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Electrochemistry of Surfactants

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Abstract

The application of different electrochemical techniques to surfactant systems, namely polarography and cyclic voltammetry, differential capacitance, chronocoulometry and electrochemical impedance spectroscopy, is reviewed.

Keywords: cyclic voltammetry, polarography, differential capacitance, chronocoulometry, electrochemical impedance spectroscopy, monolayers, micelles, microemulsions

1. Introduction

This chapter addresses the application of several electrochemical methods to the study of surfactant assemblies in both monolayers adsorbed on solid surfaces and free aggregates such as micelles, vesicles and microemulsions. The reviewed techniques are polarography and cyclic voltammetry for free aggregates and differential capacitance, chronocoulometry and electrochemical impedance spectroscopy for adsorbed monolayers.

In some cases, the reliability of the results can be verified with other techniques such as light scattering. However, when alternative methods cannot be applied such as in concentrated or coloured systems, these techniques give complementary and valuable information.

In this work, only some specific details concerning the use of these methods on surfactant systems are explained, while for a general description of the techniques, the reader is referred to electrochemistry books.

2. Polarographic and voltammetric methods applied to surfactant solutions

Polarographic and voltammetric methods allow for the determination of the diffusion coefficient of an electroactive probe. If the electroactive species is attached to a micelle, the measured diffusion coefficient is that of the micelle (D_M), which is related to the size and the shape of the micelles. Therefore, useful information can be derived from these experiments such as the aggregation number or changes in the shape with the concentration. The procedures are simple and can be applied when light scattering cannot be used, such as in coloured, absorbent or very concentrated samples or in systems showing very low refringence index contrast.

The diffusion coefficient (D), together with other properties, such as the intrinsic viscosity, may give information about the particle dimensions. The aggregation number can be obtained from the particles' dimensions and the partial molar volume of the surfactant. If the density of the surfactant is known, the aggregate weight may be computed.

The diffusion coefficient gives a hydrodynamic radius R_H . If the aggregate is a sphere, this radius is that of the particle. Otherwise, R_H is that of a sphere whose hydrodynamic behaviour is equal to that of the actual particle.

The diffusion coefficient is a function of the solute concentration and the temperature. There are two kinds of diffusion coefficients. The mutual or of pair (D_m) diffusion coefficient is obtained measuring the rate of reduction of an imposed concentration gradient of the solute.

On the other hand, the lone particle or self-diffusion coefficient, (D_T) [1] is obtained by following one or several tagged particles through the matrix formed by the other untagged particles and components in a solution with uniform concentration.

Both D_T and D_m quantify different physical processes and have different dependence on concentration. The D_M obtained with the techniques studied here is a self-diffusion coefficient and thus the Einstein's equation applies [2], which is not appropriate for diffusion over very small distances [3]:

$$D_T = k_B T / f_T \quad (1)$$

The coefficient f_T depends on the concentration. There is a theoretical dispute about the role of the '*dynamic friction*', i.e. the increase of f_T arising from direct interactions such as collisions. Several authors [4] are of opinion that the dynamic friction affects f_T Mazo [5] demonstrated that the dynamic friction may have a greater effect on D_T in micellar solutions with scarce swamping (or support) electrolyte.

The accuracy of Eq. (1) to predict the diffusion of macroparticles has been experimentally verified [6].

Stokes stated that the diffusional frictional coefficient for a sphere with radius a_0 moving through a continuous medium with viscosity η is given by $f_T = 6\pi\eta a_0$. Introducing this in Eq. (1), the Einstein-Stokes equation for spherical particles is obtained:

$$D = k_B T / 6\pi\eta a_0 \quad (2)$$

2.1. The determination of the micelle dimensions from self-diffusion coefficients

The hydrodynamic radius (a_0) of the micelles, computed with the Stokes-Einstein equation (2), is influenced by two factors: the effect of the intermicellar interactions and the possible change in size and shape of micelles when the surfactant and/or the supporting electrolyte concentration changes.

