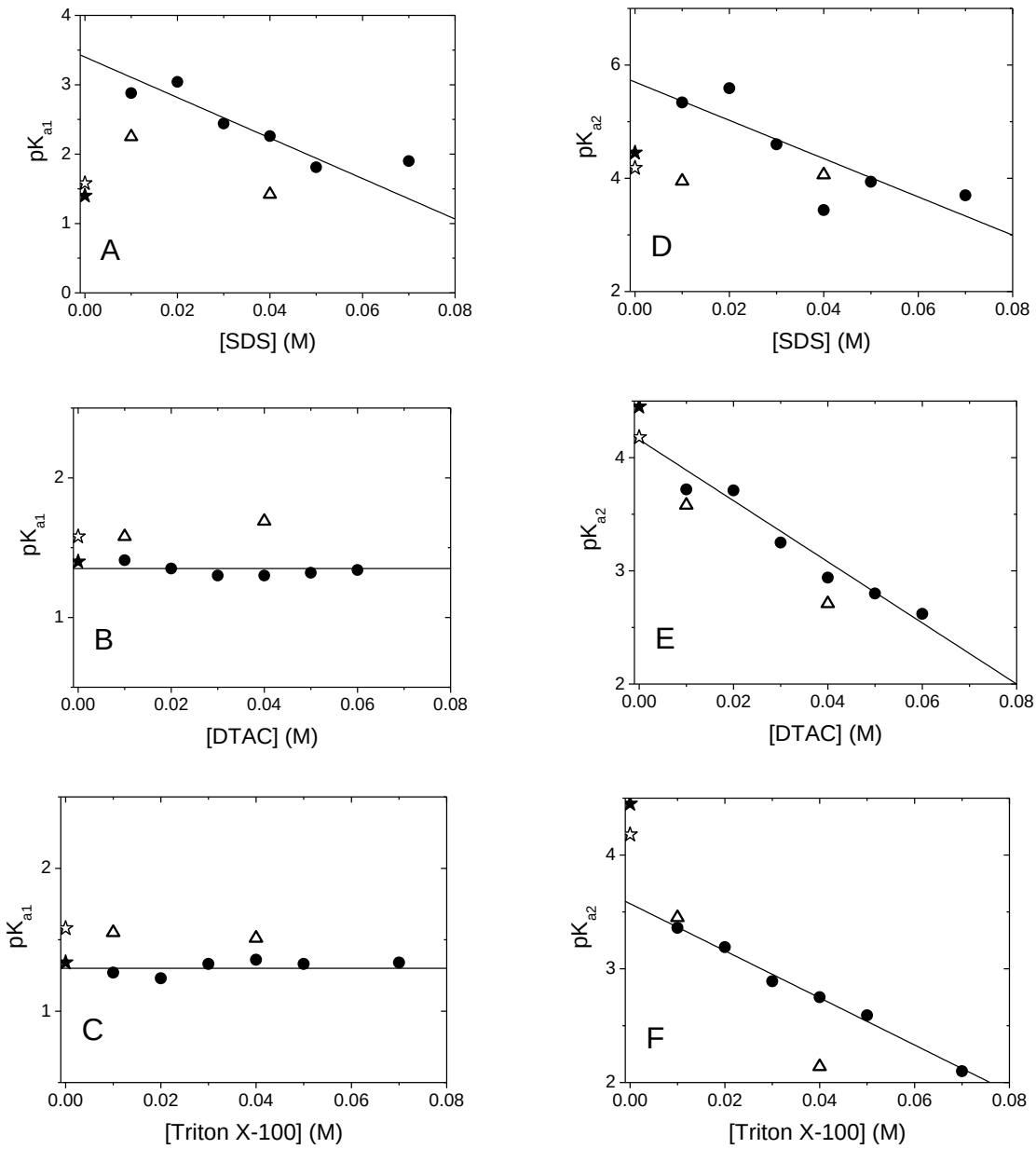

Figure 4 Plots of pK_{a1} of PADA at different surfactant concentrations (A) SDS, (B) DTAC, (C) Triton X-100 and plots of pK_{a2} of PADA at different surfactant concentrations (D) SDS, (E) DTAC, (F) Triton X-100; (●) in the absence of added salt, (**Δ**) 0.2 M NaCl; 25°C. Stars (full and empty) indicate the values in water (without salt and in 0.2 M NaCl respectively).

