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Voltammetric determination of the critical micellar concentration of surfactants by using a boron doped diamond anode

Charlotte Racaud · Karine Groenen Serrano ·
André Savall

Abstract The electrochemistry of three surfactants has been studied by voltammetry at boron doped diamond (BDD) electrode in sodium sulphate solutions. The electrochemical behaviour of these surfactants is characterized by an oxidation signal (peak or wave) situated before the electrolyte oxidation. The anodic current is found to follow a linear relation with the concentration of the surfactants; the slope decreases abruptly above the critical micellar concentration (CMC) of the surfactants. The CMC values obtained for an anionic (sodium dodecylbenzenesulfonate, SDBS), a cationic (polyoxyethylene-23-dodecyl ether, BRIJ 35) and a neutral (1-(hexadecyl)trimethylammonium bromide, CTAB) surfactant are found in good agreement with those measured by the classical technique of surface tension. This voltammetric method has the advantage not to require the use of a redox active electrochemical probe.

Keywords Surfactants · Critical micellar concentration · Boron doped diamond · Voltammetry

1 Introduction

Surfactants are organic compounds endowed with amphiphilic structure; their molecules contain both polar (hydrophilic) and nonpolar (hydrophobic) groups making them surface-active agents. This property provides to surfactants important applications as active cleaning

agents for all kinds of washing [1 and ref. therein]. Indeed, most water insoluble materials can be readily solubilized in the presence of a suitable surfactant. The concept of critical micellization concentration is of importance and the value of the CMC is a characteristic feature of each micelle-forming compound. The CMC is usually defined as a concentration below which only original molecules (called unimers) exist in a solution, and above which unimers and associates coexist [2]. The CMC depends mainly on the surfactant structure but is also affected by temperature, and the presence of other substances like strong electrolytes [1, 3]. An accurate value of a CMC is essential for studies of detergency, solubilisation, catalysis, and thermodynamic properties of a given surfactant [3, 4].

The CMC is usually determined from the sudden change of a physical property over a very small concentration range. A number of methods, including for examples the measurements of surface tension [5–7], light scattering [8], speed of sound [9], have been used. A review of electrochemical methods was recently published by Nesmerak and Nemcova [10]; potentiometry, electrical conductivity, voltammetry, capillary electrophoresis, have been successfully used for the determination of the CMC of various surfactants. Conductimetry is the most often used because its advantage is simplicity and standard instrumentation. In the simplest approach the specific conductivity is plotted as a function of the surfactant concentration to obtain almost straight lines whose intersection gives the CMC. However, for difficult cases, more sophisticated methods have been proposed [4, 10]. Anyway, conductimetry is not helpful to measure the CMC of neutral surfactants.

Voltammetry is a typical method for the CMC determination [10]. The measurement is based on the fact that

C. Racaud · K. Groenen Serrano · A. Savall (✉)
Laboratoire de Génie Chimique, CNRS, Université Paul
Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex 9,
France
e-mail: savall@chimie.ups-tlse.fr

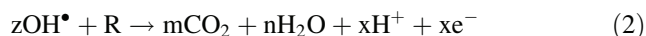
formation of micelles in a solution changes the mass transport flux towards the working electrode [11, 12]. Mandal proposed to introduce in solution, metal complexes or ferrocene as redox-active electrochemical probes to detect CMC in a variety of micellar systems [13 and ref. therein]. Several other electrochemical probes were proposed since the work of Mandal et al. [10]. The CMC value is obtained from the discontinuity on the plot of limiting current of species as function of concentration. The basic idea of this method rests on the assumption that the introduction of a small amount of an electrochemically active additive (the probe) into the system does not substantially alter the size and shape of the micelles. According to Mandal [13] the ideal probe is one which is completely solubilized (encapsulated) in micelles and insoluble in water; however, the distribution of the probe facilitates the observation of the onset of micelle formation [6, 13, 14]. Consequently, some efforts have been done for the direct voltammetric CMC determination without any probe. In this aim, Liu et al. [15] determined the first CMC and the second CMC of Triton X-100 by cyclic voltammetry on a Pt anode without any probe. Some other voltammetric techniques were developed with particular surfactants containing in their chemical structure a redox active group [10]. Nevertheless, except the use of a grafted electroactive probe, the direct voltammetric method did not know of wide development because of the relative electrochemical inactivity of surfactants on classical electrode materials.