The intermicellar interactions may be computed considering a hard sphere and Coulomb repulsions, and a van der Waals attraction through a model proposed by Pusey [6]. The interaction is represented by a unique parameter defined by the effective radius of the hard sphere a_{eff} , and the hydrodynamic radius a_0 obtained from the Stokes-Einstein equation, giving:

$$D_M = D_{M,0} [1 + k_D(c - \text{CMC})] \quad (3)$$

where D_M and $D_{M,0}$ are the micelle diffusion coefficient at concentration c and without the effect of interactions, respectively, and

$$k_D = \left[0.5 + 2(1+x)^2(1+4x) - 15/8(1+x)^{-1} \right] v \quad (4)$$

where $x = a_{\text{eff}}/a_0 - 1$ and v is the partial specific volume of micelles. In this model, $a_{\text{eff}} \approx a_0 + \kappa^{-1}$, κ^{-1} being the Debye length. In SDS rod-like micelles at 25°C in 0.1 M NaCl $a_{M,0} = (9.6 \pm 0.2) \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ and $k_D = 15 \pm 1 \text{ cm}^3 \cdot \text{g}^{-1}$, when c is measured in $\text{g} \cdot \text{cm}^{-3}$.

In order to compute the ionic strength and then the Debye length, the concentration of free counterions and surfactant ions in equilibrium with micelles must be known. In absence of actual data from ion-selective electrodes, the free surfactant ions concentration $[S]$ is usually taken as the CMC ($[S] = \text{CMC}$) and the free counterions concentration $[X]$ as $[X] = \text{CMC} + (c - \text{CMC})\alpha$, where α is the ionization degree of micelles, which is usually almost invariant in a homologous series.

The ionization degree has been extensively reported in literature and may be readily obtained from conductivity measurements. It is usually assumed that the free surfactant concentration and α are invariant at any concentration above the CMC but it has been demonstrated with ion-selective electrode measurements that this is not always true. In general, α and $[S]$ do not remain constant with concentration. For instance, in disodium *n*-decane phosphonate solutions the free surfactant and the counterion concentrations increase, while the micelle ionization degree strongly decreases when increasing the concentration above the CMC [7]. The same behaviour of α was observed in amiodarone micelles [8]. In cationic surfactants $[S]$ strongly decreases and counterions concentration $[X]$ monotonically increases at concentrations above the CMC [9–11]. The same behaviour was observed in sodium dehydrocholate micellar solutions [12]. However, in some anionic surfactants, such as SDS [9] sodium perfluorooctanoate [13], and *n*-alkane phosphonic acids [14, 15] the $[S]$ and $[X]$ values above the CMC are almost constant and equal to the CMC. The proper procedure is to measure $[S]$ and $[X]$ by using ion-selective electrodes at each concentration, c . The contribution of micelles to the ionic strength is negligible and may be ignored [16].

If the micellised surfactant molar partial volume V ($\text{cm}^3 \cdot \text{mol}^{-1}$) is known, the volume fraction of micelles can be computed as $\nu = V \cdot c_M/1000$, where c_M is the micellised surfactant concentration on a monomer basis, $c_M = c - [S]$. If V is not known, it may be computed from tables of group contributions to the partial molar volume and procedures from literature [17].

If no experimental surfactant molar partial volumes are available, a good estimation may be obtained from the equation [18]:

$$V_{S,m} = V_{CH3} + (n_C - 1) V_{CH2} + V_{ph} + n_W V_W \dots \quad (5)$$

where $V_{CH2} = 0.02669 + 0.0000143t \text{ nm}^3$ and $V_{CH3} = 0.05108 + 0.0001311t \text{ nm}^3$, t being the temperature in $^\circ\text{C}$ [19], V_W is the volume of the hydration water molecule in the Stern layer ($=0.01038 \text{ nm}^3$ [20]); n_W is the number of water molecules per hydrated micellised surfactant molecule (which is an approximately constant value in an homologous series); V_{ph} is the volume of the polar head group computable on the basis of its structure.