The data in the presence of NaCl 0.2 M are significantly different to those obtained in the absence of added salt, both as concerns the numerical values and as regards their dependence on the surfactant content that, in 0.2 M NaCl, is strongly reduced in the case of SDS. This result can be

obtained also on the basis of visual observations. Figure 5A shows PADA/SDS solutions where the acidity level is kept constant (pH = 5.5) and the NaCl concentration is increased. The colour of PADA changes from pink (H_2L^{2+}) to orange (HL^+) on increasing the salt content. Figure 5B demonstrates this effect is due to [Na^+] and not to chloride ions, as the increase of [Cl^-] does not produce any colour change, provided that the sodium content is kept constant.

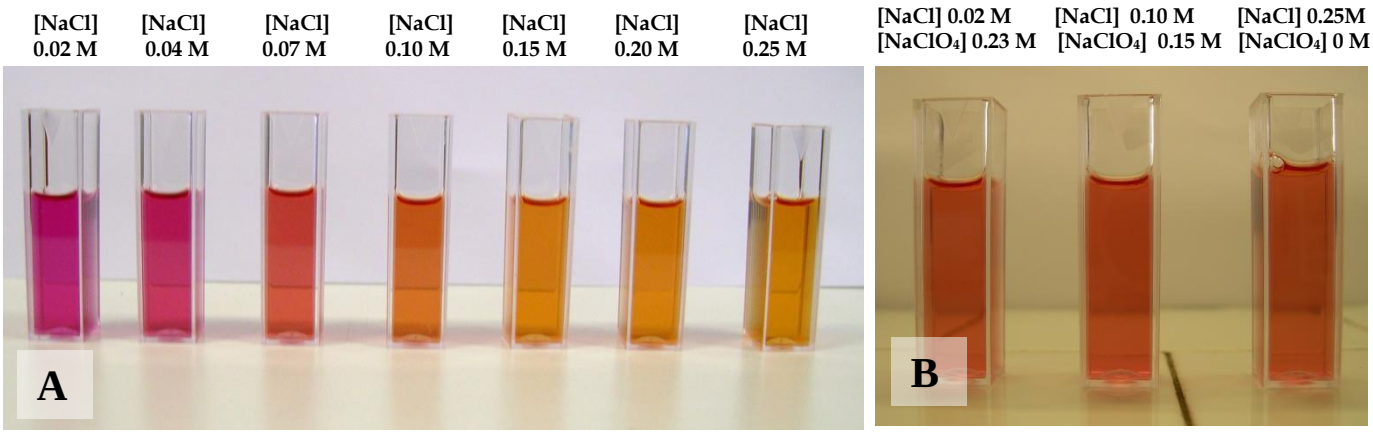

Figure 5. Colour of PADA solutions (A) at constant pH and different added NaCl (B) at constant pH and [Na^+] and different Cl^- content. [PADA] = 4×10^{-5} M, [SDS] = 0.02 M, pH = 5.5, T = 25 °C.

4. Discussion

It has been assumed in this work that that the addition of the dye to solutions containing the surfactant does not alter the surface properties of the micelles, owing to the very low values of the employed [dye]/[micelle] ratio. The data reported in Figure 4 show that the surfactants here investigated affect the acid dissociation constants of PADA in different ways. Actually, the pK_{a2} values display a decrease for all the studied systems as the surfactant concentration is raised (Figure 4D,E,F). Similar behavior is displayed by pK_{a1} in the presence of SDS (Figure 4A). By contrast, in the presence of DTAC and Triton X-100 the pK_{a1} values are independent on the surfactant concentration and similar to the value in water (Figure 4C,D). We find convenient to discuss the obtained results in terms of the pK_a shifts, as shown in Table 1 which, in principle, allow

separating the "intrinsic" shift $\Delta pKai^0$ from the surface potential effect. The values of pK_{a1} and pK_{a2} reported in Table 1 have been derived by extrapolating the data of Figure 4 to [surfactant] = 0 M (straight line in the figures).

Table 1. Values of pK_{a1} and pK_{a2} of PADA in water, SDS, Triton X-100 and DTAC extrapolated at zero micelle concentration and of the relevant shifts with respect to water ($\Delta pK_a^w = pK_a - pK_a^w$) and with respect to uncharged Triton X-100 taken as a reference ($\Delta pK_a^0 = pK_a - pK_a^0$). $pKa_1^w = 1.4$, $pK_{a2}^w = 4.5$, T = 25 °C.