The objective of the present study is to propose a general voltammetric method without adding a probe in solution in view to determine the critical micellar concentration of surface-active agents. In this purpose, an electrode material which is electroactive whatever the surfactant used is required. Boron doped diamond (BDD) could be a good candidate due to its unique electrochemical properties: wide electrochemical potential window, high chemical stability, great stability towards oxidation, low capacitance, poor adsorption capacity. BDD was used in electroanalysis [16, 17] and in electrochemical processes for disinfection [18, 19] or treatment of wastewaters by mineralization of organics [20–23]. Electrochemical oxidation of organics into CO₂ and H₂O occurs with a significant rate in the potential region of oxygen evolution. It is commonly assumed that the electrogenerated hydroxyl radical, the most powerful oxidant in water [24], is very active in the degradation of organic molecules. Hydroxyl radicals are produced in the anodic reaction directly from water according to:



It is assumed that there is a very weak interaction between the hydroxyl radicals and the BDD electrode

surface [24]. In this case, the oxidation of organics is mediated by hydroxyl radicals (Eq. 2) and may result in fully oxidized reaction products such as CO₂:



It has been shown by means of electrochemical oxidation that, sodium dodecyl benzensulfonate (SDBS), a very common anionic surfactant, can be completely mineralized using BDD anodes [22, 25–27]. The active potential range is close to water discharge, implying that reaction with hydroxyl radicals can occur during electrolyses [22]. Furthermore, it was observed that mineralization is under mass transfer control: the removal rate of chemical oxygen demand depends on the electrolyte flow rate that could be explained by the low concentration of the surfactant [22, 26].

This paper considers the performance of the BDD anode to determine the CMC of various surface-active agents in aqueous solutions containing moderate concentrations of Na₂SO₄ (0.01–0.5 M). Attempts were made with three common surface-active agents chosen, respectively among anionic, cationic and neutral surfactants.

2 Experimental details

The cell made with Teflon[®] was a parallelepiped of capacity 5 mL. The diamond electrode (supplied by CSEM, Neuchâtel, Switzerland) which constituted the bottom of the cell was rectangular (1.5 cm × 1.9 cm) and connected to the feeder made of a copper blade by means of conductive silver glue. The cathode was a platinum wire (surface 0.66 cm²). The electrolyte was not agitated. The saturated calomel electrode was used as reference. The working electrode used for voltammetric experiments on platinum was a wire of 0.66 cm². Linear voltammetry was carried out using a computer controlled Radiometer Tacussel potentiostat Model PGZ 100. Before each voltammogram, the BDD electrode was treated under galvanostatic conditions into a sulphuric acid solution 1 mol L⁻¹ (anodic polarization at I = 5 mA during 3 min). Then several scans were successively plotted in the surfactant solution on the BDD anode from 1.5 V to 2.4 V vs. SCE, at 50 mV s⁻¹.

For the measures of surface tension the equipment was a 3S tensiometer by GBX Instruments (Romans sur Isère, France) connected with the Winddripp software.

The surface-active agents were chosen with a hydrophilic group belonging to one of the following categories: anionic, cationic, uncharged (Table 1). SDBS (rectapur) from Prolabo, CTAB (98%) from Alpha Aesar, BRIJ 35 from Alpha Aesar, and sulphuric acid (95%) were used as-received.

