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ORIGINAL PAPER

Electrochemical mineralization of sodium dodecylbenzenesulfonate at boron doped diamond anodes

Elsa Weiss · Karine Groenen-Serrano · André Savall

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Abstract Results are reported of the electrochemical oxidation of sodium dodecylbenzenesulfonate (SDBS), a common surfactant, at boron-doped diamond anodes. The measured critical micelle concentration (CMC) for SDBS in water at 24 °C was almost 150 mg dm^{-3}, but this decreased to almost 30 mg dm^{-3} in 0.1 M sodium sulfate. Cyclic voltammetry of a boron doped diamond (BDD) electrode in aqueous SDBS solutions exhibited oxidation current densities at very positive potentials; however, solutions of monomers at concentrations <CMC gave rise to higher current densities than in higher concentration solutions that formed micelles. Galvanostatic electrolyses, with samples analyzed for Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD), were performed in an electrolytic flow cell without separator, operating in batch recycle mode, using solutions containing SDBS at initial concentrations of 25 and 250 ppm. SDBS in basic media (pH = 12) exhibited lower TOC removal rates than in acidic or neutral solutions, due to concurrent oxidation of dissolved carbonates at potentials less positive than required for water oxidation, as evident in cyclic voltammograms. Decreasing the [electrolyte]/[surfactant] ratio from 200 to 10 increased TOC removal rates. For solutions containing monomers, TOC removal rates also increased with flow rate in the second part of the electrolysis, corresponding to reaction of smaller, fragmented organic compounds. When COD removal from a solution containing SDBS micelles was mass transport controlled, current efficiencies were constant at ca. 50%, due to dimerisation of hydroxyl radical to H_2O_2 and its oxidation to dioxygen.

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1 Introduction

Many industrial wastewaters contain organic contaminants. Nowadays, biological treatment is the most important, well established and relatively cheap method to remove chemical oxygen demand (COD) from wastewaters. Some compounds are not easily biodegradable and certain substances, which are toxic, can de-activate microorganisms and slow down biological processes. Electrochemical oxidation which is a possible treatment technique has important advantages. Using only electrons as reactant, direct degradation of organics into carbon dioxide and water can be achieved via electrogenerated hydroxyl radicals [1–4], which are very reactive to organic molecules in aqueous media, as reflected in the redox potential $E^0_{OH^\bullet/H_2O} = 2.74\,V\ vs.\ SHE$ [5, 6]. Hydroxyl radicals are produced on an anode by direct oxidation of water according to reaction (1):

$$H_2O \rightarrow OH^\bullet + H^+ + e \qquad (1)$$

Consequently, electrochemical oxidation of organics into CO_2 occurs with a significant rate in the potential region of oxygen evolution. Materials which have been suggested to destroy organics in aqueous effluents are graphite [7], tin dioxide [1, 8, 9], lead dioxide [10] and also the recently developed synthetic boron-doped diamond electrodes [4, 11, 12]. Among these materials, boron doped diamond (BDD) has very interesting electrochemical properties: its electrochemical window is about 3 V for a 1 mol dm^{-3} sulfuric acid solution and its chemical resistance in acid and caustic media is very high [11, 13]. BDD is known to have weak adsorption properties, meaning weak interactions between the electrode surface and both the reactant H_2O and the product $OH^\bullet$ (reaction 1). This material acts mainly via outer sphere reaction to produce hydroxyl radicals (reaction 1) free from the electrode surface and which are considered to be involved in the oxidation of organics in aqueous solutions. The weak interaction of $OH^\bullet$ radicals with BDD leads to high chemical reaction rates with organic substrates and slow oxygen evolution, due to BDD's high oxygen overpotential.

Many effluents from metallurgical industries are formed of emulsions composed from water, surfactants and lubricants. Potentially, electrochemical processes could avoid such polluted effluents and, even better, could enable recycling of process waters. Electrochemical oxidation of alkylbenzenesulfonates, and particularly sodium dodecylbenzenesulfonate (SDBS), has been studied using different electrode materials: cast-iron [14], carbon-based anodes [15], Ti–Ru–Sn oxide [16] and lead dioxide [17]. Total mineralization of SDBS is possible in the presence of chloride mediator on cast iron and Ti–Ru–Sn oxide anodes [14, 16]. However, BDD anode does not necessarily need an added mediator to mineralize SDBS solutions [15–17], the total electrochemical oxidation of which with hydroxyl radicals can be written as:

$$C_{18}H_{29}SO_3^- + 37OH^\bullet \rightarrow 18CO_2 + SO_4^{2-} + 66H^+ + 65e \qquad (2)$$

In solutions containing a low SDBS concentration, the conductivity is too low to achieve acceptable specific electrical energy consumption, so a supporting electrolyte is required. However, the interfacial activity of SDBS depends not only on its own concentration, but also on the electrolyte concentration. The most important physicochemical property of a surfactant is its critical micelle concentration (CMC), below which the surfactant molecules cover the air/water interface, and as those remaining are dispersed into the bulk as monomer or little clusters. Above the CMC, molecules aggregate to form micelles. Temperature and concentrations of ionic species, particularly counter ions, are the main factors influencing the CMC value. Using surface tension measurements, Rybicki has reported the dependence of the CMC of SDBS on temperature and concentration of Na^+ counter ions [18].

