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A MICELLAR DECONTAMINATION STRATEGY FOR REMOVING POLYCYCLIC AROMATIC HYDROCARBONS FROM THE ENVIRONMENT

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Abstract

Environmental decontamination requires strategies for removing organic contaminants from the ecosystem. Polycyclic aromatic hydrocarbons (PAHs) with toxic and carcinogenic properties are potentially hazardous pollutants. One suitable method for PAHs removal is their solubilization by micelles. This paper evaluates the effect of borax upon the aggregation ability of sodium dodecyl sulfate (SDS) with consequence over the micellar solubilization of naphthalene. Various techniques, such as micellar electrophoretic chromatography (MEKC), surface tension, UV-Vis and steady-state fluorescence were used to assess the micelle formation. The results show that borax decreases the critical micelle concentration of SDS and enhances the naphthalene solubilization. The work recommends borax as an efficient booster in the micellar decontamination strategy of PAHs.

Key words: aggregation, borax, naphthalene, sodium dodecyl sulfate, solubilization power

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1. Introduction

Due to their amphiphilic character, surfactants have peculiar properties such as the ability to self-assemble in solution forming micelles (*i.e.*, regular in aqueous solution). The concentration range beyond which the micelles start to form is appointed as critical micelle concentration (CMC). The knowledge of the aggregation ability and CMC of amphiphilic molecules is of paramount importance for chemists working either in research, industry or environment. CMC determination can be achieved by many techniques such as: surface tension (Sharma et al., 2003, 2013), conductivity (Alawi and Akhter, 2011; Sharma et al., 2013; Zdziennicka et al., 2012), dye absorption (Anand et al., 2011; Prazeres et al., 2012; Thorsteinsson et al., 2005; Topel et al., 2013), light

scattering (Topel et al., 2013; Zdziennicka et al., 2012), refractive index (Tan et al., 2010), electrophoretic mobility (Lin et al., 1999), etc.

Environmental pollution by organic contaminants represents a global problem. Removing the pollutants from soil, water or air constitutes a major item on any environmental agenda. Most of the polycyclic aromatic hydrocarbons (PAHs) are included in the pollutant list of U.S. Environmental Protection Agency, on account of their low water solubility, carcinogenicity and toxicity (Srivastava and Ismail, 2014). Natural (Wong et al., 2010) or antropogenic (petrogenic or pyrogenic) (Dong and Lee, 2009) sources can contribute to PAHs production.

One suitable approach towards PAHs removal from the environment is their solubilization by

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micelles. The enhancement of PAHs solubilization by surfactant micelles is still a challenge (Masrat et al., 2013; Srivastava and Ismail, 2014). On the other hand, surfactants are a potentially toxic hazard to the environment. For this reason, the researchers look for green surfactants of low CMC, which bring ecological and economic benefits. The decrease of CMC can be achieved by mixing surfactants with inorganic salts like borates. Among them, borax is widely used in cosmetic, biomedical, pharmaceutical, agricultural or industrial applications (Lihua, 2011; Turkeza et al., 2012; Spoljaric et al., 2014).

The present work aims to evaluate the role of borax upon the aggregation ability of the most commonly employed anionic green surfactant, sodium dodecyl sulfate (SDS). The methods used are micellar electrophoretic chromatography (MEKC), surface tension, UV absorption and steady-state fluorescence. The study correlates the SDS aggregation ability with the surfactant efficiency to solubilize naphthalene in aqueous systems, with and without borax.

2. Experimental

2.1. Materials

All the chemicals and solutions were used as received. Sodium dodecyl sulfate (SDS) and naphthalene (Np) were supplied by Fluka. Dinatriumtetraborat-decahydrat (borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) was purchased from Merck. Analytical grade acetonitrile was obtained from Sigma-Aldrich and used as an electroosmotic flow marker. The analytical grade alkaline solutions of 0.1 N and 1 N NaOH - for capillary conditioning in MEKC technique - were provided by Agilent Technologies.

2.2. Solution preparation

In order to prepare the buffers for MEKC experiments, adequate amounts of stock solutions of borax and surfactant were mixed. The final concentration of borax in those solutions was of 5×10^{-3} M. Naphthalene-saturated water represented "the sample" in all MEKC experiments. For UV-Vis absorption and steady-state fluorescence techniques, SDS solutions with and without 5×10^{-3} M borax were saturated with Np. The SDS concentration range was chosen to be between 0.6 and 50 mM. All solutions were prepared with ultra pure deionized water using a Millipore MilliQ system.