Table 1 List of surface-active agents

Category	Name	Formula
Anionic	Sodium dodecylbenzensulfonate (SDBS)	$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^-, \text{Na}^+$
Neutral	Polyoxyethylene-23-dodecyl ether (BRIJ 35)	$\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{23} \text{OH}$
Cationic	1-(hexadecyl)trimethylammonium bromide (CTAB)	$\text{CH}_3(\text{CH}_2)_{15} \text{N}^+(\text{CH}_3)_3, \text{Br}^-$

3 Results and discussion

3.1 Polyoxyethylene-23-dodecyl ether (BRIJ 35)

Figure 1 shows typical voltammograms recorded for Pt and BDD electrodes in a solution containing BRIJ 35 (300 mg L^{-1}) and Na_2SO_4 (0.05 mol L^{-1}) as supporting electrolyte. Contrary to platinum a well defined oxidation wave appears on BDD (curve c, Fig. 1). This wave is due to BRIJ 35 oxidation which starts before the potential region of water discharge. The cyclic voltammogram evidences an irreversible phenomenon (return scan not shown).

The BRIJ 35 molecule possesses a hydroxyl group which is considered as difficult to oxidize by direct electron transfer on a classic electrode material like Pt [28]. As a matter of fact, Fig. 1 (curve a) demonstrates the sluggishness of the BRIJ 35 oxidation on Pt. This low activity results probably from the slow oxidation rate of adsorbed BRIJ 35 on the surface of Pt.

Figure 2 presents voltammograms recorded on the boron doped diamond electrode in Na_2SO_4 0.1 mol L^{-1} containing different concentrations of BRIJ 35. Figure 2 shows that each oxidation wave starts around 1.6 V and presents a broad peak between 1.7 and 1.9 V; the peak intensity increases with the concentration of surfactant as well as its potential. As a consequence it is likely that the wave

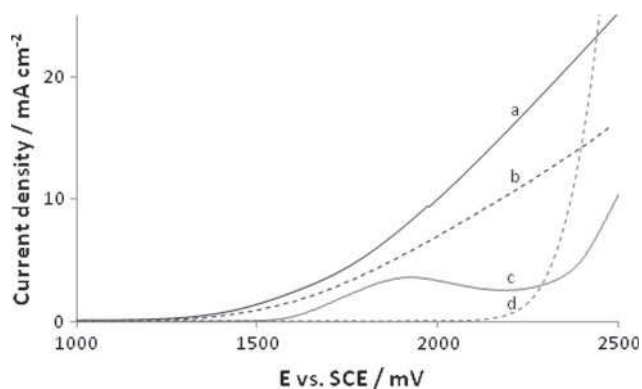


Fig. 1 Linear potential sweep voltammetry on Pt (a, b) and BDD electrodes (c, d). Curves b and d: Na_2SO_4 0.05 mol L^{-1} ; curves a and c: Na_2SO_4 0.05 mol L^{-1} and 300 mg L^{-1} of BRIJ 35. Scan rate: 50 mV s^{-1} ; $T = 25 \text{ }^\circ\text{C}$

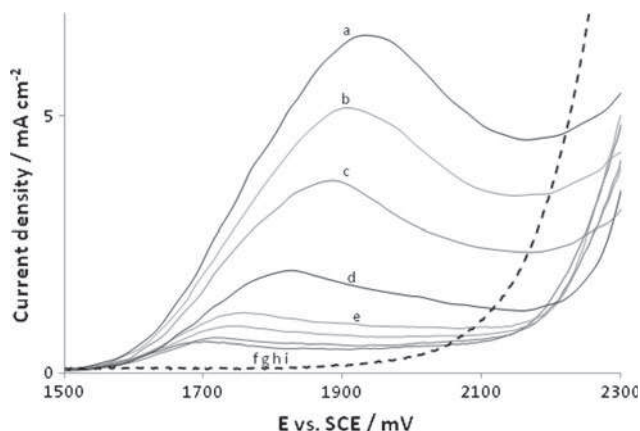


Fig. 2 Voltammograms recorded on a BDD electrode in Na_2SO_4 0.1 mol L^{-1} containing BRIJ 35 at different concentrations (mg L^{-1}): (a) 900; (b) 600; (c) 300; (d) 105; (e) 50; (f) 30; (g) 25; (h) 21; (i) dotted line: voltammogram without surfactant in Na_2SO_4 0.1 mol L^{-1} . Scan rate: 50 mV s^{-1} ; $T = 25 \text{ }^\circ\text{C}$

observed on the BDD anode is due to the direct oxidation of the BRIJ 35 by electron transfer. However, we can also consider a weak contribution of hydroxyl radicals formed by Reaction (1) [29]. But, since at 1.7 V the ground current value is 0.1 mA cm^{-2} it is assumed that contribution of OH radicals is not very important in the oxidation process. Let us remark that oxidation of the carbon structure of BRIJ 35 leading to its complete mineralization until CO_2 and H_2O via OH radicals should involve the transfer of 151 oxygen atoms per molecule of BRIJ 35 (Eq. 2).