	SDS	DTAC	Triton X-100		SDS	DTAC	Triton X-100
pK_{a1}	3.4	1.35	1.3	pK_{a2}	5.7	4.2	3.6
ΔpK_{a1}^w	2.0	-0.05	-0.1	ΔpK_{a2}^w	1.2	-0.3	-0.9
ΔpK_{a1}^0	2.1	0.05	-	ΔpK_{a2}^0	2.1	0.6	-

4.1 The PADA/Triton X-100 system

The second dissociation of PADA ($HL^+ = L + H^+$) in the presence of Triton X-100 displays a value of ΔpK_{a2}^w of -0.9. Since in the neutral micelle the potential effect can be disregarded, this shift should coincide with ΔpK_a^0. A similar shift (ΔpK_a^w = -1.1) was observed by Fromherz and Fernandez for the nitrogen acid Aminocoumarin (in the form HL^+) in the presence Triton X-100. By comparison with pK_a measurements in water-dioxane mixtures the above authors concluded that the negative value of ΔpK_a^w should be ascribed to a decrease of the dielectric constant at the water-micelle interface, where the reaction site is located. Support to the above conclusion is provided by a study which shows that the pK_a of protonated amines decrease with decreasing the dielectric constant of the medium [25]. The sign of ΔpK_{a2}^0 of PADA depends on the charges of the species participating in the reaction involved. Actually, ΔpK_a^0 is proportional to the free energy required to transfer the acid (HL^+) and the corresponding base (L) from water to the hydrophobic core of the micelle (equation (5))

$$\Delta pK_a^0 = [(\mu^{\circ m}_L - \mu^{\circ w}_L) - (\mu^{\circ m}_{HL} - \mu^{\circ w}_{HL})]/2.3RT \quad (5)$$

where $\mu^{\circ m}_L$, $\mu^{\circ w}_L$, $\mu^{\circ m}_{HL}$, $\mu^{\circ w}_{HL}$ are respectively the chemical potentials of L and HL^+ in the micelle(m) and in water (w). Since a decreased dielectric constant favors the transfer of charged species, in the case of the PADA it results that $(\mu^{\circ m}_{HL} - \mu^{\circ w}_{HL}) > (\mu^{\circ m}_L - \mu^{\circ w}_L)$, thus, according to equation (5), the value of ΔpK_{a2}^0 is negative. Equation (5) can also explain the smaller shift of pK_{a1} shown in Table 1. Here, the acid (H_2L^{2+}) and the base (HL^+) are both charged, so the energetic requirements for the transfer can be similar. As a consequence, the resulting ΔpK_{a1}^0 value is small.

4.2 The PADA/SDS system

It should be noted that in systems involving neutral micelles only the dielectric polarization is present, whereas in systems with charged micelles an additional contribution due to the ionic polarization may have be present. In such a case equation (5) is no more applicable. The results concerning the dissociations of PADA in SDS are conveniently interpreted according to equation (3) which states that the pK_a shift directly yields the surface potential of the micelle. Actually using the values of ΔpK_{a2}^0 reported in Table 1 one obtains ψ = -126 mV for the second dissociation and from the value of ΔpK_{a1}^0 one obtains ψ = -126 mV for the first dissociation as well. This value is in excellent agreement with the literature data obtained using other indicators as probes of electrical potential in SDS and lies between the inner potential (Ψ) and the zeta potential (ζ) of SDS micelles [12]. The intermediate value of ψ suggests that both the deprotonation sites of PADA are located neither at the inner nor at the outer surface of the double layer. They presumably stay out of the core but at a distance from it less than the shear layer.

4.3 The PADA/DTAC system

Concerning the results obtained in the presence of the positively charged surfactant DTAC, we note that the value of pK_{a1} is similar to that of the PADA/Triton X-100 (pK_{a1}^0). As a consequence, ΔpK_{a1}^0 is very small (Table 1), meaning that, according to equation (3), the potential effect is

strongly reduced compared to that of the PADA/SDS system; actually, the resulting value of ψ is negligible. Looking now at the second dissociation, the value of ΔpK_{a2}^{0} (0.6) yields ψ = -36mV, a negative, and therefore meaningless, value. In order to rationalize these findings one can make the hypothesis that, owing to the positive charges present on PADA, the deprotonation sites stay away from the positive surface of DTAC, protruding towards the bulk water. Such an hypothesis is strengthened by the observation that both the pK_{ai} values of PADA in DTAC are very similar to the respective aqueous pK_a^w values.