It is necessary to compare the value of a_0 obtained from Eq. (2), with $D_{M,0}$ from Eq. (3) ($= a_{M,0}$) with the length of the completely extended surfactant molecule that may be estimated with the equation [20]: $l_s \text{ (nm)} = 0.13n_C + 0.1704 + 2r_{ph}$, where n_C is the number of carbon atoms in the hydrocarbon chain and r_{ph} is the radius of the hydrated polar headgroup that can be estimated from its structure or from the size of a related ion. For instance, for the carboxylate ($-\text{COO}^-$) group, r_{ph} is estimated to be 0.168 nm using the limiting equivalent formate ion conductance (λ_o): $r_{ph} = ZeF/6\pi\eta\lambda_o$, where F is the Faraday constant and Z the ion charge. For formate, this yields $r_{ph} = 0.168 \text{ nm}$ [21].

As a refinement, the effective length of the surfactant molecule can be calculated as ρl_s , employing the chain flexibility factor ρ ($\rho \leq 1$); ρ is approximately 0.75 for sodium dodecyl sulphate (SDS) [22].

If $a_{M,0} \leq l_s$, it may be assumed that the micelles are spherical. Thus, a_0 is its actual radius and the volume is $V_{sph} = 4\pi a_{M,0}^3/3$.

The micelles are generally not spherical for high surfactant and/or supporting electrolyte concentrations. If $l_s < a_o$, micelles cannot be spherical but they can be rod-like or disk-like. Moreover, the aggregates may not be micelles but vesicles, microemulsion droplets or liposomes. This may be elucidated with turbidity measurements, even with a common photospectrometer. Except for coloured surfactants, micelles are optically transparent, while vesicles and microemulsions show some absorbance. If the system is composed of micelles, they may be rod-like or disk-like.

In this case the hydrodynamic radius is not the true radius of the micelle, but that of a sphere having the same hydrodynamic behaviour. They generally are prolate or (rarely) oblate ellipsoids [21]. Non-spherical micelles are commonly rod-like and may be assumed as prolate ellipsoids and analysed with Eq. (5). In this case it may be taken $b = l_s$, and then the length of the rod may be computed as $L = 2a$.

When micelles are rod-like or disk-like, the hydrodynamic radius is not the true radius of the micelle, but that of a sphere having the same hydrodynamic behaviour. They generally are

prolate or (rarely) oblate ellipsoids [21]. Non-spherical micelles are commonly rod-like and may be regarded as prolate ellipsoids and analysed with Eq. (6), considering the transversal radius $r = l_s$ and the length of the rod $L = 2a$.

Eq. (6) can be numerically solved to obtain the length of a micelle (L) of hydrodynamic radius a_0 [23]:

$$a_0 = \frac{L}{2\sigma - 0.19 - \frac{8.24}{\sigma} + \frac{12}{\sigma^2}} \quad (6)$$

where $\sigma = \ln(L/r)$ and r is the transversal section radius ($r = l_s$).

Disk-like micelles are uncommon [24]. They may be treated as oblate revolution ellipsoids with principal axes a ($a = l_s$) and b ($b > a$), that can be obtained with Eq. (7) [23]. The volume of the micelle is $V_d = \pi b^2 l_s$.

$$a_0 = \frac{a (b^2/a^2 - 1)^{1/2}}{\tan^{-1} [(b^2/a^2 - 1)^{1/2}]} \quad (7)$$

Rod-like micelles are rigid if L is less than 100 nm, whilst longer micelles are flexible. The flexibility has been compared with that of a caterpillar [25].

The volume of a rod-like micelle may be calculated as a cylinder with radius l_s and length $L - l_s$, capped in its extremes by hemispheres with radius l_s [26]: i.e. $V_{\text{rod}} = \pi l_s^2 (L - 2l_s) + 4\pi l_s^3/3$.