Figure 3 shows the variation of the current for the oxidation peak as a function of the surfactant concentration in Na_2SO_4 0.1 mol L^{-1} . Current increases at first quickly with the concentration of BRIJ 35 then much more slowly. The two series of points can be regrouped on two straight lines; the change of slope between these two lines occurs at 49.9 mg L^{-1} . In order to check this particular point, the CMC value of BRIJ 35 was determined, by a classic and reliable method; the surface tension γ of these solutions was determined under the same conditions (Na_2SO_4 0.1 mol L^{-1}) for BRIJ 35 concentration up to 1 g L^{-1} . The surface tension rapidly decreases with increasing the BRIJ 35 concentration and remains almost constant after the CMC has been reached. The transition indicates a CMC of 46.6 mg L^{-1} , a value very close to that found by voltammetry.

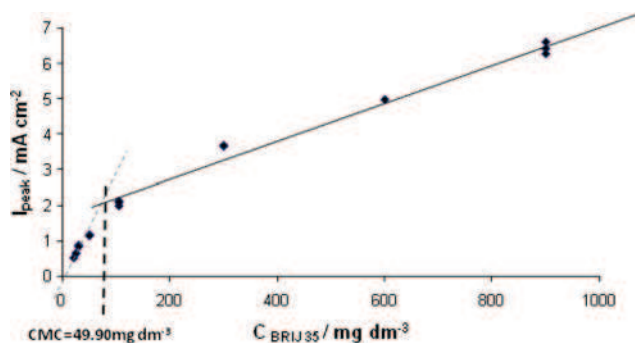


Fig. 3 Effect of BRIJ 35 concentration in Na_2SO_4 0.1 mol L^{-1} on the peak current density. Dotted line: monomer state; continuous line: micellar state. $T = 25 \text{ }^\circ\text{C}$

3.2 Sodium dodecylbenzenesulfonate (SDBS)

Electro-oxidation of alkylbenzene sulfonates has given rise to few studies. Concerning SDBS Lissens et al. [25] have studied by voltammetry its activity on anodes of carbon and BDD in the objective to mineralize this surfactant. Figure 4 shows a series of voltammograms recorded for solutions of SDBS at different concentrations in Na_2SO_4 0.05 mol L^{-1} . Voltammograms are characterized by an oxidation wave starting at 1.75 V and followed by a well-formed plateau between 2.0 and 2.2 V . SDBS oxidation appears clearly before the beginning region of water discharge (at 2.2 V the ground current is still rather low: 0.6 mA cm^{-2}). The same behaviour was observed in 0.1 mol L^{-1} Na_2SO_4 solutions. In return, it was verified that there is no significant oxidation signal for a SDBS