4.4 pK_a dependence on the micelle concentration

Figure 4D,E,F show that the pKa_2 values decrease as the surfactant concentration is raised. The decreasing trend can be explained on a kinetic ground. Consider the two proton transfer reactions occurring on the surface of the micelles: $H_2L^{2+} \leftrightarrows HL^+ + H^+$ and $HL^+ \leftrightarrows L + H^+$. Both are characterised by an association rate constant k_{ass} (M s^{-1}) and by a dissociation rate constant k_{diss} (s^{-1}). As the micelle concentration increases the reaction partners distribute over a larger surface area. Such a dilution effect results in a decrease of the specific rate k_{ass} while k_{diss} remains unchanged. The conclusion is that pK_{a2} experiences a decrease. Such a behavior has been observed several times in complex formation reactions in micellar media [15, 20, 26, 27]. Also, it should be noted that the ζ potential, and therefore ψ, shows a reduction as the micelle concentration increases, which reflects on a change of pK_a [8]. The decreasing trend is displayed by pK_{a1} in the case of SDS, but not for DTAC. The kinetic explanation given above could confirm the hypothesis that in the latter system the protonation sites protrude towards the bulk water. Under these circumstances, the reaction sites of the adsorbed dye become similar to the reaction site in the bulk, i.e. $pK_{a1} = pK_{a1}^w$ so that the variation of micelles concentration does not affect the value of pK_{a1}. It should also be noted that, if the above hypothesis is valid, the location of the sites falls in a region where the surface potential is negligible, i.e. $pK_{a1} = pK_{a1}^w$.

4.5 pK_a dependence on the NaCl concentration

Figure 4 shows that salt induces significant changes in the investigated systems. Moreover, the experiment of Figure 5 shows that, in the case of the negatively charged SDS micelle, it is the positive Na^+ ion that drives the color (i.e. the pK_{ai}) differences. An explanation for this behavior could be found in the competition between the H^+ and the Na^+ ions for the SDS surface. As $[Na^+]$ is increased, the protons adsorbed are expelled from the surface. As a consequence, the species HL^+, undergoes deprotonation with concomitant change of color.

Let's now analyze the behaviors of the individual systems. As far as the first dissociation is concerned, the data of Figure 4 show that, addition of 0.2 M NaCl to the PADA/SDS system induces a down-shift of pK_{a1} of about 0.8 units. Such a shift can be explained in terms of reduction of the surface potential by the Na^+ ions which neutralize the negative charges of the SDS micelles. Actually, it has been found that in NaCl 0.2 M ψ of SDS is reduced to -75 mV [13]. The value obtained from ΔpK_{a1}^0 in Table 1 is ψ = -60 mV.

The behavior of the PADA/DTAC system is different. Figure 4B shows that, concerning the measurements in the absence of surfactant, pK_{a1}^w experiences a small upward shift of 0.23 units on adding 0.2 M NaCl. The observed effect can be explained on the basis of the classic electrostatic theory. Actually, application of the Davies equation with B = 0.3 [28, 29] reveals that pK_{a1}^w should increase by 0.25 units. The shift remains the same in spite of the addition of increasing amounts of surfactant. The latter observation again supports the idea that the reaction site of the first deprotonation protrudes towards the aqueous phase. Similar behavior is displayed by the PADA/Triton X-100 system. Concerning the second dissociation, the pK_{a2}^w is less sensitive to the salt effect than pK_{a1}^w. The electrostatic theory predicts that the second dissociation process should be independent of the ionic strength. In effect, a small shift of less than 0.1 units can be observed on adding 0.2 M NaCl which could be ascribed to salting out of the neutral HL species [30]. As concerns the PADA/SDS system, Figure 4D shows that raising the NaCl level to 0.2 M induces a dramatic change of pK_{a2}. This parameter, however, is insensitive to changes of the SDS

concentration. The large downward pK_{a2} shift is explained by the decrease of ψ caused by the addition of NaCl. The independence of pK_{a2} of the SDS level is rationalized by the fact that, at high salt level employed, the surface potential is made constant. The situation of the PADA/ DTAC and PADA/Triton X-100 systems is different. It has been shown that in DTAC the surface potential plays a much more limited role compared to SDS, and in Triton X-100 does not play any role. Hence, it might be reasonable to advance the hypothesis that negative pK_{a2} shifts exhibited by the two systems could be ascribed to a further decrease of about 8% of the solvent dielectric constant at the reaction sites induced by addition of 0.2 M NaCl [31].

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