The partial molar volume of the micellised surfactant ($PMV_{s,m}$) can be obtained from literature or computed from solution density measurements or with the contributions of the different groups taken from literature [17]. The hydration water of micelles must be added to the surfactant molecule volume in the calculations.

The aggregation number n can be estimated as V_{micelle}/v_s , where v_s is the molecular volume of the surfactant, $v_s = PMV_{s,m}/N_A$; N_A is the Avogadro's number. The aggregation numbers obtained in this way are in good concordance with those obtained with other methods as light scattering, even with rod-like micelles [21].

It must be taken into account that the above equations are based on simplified models, although they are good approximations. So, it is possible to obtain, from hydrodynamic measurements, the dimensions of an equivalent particle that behaves hydrodynamically as the actual particle [27]. However, in general the approximation is good.

An illustrative application of the above procedures is the study by polarography of the effect on the size, shape and diffusion of disodium *n*-decane phosphonate micelles when adding two different electrolytes [28]. Under equal conditions, the addition of NaCl produces micelles with an aggregation number one order of magnitude larger than those produced when adding NaOH. This has been attributed to an increase in the effective charge per micellised head group caused by the reaction of OH^- ions with the hydrolysed head groups, mainly present as $-\text{PO}_3\text{H}^-$ in the micelle Stern layer. This is an uncommon effect since co-ions do not normally affect the size and shape of the micelles.

It can be seen by cross checking the results from voltammetric and polarographic methods with other techniques that the information obtained is very reliable.

2.2. Some applications

Spherical micelles have self-diffusion coefficients of the order of 1.5×10^{-6} – $0.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, whereas for rod-like micelles it is about $10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ [21, 28]. The changes in the structure of the aggregates when modifying the system conditions, such as temperature, concentration or added salts, can be followed through the determination of D .

Long rod-like micelles entangle and the diffusion coefficient drops sharply. The length at which sodium hexadecanoate micelles entangle was determined by plotting (in logarithmic scales) the aggregation number n as a function of the counterion concentration $[X]$ (Figure 1).

A change in slope indicates the entanglement and the aggregation numbers obtained at higher concentrations were unrealistically high [21].

Cyclic voltammetry has been used to test some assumptions commonly accepted in the study of mixed micelles [29]. The dependence of n on the composition of the surfactant mixture and the total concentration of the catanionic mixed micelles of sodium oleate and hexadecyltrimethylammonium bromide has been analysed under thermodynamic and steric considerations, including the affinity of water molecules with the double bond of the chain of oleate ions. Results suggest that the mixed micelles' composition also will change with c . Therefore, the techniques based on the assumption that the composition of the mixed micelles does not change with concentration must be used with precaution.

As shown in Figure 2, the diffusion coefficient of mixed micelles as a function of the total composition and the concentration of the system has a complex behaviour. In Figure 3, the largest dimension of the micelles is plotted as a function of the concentration and the composition of the mixtures, showing the evolution from spheres to stiff rods, then to flexible rod-like micelles and finally to entangled micelles. As already mentioned, when the micelles are entangled the values of L are unrealistic due to the restricted movement. Besides, these huge micelles probably include more than one probe molecule and some of these probe molecules may not probably access to the electrode.

Polarography has been also used to study concentrated microemulsions that cannot be studied by light scattering [30]. Zana and Mackay [31] demonstrated that these methods may not only be used to obtain the size of aggregates but also to study the inter-aggregates interactions and the partition of electroactive substances between the aggregates and the solvent.

Polarography and cyclic voltammetry can also be used to determine the critical micelle concentration (CMC). However, this method has no advantage over other simpler methods. Moreover, the inclusion of a hydrophobic probe in the system may induce the formation of micelles at concentrations below the CMC of the pure surfactant.