2.3. Methods

2.3.1. Micellar Electrokinetic Chromatography (MEKC)

The electrophoresis experiments were performed on a 7100 CE Agilent Technologies system with UV diode array detection, using a standard fused-silica capillary (40/48.5 cm x 50 μm I.D.). The 40 cm length corresponds to the distance between the point of injection and the point of detection and represents

the effective length, while the 48.5 cm is the total capillary length. To detect the UV signal of Np, the wavelength was set at 221 nm. The injection was programmed in hydrodynamic regime. The voltage applied was + 15 kV, while capillary temperature was kept constant at 25°C. Special consideration was given to capillary conditioning before each measurement and in-between each buffer change. In this respect, the capillary was consecutively rinsed with sodium hydroxide solution, ultra pure deionized water and buffer. To ensure a good reproducibility, all experiments were run in triplicate.

2.3.2. Surface tension

Surface tension measurements were carried out on a K11MK3 Krüss tensiometer (0.01 mN/m resolution), using the ring method at a working temperature of 25°C.

2.3.3. UV-Vis Spectroscopy

All UV absorption measurements were performed on a Cary 100 Bio Varian spectrophotometer.

2.3.4. Fluorescence Spectroscopy

Photophysical determinations were recorded on a Fluoromax-4 Horiba Jobin Yvon apparatus. The excitation wavelength of Np was set at 290 nm. Excitation and emission slits were 2 and 1 nm, respectively.

3. Results and discussion

MEKC was first introduced by Terabe (Terabe et al., 1984) as a separation technique of neutral compounds using surfactants. Being a hybrid between electrophoresis and liquid chromatography, this method uses surfactants as a pseudo-stationary phase. A hydrophobic and detection responsive compound, passing throughout the capillary, interacts with it. The stronger the interaction between solute and surfactant, the longer it takes the marker to reach the detection zone. A variety of neutral substances that could not be separated using "classical" capillary electrophoresis (CE), were partitioned quite easy. The separation mechanism is similar to the one used for CMC determination, with the exception that it monitors the migration time of the solute when modifying the surfactant concentration in the electrophoretic buffer. Thus, the critical micelle concentration of both ionic (Chen et al., 2000; Fuguet et al., 2005; Lin et al., 2001, 2004; Nakamura et al., 1998;) and non-ionic surfactants (Lin, 2004) can be determined.

Choosing a suitable detection responsive solute to interact with the surfactant in MEKC, is of paramount importance. It must be sufficiently lipophilic, but not completely water-insoluble. The compound should have high UV absorptivity, but a short residence time in the micelle. Different markers such as: naphthalene (Fuguet et al., 2005; Lin, 2004), 2-naphthalenemethanol (Fuguet et al., 2005; Nakamura et al., 1998), butyrofенone (Fuguet et al.,

2005), as well as chloropyridines, chlorophenols and cephalosporins (Lin et al., 2001) have been proposed.

In our MEKC work, we have chosen Np as UV marker, since it is a PAH with high molar extinction coefficient at 221 nm ($\epsilon_{Np} = 117000$), acceptable water-solubility (2.2×10^{-4} M) and adequate residence time in micelles (4 μ s) (Jacquier and Desbène, 1995). For a good efficiency of the electrophoretic system, we used borax as buffer. It is able to conduct the electric current and to induce suitable buffer characteristics. At a concentration of 5×10^{-3} M borax, the ionization state of the silanol groups of the silica capillary is maintained constant.

In order to obtain information on the aggregation and CMC of SDS in borax buffer we plotted the effective electrophoretic mobility of naphthalene (μ_{eff}) as a function of surfactant concentration. We found out the μ_{eff} by taking into account the migration time (t_a) of Np and the electroosmotic flow (μ_{EOF}) determined with acetonitrile, using the following equations (Eqs. 1-2):

$$\mu_a = lL/t_aV \quad (1)$$

$$\mu_{eff} = \mu_a - \mu_{EOF} \quad (2)$$

where μ_a is the apparent mobility of the solute, l is the effective length of the capillary, L is the total capillary length, and V is the applied voltage.

