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

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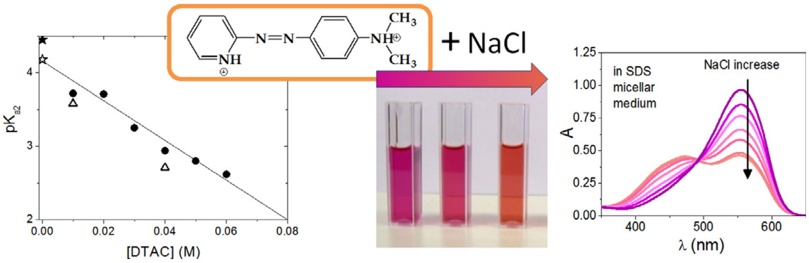
HIGHLIGHTS

- SDS (−), DTAC (+) or Triton X (non-ionic) micelles differently affect PADA's pK_as.
- 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 surface potential (SDS) or of dielectric constant (others).

GRAPHICAL ABSTRACT

The pK_as of PADA dye shift in the presence of micelles, depending on equilibrium involved, charge and concentration of the micelles and added salt.



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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^0_{ai}) are compared. For PADA/DTAC $\Delta pK^0_{a1} = 0.05$ and $\Delta pK^0_{a2} = 0.6$. For PADA/SDS $\Delta pK^0_{a1} = 2.1$ and $\Delta pK^0_{a2} = 2.1$ 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^w_{ai}) have also been analysed. Concerning PADA/Triton X-100, the shifts $\Delta pK^w_{a1} = -0.1$ and $\Delta pK^w_{a2} = -0.9$ are rationalized in terms of dielectric constant reduction at the reaction sites. Concerning PADA/DTAC, $\Delta pK^w_{a1} = -0.05$ and $\Delta pK^w_{a2} = -0.3$ whereas, for PADA/SDS, $\Delta pK^w_{a1} = 2.0$ and $\Delta pK^w_{a2} = 1.2$. The pK^w_{a2} values decrease on raising the surfactant concentrations for all the investigated systems. This behaviour is explained assuming that the increase of the overall micellar

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Abbreviations: PADAp, yridine-2-azo-*p*-dimethylaniline; SDS, sodium dodecyl sulphate; DTAC, dodecyl trimethyl ammonium chloride; Triton X-100, p, polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether; ΔpK^0_{ai}, pK_{ai} shift of the charged systems from that of the PADA/Triton X-100 reference system; ΔpK^w_{ai}, apparent pK_{ai} shift from the value in water.

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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.

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 $(a_{H^+S})/(a_{H^+W}) = \exp(-F\psi/RT)$ which, at 25 °C, can be rewritten as Eq. (1)

$$pH_s - pH_w = \frac{\psi}{59.2} \tag{1}$$

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 Eq. (2) valid at 25 °C [8,10].

$$pK_a^s - pK_a^w = \frac{-\psi}{59.2} \tag{2}$$

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 blue and methyl red were shifted by neutral micelles [11]. Such an observation makes Eq. (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 [12], 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) in Eq. (2) can be replaced by (pK_a^0), the probe pK_a measured in the presence of uncharged micelles [13,14] (Eq. (3), where F is the Faraday constant, R is the gas constant and T the temperature).

$$pK_a^s - pK_a^0 = \frac{-\psi F}{2.3RT} \tag{3}$$

Pyridine-2-azo-*p*-dimethylaniline (PADA) is a diprotic acid that dissociates as shown in Fig. 1 [15]. It is widely used as a metal extractor in micellar enhanced extraction processes [16,17] 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 [18–21] 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 [22] 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.

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. Stock solution of PADA was prepared by dissolving weighed amounts of solid in ethanol and diluting with water so such a level than the ethanol content was reduced to less than 1%. Ultrafiltration membranes made of regenerated cellulose (YM 3, Millipore) of 4.5 cm diameter, with

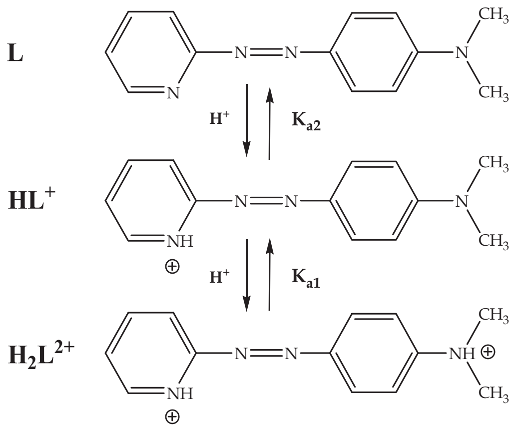

Fig. 1. Pyridine-2-azo-*p*-dimethylaniline (PADA) in its neutral (L) and protonated forms (HL^+ and H_2L^{2+}).