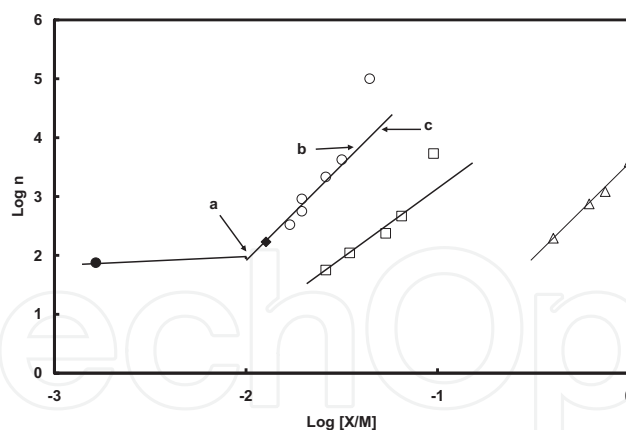


Figure 1. $\log n$ vs. $\log [X]$ (counterion concentration), for \square : sodium dodecanoate; \circ : sodium hexadecanoate, Δ : potassium dodecanoate, *a*: maximum concentration for spherical micelles, *b*: upper limit for stiff rod-like micelles, *c*: upper limit for non-entangled rod-like micelles, Redrawn from [21].

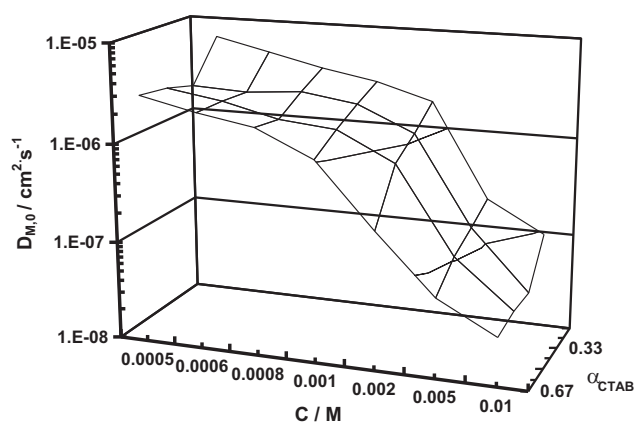


Figure 2. The values of $D_{M,0}$ as a function of concentration and the mole fraction of hexadecyltrimethylammonium bromide (α_{CTAB}) [29].

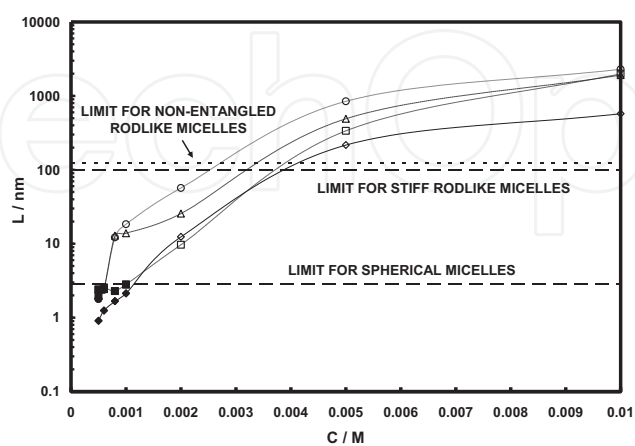


Figure 3. The largest dimension of micelles L as a function of concentration and $\alpha_{CTAB} = 0$ (\diamond, \blacklozenge), 0.33 (\square, \blacksquare), 0.5 (Δ, \blacktriangle) and 0.667 (\circ, \bullet). Open symbols represent rod-like micelles, while closed symbols correspond to spherical ones [29].

2.3. Conditions to study micelles

It is necessary to tag the micelles with an electroactive probe in order to study their diffusion coefficient. Hoyer and Novodoff [32] were pioneers using polarography and employing solid cadmium dodecanoate as a probe since the wave of Cd^{+2} is not in the region of the studied surfactant.