The variation of μ_{eff} with the surfactant concentration is presented in Fig. 1. One may observe that at low SDS concentration, the Np has a low electrophoretic mobility. A dramatic change in the slope of the marker's electrophoretic mobility is observed when the surfactant concentration reaches 5 mM. This was considered to be the starting point of micellization by surfactant aggregation and it marks the CMC of SDS. The value found in borax buffer is smaller than that reported in water ($CMC_{SDS/water} = 8 \times 10^{-3}$ M) (Honda et al., 2004). This result is expected

because the inorganic electrolyte decreases the CMC (Chatterjee et al., 2001). Our results can be explained by taking into account that after the surfactant reaches a concentration of 5 mM in the MEKC buffer, it takes longer for the marker to migrate towards the detection zone, due to its higher solubility in the system, and the greater partition between aqueous and micellar phases. Above CMC, the dye molecules enter into the micelles followed by a more Np confinement and concentration in the Stern layer.

The result of surfactant aggregation obtained by capillary electrophoresis was verified by surface tension measurements. We investigated the adsorption ability of surfactant molecules at air/water interface, in both absence and presence of borax.

Fig. 2 shows the surface tension of the surfactant (σ) obtained by varying the SDS concentrations between 0.6 and 50 mM, without Np. As shown, in both cases the surface tension decreases by increasing the surfactant concentration, until the adsorption of SDS molecules at air/water interface is constant. The break point in the surface tension plots corresponds to the CMC of the surfactant. The CMC obtained in the presence of 5 mM borax was of 4 mM SDS being very close to the MEKC value.

For a common inorganic electrolyte like sodium chloride, a smaller tendency of surfactant's aggregation was evidenced (Maxim, 2012). In this case, using 5 mM sodium chloride a CMC of 6.5 mM SDS was obtained. At the same concentration, borax has an ionic strength three times higher than sodium chloride and entails a lower value of CMC. In the absence of borax, the CMC was found to be 7 mM, which is lower than the value reported in the literature (8×10^{-3} M) (Honda et al., 2004). The minimum appearing in the surface tension isotherm of SDS without borax, is attributed to hydrophobic impurities in SDS (most likely dodecanol that came from surfactant's synthesis (Holmberg et al., 2002)).

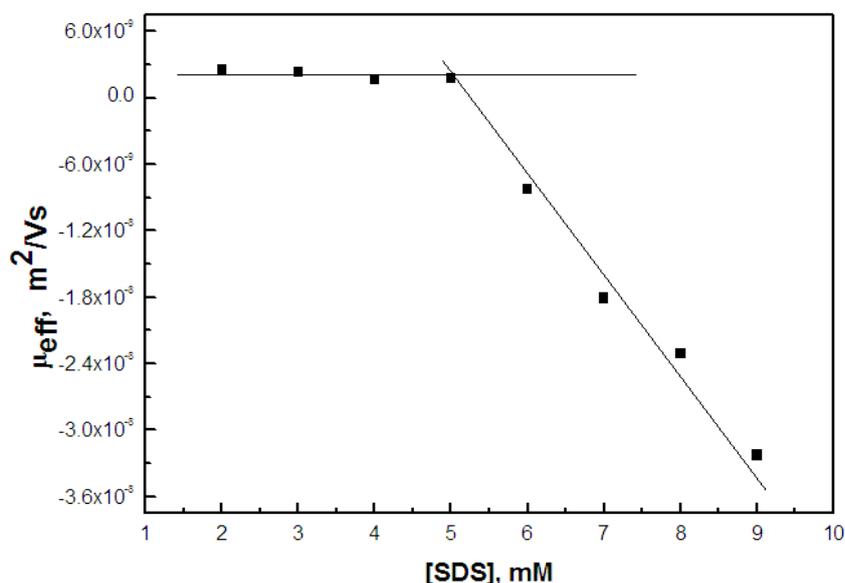


Fig. 1. The electrophoretic mobility of naphthalene as a function of SDS concentration in 5 mM borax buffer