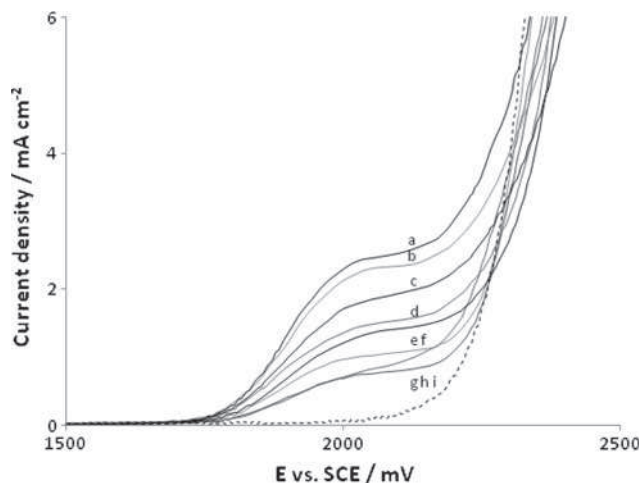


Fig. 4 Voltammograms recorded on a BDD electrode in Na_2SO_4 0.05 mol L^{-1} containing SDBS at different concentrations (mg L^{-1}): (a) 1000; (b) 600; (c) 300; (d) 105; (e) 60; (f) 50; (g) 30; (h) 25; (i) dotted line: voltammogram without surfactant in Na_2SO_4 0.05 mol L^{-1} . Scan rate 50 mV s^{-1} ; $T = 25 \text{ }^\circ\text{C}$

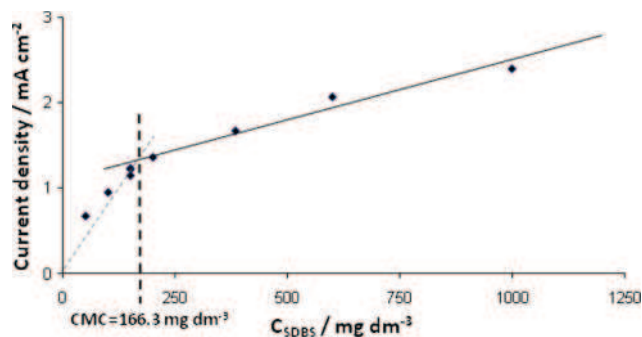


Fig. 5 Effect of SDDBS concentration in Na_2SO_4 0.05 mol L^{-1} on the limiting current density. Dotted line: monomer state; continuous line: micellar state. $T = 25 \text{ }^\circ\text{C}$

solution on a Pt electrode (not shown). On the other hand, only the first recording was retained because, during successive scans, the interface was gradually inhibited probably by polymers formation in reason of the presence of the aromatic ring in the alkylbenzylsulfonate anion [30]. Fortunately, the anode activity can be restored after a short period of polarization at potential $E = 2.25 \text{ V}$ [30].

Values of the current density measured on the plateau (at $E = 2 \text{ V}$) are represented as function of SDDBS concentration in Fig. 5. The intersection of the two straight lines indicates a CMC value of 166.3 mg L^{-1} which is in good accordance with that (185.8 mg L^{-1}) determined by surface tension measurements at the same Na_2SO_4 concentration (0.05 mol L^{-1}).

Results show also that increasing sulphate sodium concentration induced a marked decrease of the CMC of SDDBS solutions (Table 2). Although the significance of salt addition in promoting ionic surfactant adsorption was demonstrated long ago [31] the general understanding of this effect still remains fairly incomplete. One can find in the literature only a few systematic works dealing with the effect of the ionic strength on interface tension of ionic surfactants [31, 32]. This effect was pointed out by Rybicki in the case of SDDBS– Na_2SO_4 solutions [33]. Studying the CMC variation of sodium dodecylsulfate by surface tension measurements Tajima [34] reported that CMC decreased as the concentration of sodium chloride increased. Tajima concluded that this effect was due to a decrease in the molecular area of micelles and, qualitatively, interpreted it as the effect of added salt on diffuse double layers of the dodecylsulphate ion. A similar assumption could be formulated in the case of SDDBS. Let us note that among all the measurements made during the present investigation only two of them can be compared with those of other authors; and so, the CMC values measured by surface tension, for SDDBS in Na_2SO_4 solutions, respectively at 0.05 and 0.1 mol L^{-1} , are relatively close to those observed (around $\pm 25\%$) by Rybicki [33].