This paper reports results of the electrochemical degradation of SDBS at ambient temperature, using cyclic voltammetry to understand the electrochemical behavior of SDBS in the light of micelle formation. Electrolyses of SDBS solutions were carried out with a BDD anode in a one compartment flow cell, to evaluate the influence of operating parameters on current efficiencies.

2 Experimental

2.1 Reagents and surface tension measurements

Sodium dodecylbenzenesulfonate ($C_{18}H_{29}SO_3Na$, SDBS, M = 348.48 g mol^{-1}) was used as a model anionic surfactant with a 12 carbon aliphatic chain and a benzenesulfonate group. It was supplied by Fluka in 80% purity, the remaining 20% being similar linear alkylbenzenesulfonate compounds (LAS) with different lengths of aliphatic chains, assumed to have similar electrochemical properties. The production of LAS from linear alkylbenzene (LAB) depends on the quality of LAB [19]; the isomer having the best surfactant properties, i.e. the lowest CMC, is that for which the benzenesulfonate group is grafted on to the third carbon of the alkyl chain [20]. The CMC value of the surfactant mixture used in this study was determined with a tensiometer (3S, GBX Instruments) at room temperature (24 °C) in different electrolytes.

Bulk electrolyses were conducted for surfactant concentrations of 25 and 250 mg dm^{-3}, in supporting electrolyte of Na_2SO_4 (Prolabo, Normapur, 99.5% purity) at 0.01–0.1 mol dm^{-3}; the pH (2–12) was initially adjusted adding H_2SO_4 (Prolabo, Normapur, 95% purity) or NaOH (Prolabo, Normapur, 98% purity).

2.2 Electrochemical measurements

Cyclic voltammograms were carried out in a conventional three-electrode cell (30 cm^3) using a computer controlled Eco Chemie Autolab potentiostat Model 30 (Utrecht, The Netherlands). BDD was used as working electrode (0.196 cm^2), Pt as counter electrode and $Hg/Hg_2Cl_2/Cl^-$ (sat) as the reference electrode. Before each experiment, the electrode was pre-treated in molar sulfuric acid solution: galvanostatic electrolysis at 100 mA cm^{-2} for 10 min, then 10 scans in cyclic voltammetry from –1.0 V to 2.2 V vs. SCE at 50 mV s^{-1}. The limit potential of 2.2 V vs. SCE in oxidation was chosen to minimize oxygen evolution. In most of cases, the electrolyte was a 0.1 M sodium sulfate solution, for which the pH was adjusted with sulfuric acid or sodium hydroxide.

2.3 Electrolyses and electrode material

Electrolyses were performed in a one compartment electrolytic flow cell (Diacell®) under galvanostatic conditions. BDD (CSEM, Neuchâtel, Switzerland), made by chemical vapor deposition on a conductive polycrystalline silicon substrate, was used as anode and zirconium as cathode. All electrodes were discs (100 mm diameter) with a geometric area of 63.6 cm^2 each. The details of the electrolytic flow cell and the electrochemical reactor are described elsewhere [17]. The flow rate in the electrochemical cell was kept constant during each experiment (42, 168, 200 or 336 dm^3 h^{-1}). The range of constant current density values used was 0.63–40 mA cm^{-2}.

2.4 Analytical procedures

Solution samples taken during electrolyses were analyzed by Total Organic Carbon (TOC) and COD measurements. TOC analysis was carried out by means of a Shimadzu TOC-VSCN total organic carbon analyzer. The COD was determined by common photometric tests using COD test tubes and photometer Dr Lange Lasa 50 system.

The TOC value corresponding to a surfactant concentration of 250 mg dm^{-3} (SDBS molar concentration = 6.15×10^{-4} mol dm^{-3}) is 135 mg dm^{-3}, with a corresponding COD value of 430 mg dm^{-3}.

3 Results and discussion

3.1 Determination of surfactant CMC value

The CMC values for SDBS in different solutions (H_2O, Na_2SO_4 and H_2SO_4) were determined from surface tension versus surfactant concentration plots, at a constant temperature (24 °C). Figure 1 shows experimental points obtained in: water (a) 0.1 M sulfuric acid (c) sodium sulfate at 0.01 M (b) and 0.1 M (d). As shown in Fig. 1, the surface tension decreased with increasing surfactant concentration. After reaching the CMC value, corresponding to the change in gradient, the surface tension remained constant. This change of gradient occurred in the same region for curves (a) and (b) on the one hand, and for curves (c) and (d) on the other hand. The CMC values are listed in Table 1, for each of the solutions used.