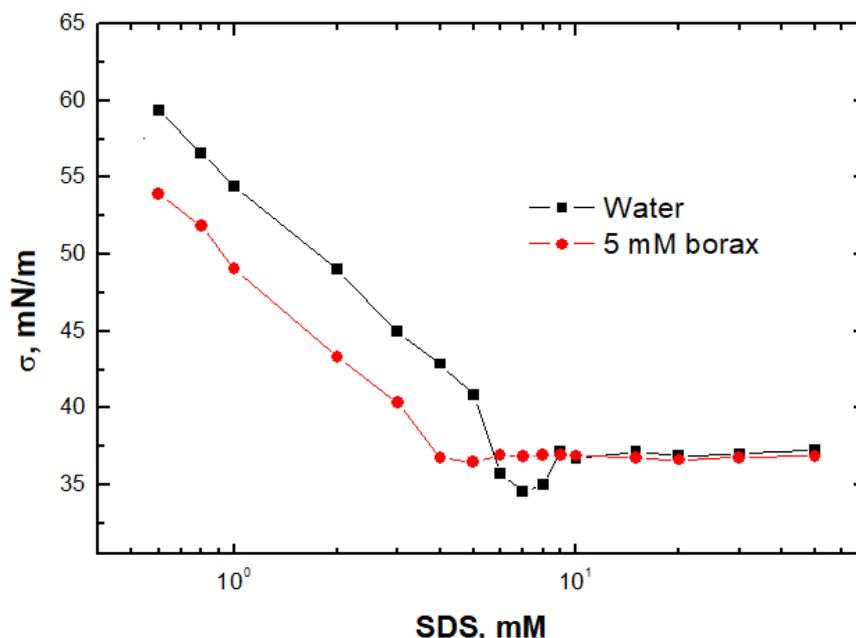


Fig. 2. Surface tension isotherms of SDS in water and in 5 mM borax

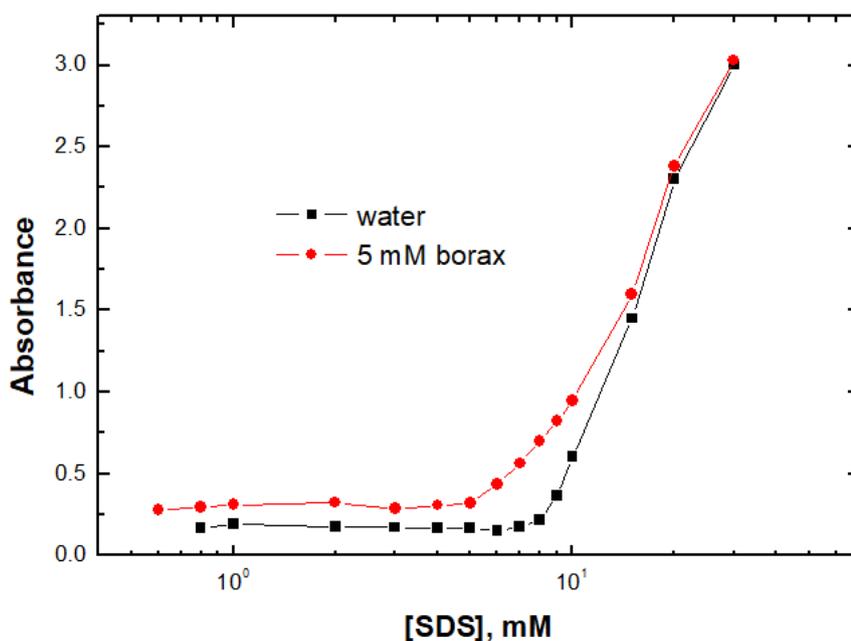


Fig. 3. The naphthalene absorbance at 275 nm vs. SDS concentration in water and in 5 mM borax

The results obtained from surface tension confirm those from literature sustaining that salt addition decreases the CMC (Chatterjee et al., 2001).

Borax, as well as other inorganic electrolytes (*i.e.*, sodium chloride), penetrates the Stern layer of the micelles, dehydrates the ionic head group region, minimizes the electrostatic repulsions, increases the aggregation number and the size of micelles (Dutkiewicz and Jakubowska, 2002). By comparing σ values at concentrations corresponding to the pre-micellar region, it can be seen that the surface tensions of the surfactant in borax solutions are smaller than those in water. The results obtained from these measurements demonstrate that the presence of inorganic electrolyte between the SDS charged head groups favors the surfactant aggregation process.

By using the UV-Vis technique, we obtained information about the surfactant aggregation and the Np solubilization into the SDS aggregates. The data were recorded at 275 nm on dye-saturated micellar solutions and are illustrated in Fig. 3. One can observe that at low SDS levels the dye has low absorbance in both water and borax solution. When the surfactant concentrations reaches 8 mM SDS (without borax) and 5 mM (with borax), a dramatic change in the slope appears, marking the CMCs of SDS. These results indicate an enhanced dye solubilization in the borax micellar system mainly in the SDS concentration range from 6 to 9 mM. To quantify, in both systems, the surfactant solubilization power and the partitioning of Np between the aqueous and micellar phases, additional absorption tests were undertaken.