Table 2 Experimental values of the CMC at T = 25 °C

Surfactant	Na ₂ SO ₄ concentration (mol L ⁻¹)	CMC using voltammetry		CMC by surface tension measurement		Δ (%)
		mg L ⁻¹	mmol L ⁻¹	mg L ⁻¹	mmol L ⁻¹	
SDBS	0.05	166 ± 15	0.477 ± 0.043	186 ± 10	0.533 ± 0.028	-10.5
	0.1	166 ± 10	0.477 ± 0.028	149 ± 5	0.428 ± 0.015	+11.5
	0.5	95 ± 13	0.273 ± 0.038	56 ± 8	0.159 ± 0.023	+71.7
BRIJ 35	0.05	180 ± 15	0.150 ± 0.013	100 ± 17	0.083 ± 0.013	+64.6
	0.1	50 ± 3	0.042 ± 0.003	47 ± 8	0.039 ± 0.007	+7.0
CTAB	0.01	69 ± 10	0.189 ± 0.026	49 ± 3	0.133 ± 0.008	+42.8
	0.05	29 ± 5	0.080 ± 0.013	27 ± 3	0.074 ± 0.008	+6.6

Δ represents the difference between CMC values given by the two methods using measurement by surface tension as reference. Standard uncertainties were estimated on the basis of a rectangular distribution; reported uncertainties provide a level of confidence of 95% [37]

3.3 1-(Hexadecyl)trimethylammonium bromide (CTAB)

Figure 6 represents a series of voltammograms recorded in solutions containing CTAB at different concentrations in Na₂SO₄ 0.05 mol L⁻¹. The curves present a stretched wave for concentrations of CTAB up to 105 mg L⁻¹; a peak arises around 1.7 V only for concentrations higher than 300 mg L⁻¹. CTAB oxidation appears also as an irreversible phenomenon situated before the potential region of water discharge (at 2.2 V). The peak formed at 1.7 V does not probably result from the oxidation of free bromide anion; indeed it was shown [35] that oxidation of NaBr at 5 × 10⁻³ mol L⁻¹ occurs as early as 1 V vs. SCE on a glassy carbon electrode (E° (Br₂/Br⁻) = 0.846 V vs. SCE). As bromide anion is strongly bound to the ammonium group in CTAB micelles [36] it may be possible that oxidation of the micelle involves oxidation of bromide;

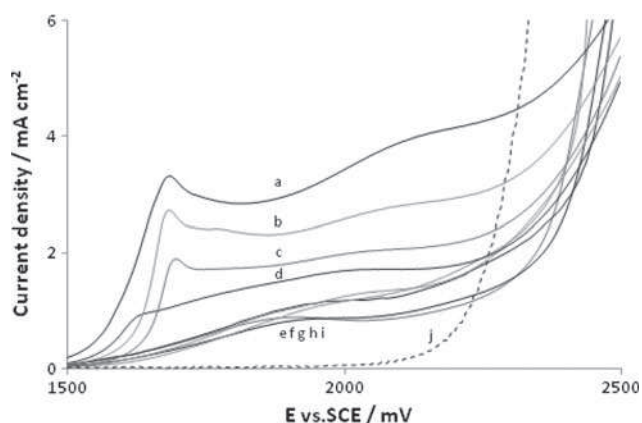


Fig. 6 Voltammograms recorded on a BDD electrode in Na₂SO₄ 0.05 mol L⁻¹ containing CTAB at different concentrations (mg L⁻¹): (a) 1500; (b) 900; (c) 600; (b) 300; (e) 105; (f) 50; (g) 30; (h) 25; (i) 21; (j) dotted line: voltammogram without surfactant in Na₂SO₄ 0.05 mol L⁻¹. Scan rate 50 mV s⁻¹; T = 25 °C

under its bonded form this needs more energy (potential of 1.7 V instead of 1 V for the Br⁻).

Figure 7 represents the variation of the current density measured on the plateau (at E = 2 V) as a function of the CTAB concentration for Na₂SO₄ 0.05 mol L⁻¹. The intersection of the two straight lines indicates a CMC value of 28.6 mg L⁻¹ which is in good accordance with the value determined by surface tension measurements at the same Na₂SO₄ concentration (26.9 mg L⁻¹).