The viscosity η used in the Stokes-Einstein equation to determine D of micellar systems is that of the intermicellar solution, which is approximately equal to that at the critical micelle concentration (CMC). If the CMC is low and there are no added salts, this viscosity is close to that of pure water.

When the electrode reaction is controlled by the mass transport, the diffusion current allows the determination of the diffusion coefficient of the electroactive species and it is that of the carrier when the electroactive species is attached to a micelle, a droplet of microemulsion or a vesicle. Polarography, cyclic voltammetry, lineal scanning voltammetry, chronocoulombimetry, amperometry and spinning disk voltammetry are the most common techniques employed not only to obtain information on diffusion, but on the kinetics and energetics of adsorption and the electrode reaction.

Both methods, polarography and voltammetry, measure the intensity of the diffusion current generated by the discharge of an electroactive particle (i_D). Then, as the electroactive particle contribution to the charge transport through the cell must be negligible, a swamping or support electrolyte is commonly used which eliminates the electroactive probe transport current contribution. This may be a problem when ionic surfactant micelles are studied because their size and shape is usually altered by the nature and the concentration of added salts. However, the intermicellar solution has enough concentration of monomeric ions to act as swamping electrolyte (except for very low CMC) because the low concentration of micelles and their large size compared with that of monomeric surfactant ions and counterions. The addition of an electrolyte does not alter their size and shape of non-ionic micelles provided if the salt concentration is not very high, much above that needed to ensure the conditions for the i_D measurement.

2.4. Experimental details

2.4.1. Electrodes

Saturated calomel electrode (SCE) (potential $E_{\text{SCE}} = 0.241$ V at 25°C) and the Ag/AgCl with saturated KCl ($E_{\text{Ag/AgCl}} = 0.197$ V at 25°C) are usually employed as reference electrodes. The working electrode is commonly of quicksilver, platinum or carbon (vitreous or pyrolytic), but other electrodes may be used. Polarography uses a mercury electrode (dropping or with a static drop). Voltammetry uses hanging quicksilver drop or solid electrodes. The electrode surface lies between 0.01 and 0.10 cm^2 . Microelectrodes or ultramicroelectrodes with areas of some square microns have been used in high high-resistivity W/O emulsions [33].

2.4.2. Time scale

The time scale involved in continuous current polarography is $1\text{--}10$ s (droplet falling time); in cyclic voltammetry and lineal scanning voltammetry is between 10^{-4} and 1 s (scanning time);

in chronocoulombimetry, amperometry and potentiometry from 10^{-3} to 10 s (transition time) and in spinning disk voltammetry, 10^{-3} –0.1 s (spinning speed).

2.4.3. The techniques

Figure 4 shows a continuous current polarogram with spinning disk electrode.

Figure 5 shows a cyclic voltagram for a reversible process, in which the half-wave potential is $E_{1/2} = (E_a + E_c)/2$ and the diffusion current i_D corresponds to E_c .

The following equations may be used for reversible and irreversible processes at 25°C:

Continuous current polarography, Ilkovič equation:

$$i_D = K n D^{1/2} C m^{2/3} t^{1/6} \quad (8)$$

where D is the diffusion coefficient in cm^2/s ; n is the number of transferred electrons; m is the flux speed of mercury in $\text{mg} \cdot \text{s}^{-1}$; C is the concentration of the electroactive probe (not that of the micelles) in $\text{mol} \cdot \text{cm}^{-3}$ and t the dropping time in s. The current is given in Ampère. The factor K

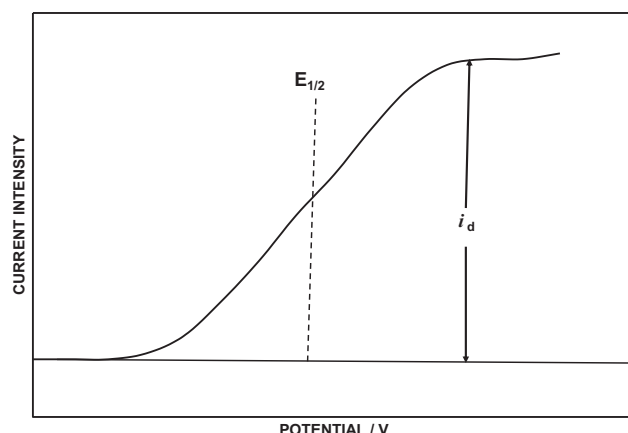


Figure 4. Continuous current polarogram with spinning disk electrode.