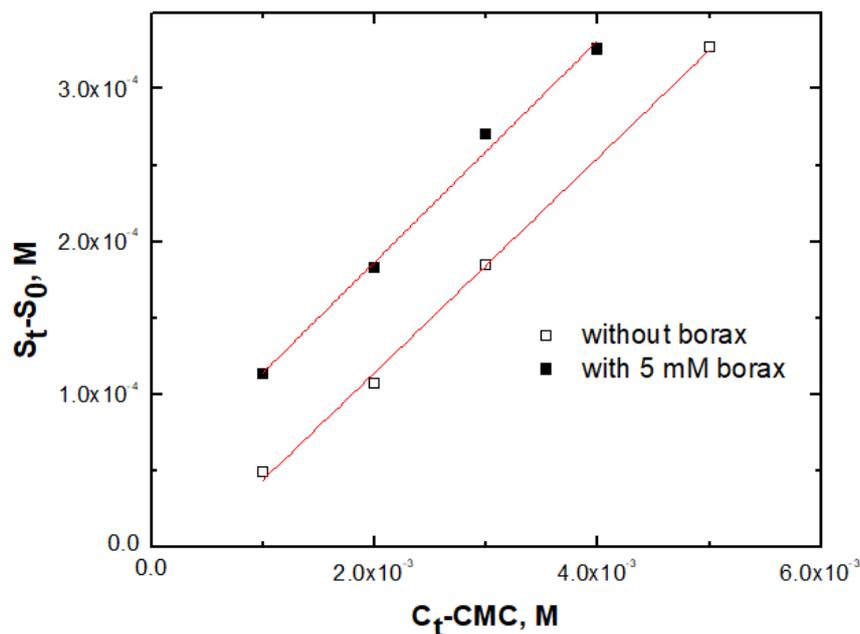


Fig. 4. The change of Np solubility in SDS micellar systems in the absence and presence of borax

For each system, five micellar solutions with appropriate concentrations, near CMC were placed in glass vials. A sufficient amount of Np was added to each vial in order to obtain saturated solutions. Each sample was stirred, and about 3 mL solution was filtrated through a 0.20 μm membrane filter into a quartz cuvette. Np's micellar solubility was determined spectrophotometrically, using the molar coefficient of solute solubilized in a good solvent such as the cyclohexane, at a wavelength of 275 nm ($\epsilon_{\text{Np}} = 6000 \text{ M}^{-1}\text{cm}^{-1}$). Surfactant concentration was kept constant in both sample and reference cuvettes to eliminate the effect of surfactant upon the UV signal.

Using Np solubility at a surfactant concentration above CMC (S_t) and its solubility at CMC (S_0), the molar solubilization ratio (MSR), can be obtained by (Eq. 3) (Masrat et al., 2013):

$$MSR = ([S_t] - [S_0]) / ([C_t] - [CMC]) \quad (3)$$

where C_t is the surfactant concentration above CMC. This ratio is a measure of the effectiveness of surfactant micelles for PAH solubilization, in mole per mole.

Fig. 4 presents the plots of the $S_t - S_0$ vs. $C_t - CMC$ for Np solubilized in the micellar systems. From both solubility curves it can be observed that above CMC the amount of solute increases linearly with surfactant concentration. It is also obvious that borax raises the ability of SDS micelles to solubilize naphthalene.

We obtained the values of MSR from the slopes of solubility curves using the least-squares linear regression method. In the micellar system without borax, MSR is 0.070, and respectively 0.073 in the one with borax. The values are comparable with those found in literature (see Table 1).

Surfactant's solubilization effectiveness can also be evaluated considering the partition coefficient

of the solute between water and micelles (K_m). This parameter is defined as the ratio between the molar fraction of solute in the micellar phase (X_m) and in aqueous phase (X_a). It is obtained using (Eq. 4):

$$K_m = X_m / X_a \quad (4)$$

where X_m is given by (Eq. 5) (Masrat et al., 2013):

$$X_m = MSR / (1 + MSR) \quad (5)$$

The molar fraction of solute in water is computed from $X_a = S_0 V_m$ taking into account that the molar volume of water (V_m) is equal to 0.018 M^{-1} .