3.4 Comparison of results

Micelles are formed by reversible aggregates of a large and finite number of monomers and the micelle-forming reaction obeys the laws of equilibrium [1]. Thus, the degree of micellization changes gradually although it may change rapidly in a relatively narrow gap of concentration. Furthermore, micelles are polydisperse, in other words there is not a unique number of monomers which can form an aggregate but a range with relatively wide limits. Furthermore, under certain conditions surfactants can exist

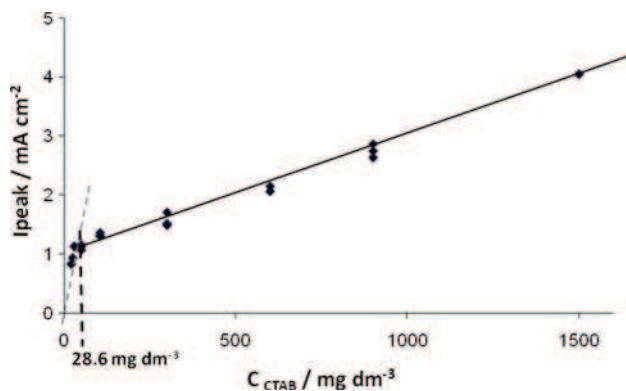


Fig. 7 Effect of CTAB concentration in Na₂SO₄ 0.05 mol L⁻¹ on the current density. Dotted line: monomer state; continuous line: micellar state. T = 25 °C

both in spherical micelles and larger rod-like micelles with concentration increasing which define, respectively the first and second CMC [1, 15]. Consequently, this is a source of uncertainty in CMC determination [5].

Table 2 summarizes the CMC values found by the two experimental methods for the three surfactants. There are some discrepancies between measurements of CMC by voltammetry and by surface tension. However it is seen that the CMC values obtained by voltammetry happen to be relatively close to some of the data resulting from surface tension measurements. If accordance (see Δ expressed in % in Table 2) varies between the two methods with the supporting electrolyte concentration, there is nevertheless no crossing between the variations observed by the two methods. In the case of BRIJ 35 the CMC value obtained by voltammetry is 64.6% higher than that measured by surface tension variations for Na_2SO_4 0.05 mol L^{-1} while it is only 7% for Na_2SO_4 0.1 mol L^{-1} . For SDBS solutions the discrepancy increases from 10% to 72% as the concentration of the electrolyte increases from 0.05 to 0.5 mol L^{-1} . Discrepancies are not unusual between methods of measurements in CMC determination. This is underlined in the review of Nesmerak and Nemcova [10]; in their Table 1 it is evident that discrepancies of the order 100% are possible between different methods.

An explanation of this difference probably lies in the adsorption of the different surfactants on the electrode surface which appears to be modified by the sodium sulphate concentration. Discrepancies observed between the two methods may also be attributed to the fact that surface tension data results from measurements which are directly linked to adsorption properties of the system while current intensities obtained by electro-oxidation are rather linked to transport properties of the tensio-active species in solution. The former properties are not affected by molecular cross-sectional areas of surfactants when the latter ones are under influence of mass-transport which depends on size of electro-active particles and on the viscosity of the solution. A more detailed investigation will be useful for a complete understanding of the discrepancy between the two methods.

4 Conclusions

Voltammetry is considered as a general method for characterizing microheterogeneous systems as micelles. However, most voltammetric studies in micellar systems used electrochemical active probes; the presence of such additives to detect the onset of micellization may affect the value of the CMC.

Boron-doped diamond is an efficient anode material for oxidizing surfactants in aqueous solutions owing to its

large electrochemical window. This work shows that voltammetry on a boron doped diamond electrode can be one of the supplementary techniques for the determination of the CMC. The present approach relies on the variation of current intensity of a peak or a plateau, measured during voltammetric scans, as a function of the surfactant concentration. Since micelles are constituted by aggregates of surfactant monomers their diffusion coefficients are much smaller than that of monomers. It results that, as the surfactant concentration increases, the enhancement of the oxidation current undergoes a strong slope decrease when the system goes through micellization. The preliminary results reported in this paper show that a BDD electrode can be used to determine the CMC of surfactant solutions. Using this electrode presents the advantage not to require the use of an electrochemical probe. It is reasonable to expect that the method can be extended to measurement of CMC under better controlled hydrodynamic conditions by using a rotating disk electrode of diamond, as well as under very low supporting electrolyte concentration, by using a micro-electrode of diamond.

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