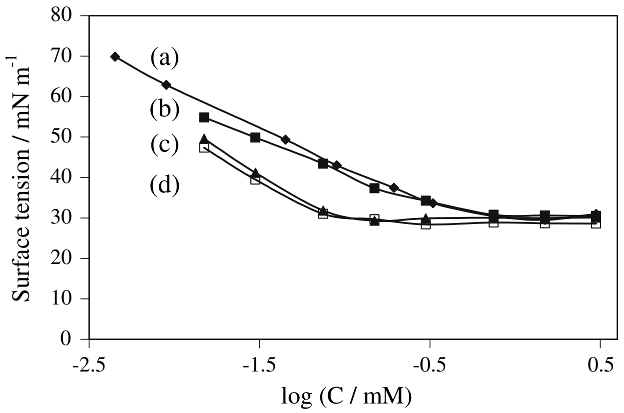

Fig. 1 Effect of SDBS surfactant concentration on surface tension at room temperature (T = 24 °C) in: (a): distilled water, (b): Na_2SO_4 0.01 M, (c): H_2SO_4 0.1 M, (d): Na_2SO_4 0.1 M

Table 1 CMC values at 24 °C in the four solutions for which results are reported in Fig. 1

	Molar concentration/ mM		Mass concentration/mg dm^{-3}	
Electrolyte	Min	Max	Min	Max
Water	0.41	0.48	142.9	167.3
0.01 M Na_2SO_4	0.39	0.46	135.9	160.3
0.1 M H_2SO_4	0.076	0.081	26.5	28.2
0.1 M Na_2SO_4	0.082	0.095	28.6	33.1

In water (curve a), the CMC value (0.41–0.48 mM) was lower than that found in the literature. Most of the CMC values were obtained from surface tension measurements [18, 21–23] or conductometric values [24]. The difference between values obtained (from 0.54 [22] to 2.1 mM [24]) results from the control of operating parameters like temperature and purification of reagents before use. In solution containing a low concentration of sodium sulfate (0.01 M), the CMC value was close to that obtained in distilled water (0.39–0.42 mM). Increasing sodium sulfate concentration to 0.1 M, the CMC value decreased to a value five times lower than in distilled water, while it is quoted as three times lower in reference [18] at the same electrolyte concentration. Curves (c) and (d) show that using sodium sulfate or sulfuric acid at the same concentration resulted in slightly different CMC values.

Although the quantity and the nature of hydrated cations were different in the two solutions, the results in term of CMC and surface tension values were the same. Danov et al. [25] had observed that pH had no influence on the CMC value in electrolytic solutions of NaCl at pH 2.5 and 6. In fact, one can conclude also that pH has no influence if the concentrations of sulfuric acid and sodium sulfate are similar. The electrochemical behavior of the surfactant can be studied with it as monomers or micelles, predominating below and above the CMC, respectively.

3.2 Influence of monomeric/micellar form on SDBS electrochemical behavior

A series of cyclic voltammograms conducted in Na_2SO_4 (0.1 M) is presented in Fig. 2, for different surfactant concentrations (25, 122, and 1220 mg dm^{-3}). At the lowest concentration (25 mg dm^{-3}), the surfactant was in its monomeric form, and at 122 and 1220 mg dm^{-3}, it was in micellar form. At the lowest concentration, the oxidation peak at 2 V vs. SCE reached the highest value; increasing concentration above the CMC value produced a dramatic decrease in current density. At the highest concentration of surfactant (1220 mg dm^{-3}), the oxidation peak increased again. Cheng and Gulari [26] showed that the diffusion coefficient of SDBS decreases with an increase in NaCl

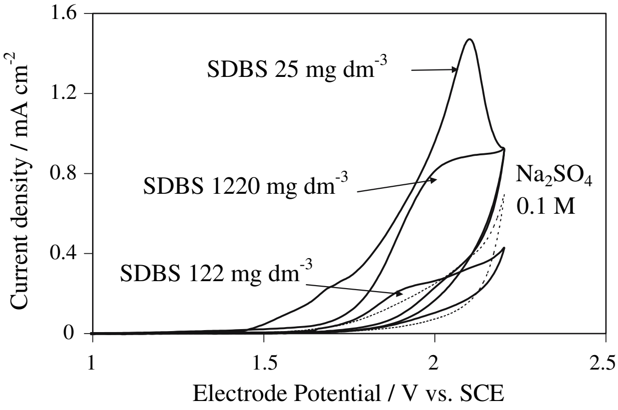

Fig. 2 Cyclic voltammograms of a BDD electrode in 0.1 M Na_2SO_4 solutions containing SDBS surfactant concentrations: (1) 25 mg dm^{-3} (monomers or aggregates); (2) 122 mg dm^{-3} (micelles) and (3) 1220 mg dm^{-3} (micelles). S = 19.6 mm^2, scan rate = 50 mV s^{-1}, T = 20 °C