Table 1 shows CMC, MSR and $\log K_m$ values of Np in the micellar systems. It reveals higher MSR and K_m values in the presence of borax. In the micellar system without electrolyte, Np migrates toward the interior of the micelles due to the electrostatic repulsion between the negative charges of the polar heads and the π -electrons of solute (Masrat et al., 2013).

In the micellar system with borax, the inorganic electrolyte shields the charges of the polar-head groups from the Stern layer. This phenomenon entails a decrease of the electrostatic repulsion and increases the solubilization of solute in the micelles. Therefore, borax enhances the solubilization ability of SDS micelles towards PAHs.

Steady-state fluorescence was also used to investigate Np solubilization in the self-assembled systems with and without borax. The SDS concentration was modified from 0.6 mM to 20 mM.

Excited at 290 nm, Np shows two emission maxima at 320 nm and 334 nm (spectra not presented here). Regardless of the peak, the evolution of emission intensity with SDS concentration remains the same.

Table 1. The values of CMC, MSR, and log K_m in SDS micellar solutions in the absence and presence of borax

SDS micellar systems	CMC, M	MSR (moles/moles)	Log K_m	References
Water	8.0×10^{-3}	0.070	4.35	Our work
	8.2×10^{-3}	0.065	4.12	(Mohamed and Mahfoodh, 2006)
	8.5×10^{-3}	0.073	4.19	(Paria and Yuet, 2006)
5×10^{-3} M borax	5.0×10^{-3}	0.073	4.50	Our work

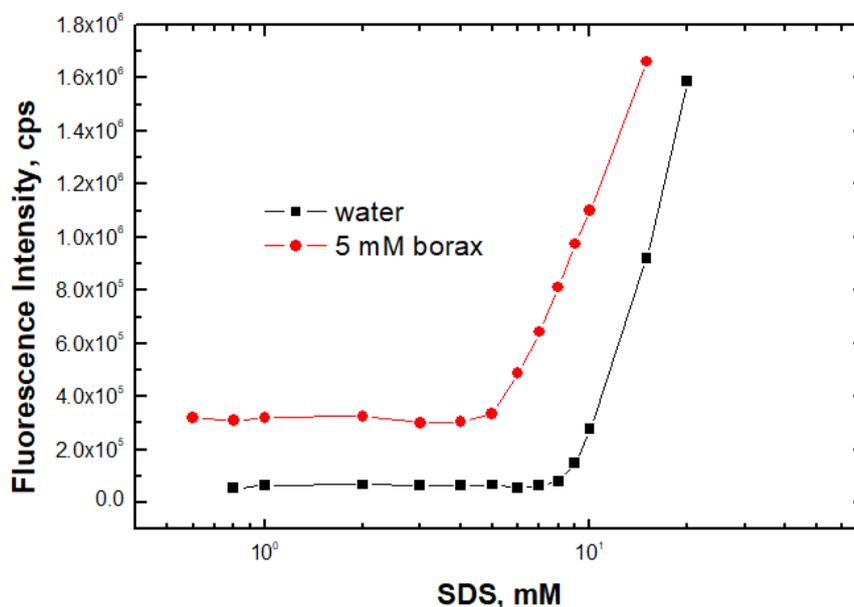
**Fig. 5.** The dependence of Np fluorescence intensity on SDS concentration in water and borax solution, $\lambda_{em}=320$ nm

Fig. 5 shows the variation of Np fluorescence intensity for the first emissive peak (320 nm) with SDS concentration in the absence and presence of borax. In both cases, the intensity remains constant until a threshold value, and thereafter, it increases sharply. The break point denotes the CMC. These points are at 8 mM SDS in water, and respectively at 5 mM SDS in borax solution. The marked enhancement of fluorescence intensity above CMC is attributed to the dye solubilization into the SDS micelles that is a more suitable microenvironment for PAH than water.

4. Conclusions

MEKC, surface tension, UV absorption and steady-state fluorescence were used to investigate the effect of borax upon SDS aggregation and solubilization of naphthalene. An excellent correlation between the CMC values obtained by these methods and by those reported into literature was found. Borax decreases the CMC, increasing the surfactant's ability to aggregate and solubilize PAHs. This signifies less SDS quantities needed to solubilize naphthalene and its removal from polluted waters.

The results of this study recommend borax as a booster in the strategy of PAHs removal from sewage by means of a green surfactant.

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