concentration at constant temperature. They assumed that this decrease was due to the change of state from monomer to micelle. Moreover, a study was carried out by Yeh and Kuwana [27] with ferrocene, which forms micelles with Tween 20 (M = 1650 g mol^{-1}). These authors highlighted that the micelles diffuse very slowly to the electrode because of their effective size. For similar hydrodynamic conditions, they evaluated the following relation between the mass transfer coefficients: $k_{micelles} = 10^{-2}\ k_{monomers}$. This ratio explains the sharp decrease in current density on increasing the surfactant concentration from 25 and 122 mg dm^{-3}, as shown in Fig. 2. However, if that concentration was increased further to 1220 mg dm^{-3}, increasing the concentration of micelles, the current density increased, but still not to the peak current value for 25 mg dm^{-3}, at which monomers predominated. This experiment shows that a monomer or micelle state has an important effect on the SDBS direct oxidation process. The following sections will treat the influence of various experimental conditions on performance of electrolyses operated in batch recycle mode.

3.3 Influence of initial pH on electrolysis performance

Fig. 3 shows the variation of TOC removal during galvanostatic electrolyses (4 mA cm^{-2}) at different initial pHs. Curves corresponding to pH 2, 4, 7, and 10 are quite similar; in this range, pH had no real influence on TOC removal rate, whereas at pH 12, that rate was significantly lower. Measurements of pH during electrolyses (Fig. 3 insert) provided evidence of net acidification. Because, at the anode, complete SDBS mineralization generates protons (reaction (3), (4), and (5)), which are consumed by hydrogen evolution at the cathode, but the overall cell reaction (7), (8), and (9) generates 1, 19 or 37 protons per surfactant molecule, depending on the pH:

Anode:

$$\text{pH} < 6.37:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18H_2CO_3 + SO_4^{2-} + 103H^+ + 102e \tag{3}$$

$$6.37 < \text{pH} < 10.25:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18HCO_3^- + SO_4^{2-} + 121H^+ + 102e \tag{4}$$

$$\text{pH} > 10.4:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18CO_3^{2-} + SO_4^{2-} + 139H^+ + 102e \tag{5}$$

Cathode:

$$H^+ + e \rightarrow 1/2H_2 \tag{6}$$

Overall reaction:

$$\text{pH} < 6.37:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18H_2CO_3 + SO_4^{2-} + H^+ + 51H_2 \tag{7}$$

$$6.37 < \text{pH} < 10.25:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18HCO_3^- + SO_4^{2-} + 19H^+ + 51H_2 \tag{8}$$

$$\text{pH} > 10.4:\quad C_{18}H_{29}SO_3^- + 55H_2O \rightarrow 18CO_3^{2-} + SO_4^{2-} + 37H^+ + 51H_2 \tag{9}$$

Furthermore, other studies on degradation of organic compounds on BDD have shown that the electrolysis performance is independent of pH [28]. In order to clarify the effect of the initial pH value on the oxidation process, the amount of carbon dioxide accumulated during the electrolyses was measured in a first step.

Figure 4 represents variation of Inorganic Carbon (IC) for electrolyses conducted with initial pH of 2, 10, and 12. The variation in IC was due to carbon dioxide dissolved into the solution, absorbed from the atmosphere in an open system, on the one hand, and produced during the mineralization process (reaction 3, 4 or 5), on the other hand. The increase of IC in the solution rose with pH and was more important at pH 12. The two pK_as of carbonic acid being respectively 6.37 and 10.25 at 25 °C, the total carbonate concentration rose with pH [29]. It should be noted that the experimental protocol required sample acidification before

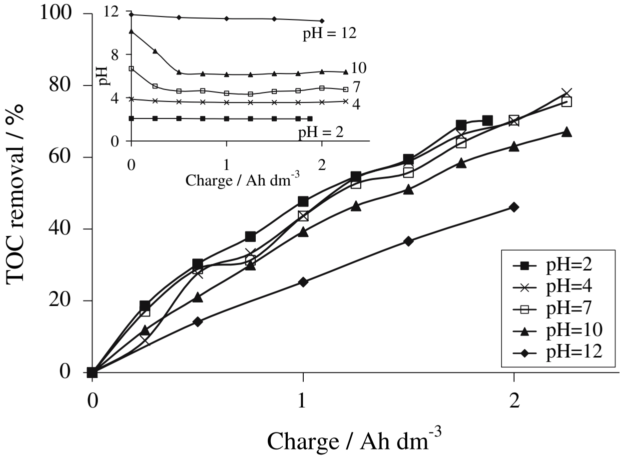

Fig. 3 Variation of TOC removal with charge and pH during electrolyses at different initial pH values. T = 20 °C, j = 4 mA cm^{-2}, flow rate = 42 dm^3 h^{-1}, electrodes: BDD and Zr (63.6 cm^2), electrolyte: 1 dm^3 of solution containing 0.01 M Na_2SO_4 and initial SDBS concentration of 25 mg dm^{-3} and pH range = 2–12

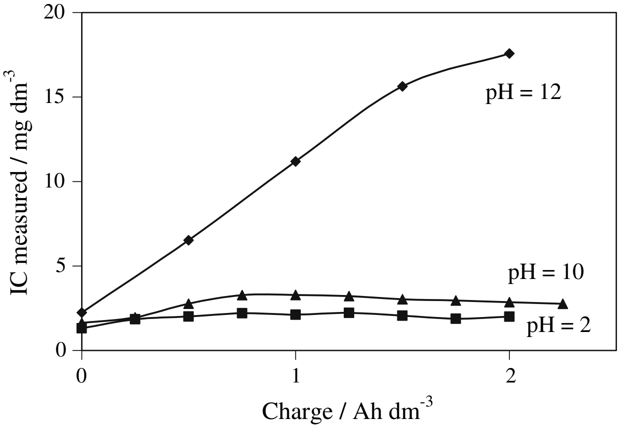

Fig. 4 Variation of inorganic carbon during electrolyses at initial pHs 2, 10, and 12. T = 20 °C, j = 4 mA cm^{-2}, flow rate = 42 dm^3 h^{-1}, electrodes: BDD and Zr (63.6 cm^2), electrolyte: 1 dm^3 of 0.01 M Na_2SO_4 containing 25 mg dm^{-3} of SDBS

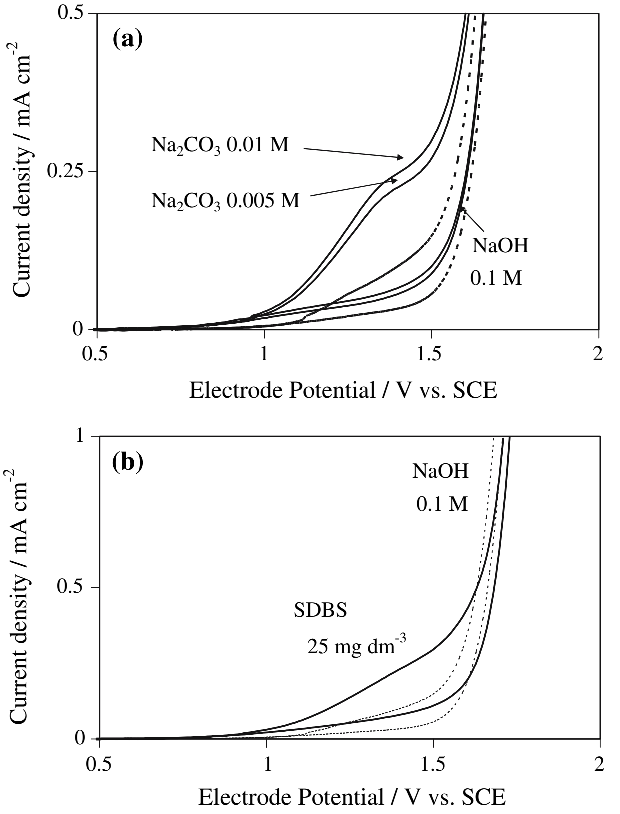

Fig. 5 Cyclic voltammograms in caustic media on BDD electrode (surface = 19.6 mm^2), scan rate = 50 mV s^{-1}, T = 20 °C. (a) continuous lines: 0.01 and 0.005 M Na_2CO_3 in 0.1 M NaOH, dotted line: NaOH 0.1 M. (b) continuous lines: 25 mg dm^{-3} SDBS in 0.1 M NaOH, dotted line: NaOH 0.1 M

IC measurement; consequently, the values reported in Fig. 4 for pH 12 are lower than the actual values.

Figure 5 (a) shows cyclic voltammograms plotted in a 0.1 M sodium hydroxide solution with and without sodium carbonate. Carbonate is oxidized to peroxodicarbonate on a BDD anode, at potentials less positive than ca. 1.4 V vs. SCE corresponding to hydroxide ion oxidation to oxygen. Moreover, Fig. 5 (b) shows cyclic voltammograms on a BDD anode of SDBS solutions in 0.1 M sodium hydroxide. The potential of current onset was less positive than that for oxygen evolution at ca. 1 V vs. SCE, due to the simultaneous oxidation of SDBS and carbonates at ca. 1–1.5 V vs. SCE on the BDD anode. Thus, the competitive oxidation of carbonate by the reaction (10) can explain the significant decrease in electrolysis performance as shown in Fig. 3 at pH 12.

$$2CO_3^{2-} \rightarrow C_2O_6^{2-} + 2e \qquad (10)$$

The low SDBS concentration (6 × 10^{-5} M) accounts for the difference on the pH dependence of the electrolysis performance between our results and those reported by Cañizares et al. [28], who studied the degradation of organic compounds at concentration higher than 1 mM. Moreover, the presence of carbonate in solution can have an effect on the CMC value: for example, Oates and Schechter [30] have shown that CMC of sodium dodecylsulfonate (SDS) decreases as the CO_2 pressure increases. Thus, the SDBS CMC value could be lower at basic pH than at acidic pH; in this case, SDBS would be in a micellar state at basic pH and then a larger part of the current could be used for the concurrent oxidation of carbonates. The following part presents a study of the combined influence of pH and electrolyte amount on the SDBS mineralization process.

3.4 Comparison of pH and electrolyte influences

The solutions were prepared with surfactant at 250 mg dm^{-3} in the presence of either sodium sulfate or sodium sulfate and sulfuric acid (pH = 2), at concentrations such as the ratio of molar concentrations R = [sulfate]/[surfactant] was equal to 10 and 200; according to Table 1, the surfactant forms micelles in the four solutions. Figure 6 shows variations of TOC removal as function of charge during galvanostatic electrolysis of these solutions (at 40 mA cm^{-2}). At the beginning of the electrolyses, the TOC removal rate was the same in all cases. However, for a volume specific charge greater than 2 Ah dm^{-3}, higher performance was obtained for lower [sulfate]/[surfactant] ratio. According to results presented in Fig. 3, the pH had no significant effect. Among the possible competitive reactions, oxidation of sulfate and hydrogenosulfate can occur on BDD anode to generate peroxodisulfates [31]:

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e \quad E^\circ = 2.12\text{V vs. SHE} \tag{11}$$

And at pH > $pK_a(HSO_4^-) = 1.99$:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e \quad E^\circ = 2.01\text{V vs. SHE} \tag{12}$$

It is assumed that the difference in TOC removal observed for the two values of the [sulfate]/[surfactant] ratio results from sulfate oxidation by hydroxyl radicals. At the beginning of all electrolyses, the surfactant was in micellar form, but as its concentration decreased by oxidation reaction (2) and reached, faster for the lowest ratio, a lower value than that of CMC (monomeric state).

3.5 Influence of applied current density on electrolyses performance

Electrochemical oxidation of organics on BDD electrodes are generally complex, with intermediate species and their concentrations are both unknown. Thus, it is convenient to define a time dependent limiting current using the global parameter COD:

$$j_{\lim,t} = nF\mathrm{k_m}[COD]_t \tag{13}$$

where $j_{\lim}$ is the limiting current density (A m^{-2}), F is the Faraday constant (96485 C mol^{-1}), $n = 4$ is the electron stoichiometry considering that the process is similar to the oxidative degradation by molecular oxygen. k_m represents the average mass transport coefficient in the electrochemical cell (m s^{-1}). For the cell used in this study, the value of k_m, determined by using the hexacyanoferrate(III/II) redox couple, varied as a function of the flow rate u (dm^3 h^{-1}) [32]:

$$\mathrm{k_m} = 2.78 \times 10^{-6}\mathrm{u}^{0.38} \tag{14}$$

Figure 7 shows the COD variation as a function of the charge per unit volume at current densities from 1 to 40 mA cm^{-2}. For a SDBS solution at initial concentration of 250 mg dm^{-3}, and flow rate of 200 dm^3 h^{-1} (in this case, $k_m = 2 \times 10^{-5}$ m s^{-1}), the corresponding limiting current density was 12 mA cm^{-2}. For these experiments, the faradaic efficiency, Φ, was calculated using the global parameter COD as followed:

$$\Phi = \frac{\Delta COD_{\exp}}{\Delta COD_{th}} = \frac{[COD^\circ - COD(t)]}{I \times t \times M_{O_2}} \times 4 \times F \times V \tag{15}$$

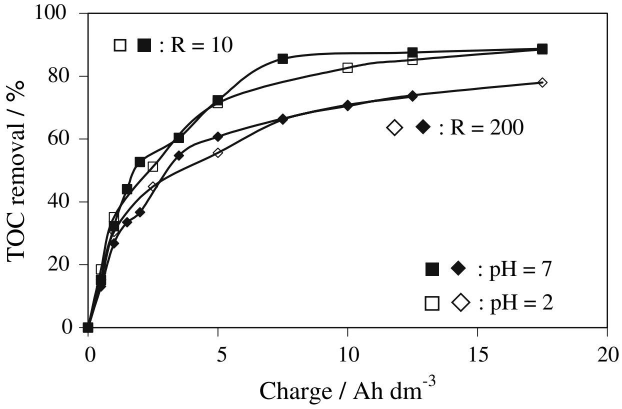

Fig. 6 Variation of TOC removal with charge per unit volume, at sulfate: SDBS molar ratios of 10 and 200. 1 dm^3 of SDBS solution at initial concentration of 6.15×10^{-4} M. Electrolyte: Na_2SO_4 (pH = 7) or Na_2SO_4 + H_2SO_4 (pH = 2), total sulfate concentration of 6.15 mM (R = 10) or 123 mM (R = 200). T = 20 °C; j = 40 mA cm^{-2}, flow rate = 42 dm^3 h^{-1}, electrodes: BDD and Zr (63.6 cm^2)

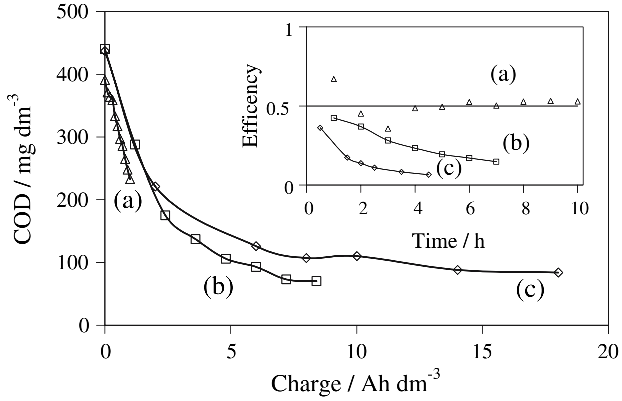

Fig. 7 Variation of COD with charge per unit volume and variation of current efficiency based on COD measurement as function of time for current densities: (a): 1; (b): 12 and (c): 40 mA cm^{-2}. T = 20 °C, flow rate = 42 dm^3 h^{-1}, electrodes: BDD and Zr (50 cm^2), electrolyte: 0.5 dm^3 of solution containing surfactant at initial concentration of 250 mg dm^{-3}; [H_2SO_4] = 0.005 M and [Na_2SO_4] = 0.118 M

COD°, COD(t) are respectively the COD concentration (g dm^{-3}) at initial time and at time t (s); I, constant current (A); M_{O2}, molecular weight of dioxygen (g mol^{-1}); V, volume of the solution (dm^3).

Curves (a), (b), and (c) in Fig. 7, show that COD decreased with increasing charge less rapidly as current density increased. Plots of current efficiencies, Φ, versus time show that the smaller the current, the higher the efficiency (insert Fig. 7); furthermore, in every case, current efficiencies did not exceed 50%. For the experiment conducted at the lowest current (curve a, Fig. 7), according to Eqs. 13, 14, and 15, all the hydroxyl radicals produced should react with SDBS and its oxidation intermediaries that should lead to 100% current efficiency. Curve (a), for the lowest current density, shows that current efficiencies did not vary during the electrolysis, but contrary to expectation, were only ca. 50%. For the experimental conditions of Fig. 7, the surfactant was in micellar form, because of the high sodium sulfate concentration (Table 1). Thus, the mass transfer coefficient of SDBS would have been much lower than that predicted by correlation (14); in fact, according to Yeh and Kuwana [27], k_m is approximately two orders of magnitude lower for micelles compared to monomers. This explains why current efficiencies were ≤50%. Though hydroxyl radicals are extremely reactive, they can combine according to reaction 16:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{16}$$

The hydrogen peroxide so formed can be further oxidized anodically to oxygen:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \tag{17}$$

Therefore, reactions (16) and (17) can explain the low current efficiencies for electrolyses shown on Fig. 7 (curves a, b, and c), the process being controlled by mass transfer of micelles; thus, current efficiencies decreased continuously during electrolysis except for curve *a*, which corresponded to a current density of 1 mA cm^{-2}. The part of the current used to oxidize the SDBS decreased progressively, other reactions producing dioxygen by reaction (17) and peroxodisulfate anions [31] by reaction (12).

3.6 Influence of SDBS initial concentration on electrolyses performance

Figure 8 shows results for electrolyses at a constant current density of 12 mA cm^{-2}, for surfactant concentrations of 25 and 250 mg dm^{-3}, at which oxidation rates were mass transfer controlled ($j°_{lim}$ = 0.68 mA cm^{-2} and 6.8 mA cm^{-2}, respectively). For the higher concentration, SDBS was in micellar form. At the beginning of the electrolysis, the mineralization rate, expressed in mg of TOC removed per time unit, was higher in the case of the lower initial concentration (curve a, Fig. 8). Bearing in mind that the diffusion coefficients are lower for micelles than for monomers, so the oxidation rate of SDBS was lower in its micellar than its monomeric form (Fig. 2), we assumed that the production rate of free hydroxyl radicals was not the limiting factor under the given conditions. After 3 Ah dm^{-3}, curve (b) reached a plateau, due to a decrease in the mineralization rate that decayed essentially to zero, the rate of TOC removal was higher for the solution containing micelles.

3.7 Influence of flow rate

Figure 9 shows the effect of flow rate *u* on the TOC removal at a BDD anode, as a function of charge passed per unit volume of 25 mg dm^{-3} SDBS solution containing 0.01 M Na_2SO_4; monomer would have predominated in such a solution, as suggested by Fig. 2. For charges less than 0.25 Ah dm^{-3}, flow rate has no significant effect on the TOC / SDBS removal rate, but for SDBS removal >40%, the TOC removal changed appreciably, depending on the flow rate. In our previous work on SDBS electro degradation [17], HPLC analyses showed that the attack of $OH^\bullet$ was made at first on the linear chain in preference to the aromatic ring. As the number of carbon atoms was higher in the aliphatic chain than in the ring, after 40% TOC removal, small molecules and aromatic components would have been present in the solution. Diffusion coefficients of these fragment molecules would be higher than

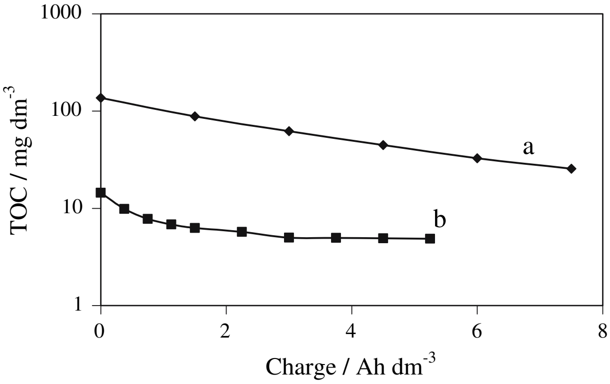

Fig. 8 TOC variation with charge per unit volume during electrolyses for: (a) [SDBS] = 250 mg dm^{-3} (micelle), (b) [SDBS] = 25 mg dm^{-3} (monomer). T = 20 °C, pH = 2 (0.118 M Na_2SO_4 and 0.005 M H_2SO_4), *j* = 12 mA cm^{-2}, electrodes: BDD and Zr (63.6 cm^2), flow rate = 42 dm^3 h^{-1}

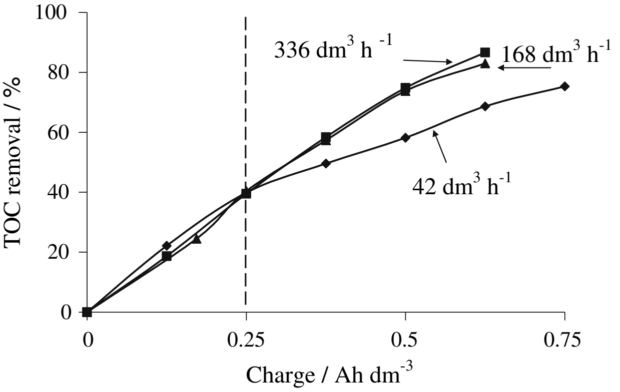

Fig. 9 TOC removal during electrolyses at different flow rates: 42, 168 and 336 dm^3 h^{-1}. T = 20°C, j = 1 mA cm^{-2}, electrodes: BDD and Zr (63.6 cm^2), electrolyte: 1 dm^3 of solution containing 0.01 M Na_2SO_4 and initial SDBS concentration of 25 mg dm^{-3}

the initial SDBS compound, so flow rate might be expected to have a greater effect on rates.

4 Conclusions

Boron-doped diamond is an efficient anode material for oxidizing and mineralizing SDBS in aqueous solutions. The active potential range is close to water discharge, implying that reaction with hydroxyl radicals can occur during electrolyses. Electrolyses conducted at different pH values (2, 4, 7, 10, and 12) showed no significant difference in the initial pH range of 2–10, whereas at pH = 12 mineralization efficiencies decreased, probably because of the concurrent carbonate oxidation in peroxodicarbonate. The effect of electrolyte concentration has been highlighted, higher performance being obtained for a 6.15×10^{-4} M SDBS solution with a [sulfate]/[surfactant] ratio of 10 than 200, in which sulfate ions were oxidized to peroxodisulfate ions. For electrolyses under charge transfer control $(j \rangle j_{\mathrm{lim},t})$, in solutions containing SDBS in micellar form, the efficiency calculated with COD measurements was constant at ca. 50%, probably because the diffusivity of micelles is lower than that of monomers, resulting in loss reactions.

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