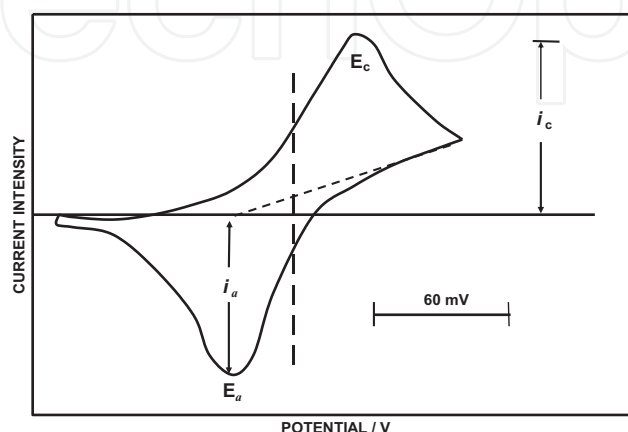


Figure 5. Cyclic voltagram for a reversible process.

is 708.1 for instantaneous current measurements and 607 for average current. Notice that for a given cell and experimental conditions, $Km^{2/3}t^{1/6}$ is constant and may be determined measuring the i_D for an electroactive probe such as Cd^{+2} , with $n = 2$ and $D_{Cd+2} = 69 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ in absence of surfactant.

Another procedure is to plot i_D as a function of the concentration of the electroactive probe in water and in surfactant solution and determine the corresponding slopes S_w and S_m of both straight lines. The ratio of the slopes is $S_m/S_w = (D_M/D_{\text{probe}})^{1/2}$, where D_M is the micelle self-diffusion coefficient

Spinning disk voltammetry, Levich equation:

$$i_D = 0.620 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C \quad (9)$$

where A is the electrode area (cm^2); F is the Faraday constant ($\text{Coulomb} \cdot \text{mol}^{-1}$); ω the spinning speed ($\text{radian} \cdot \text{s}^{-1}$) and ν is the kinematic viscosity ($\text{cm}^2 \cdot \text{s}^{-1}$).

The Randles-Sevcik equation may be used for reversible processes in cyclic or linear scanning voltammetry:

$$i_D = 2.69 \cdot 10^5 n^{2/3} A D^{1/2} \nu^{1/2} C \quad (10)$$

where ν is the scanning speed in $\text{V} \cdot \text{s}^{-1}$.

For microelectrodes:

$$i_D = 4 n F D C r \quad (11)$$

where r is the electrode radius [34, 35].

2.4.4. Probes

An ideal electroactive probe attaches to the aggregate and does not dissolve in the interparticle solution, i.e. the probe must be soluble in the micelle and water insoluble. In order to avoid any modification of the size and shape of micelles, there must be less than one probe molecule per micelle. The diffusion current must be caused only by micelle translational diffusion, with its attached probe directed to the electrode surface.

The hydrophobicity of the electroactive probe plays an important role in their inclusion in the aggregate [36]. It is necessary that the micelle does not carry more than one probe molecule in order to obtain proper i_D values. The probe/micelle ratio can be less than unity.

The probe must be always electroactive, i.e. it must be able to exchange electrons with the electrode whatever the location in the micelles. This condition is almost always fulfilled when solubilized in micelles and microemulsions droplets, but it may not be the case in macroemulsions or vesicles [37, 38].

When a probe is dissolved in a very hydrophobic region of an aggregate, where it is not available for the electrons transfer, it does not remain electroactive. This is the case for 1-dodecyl-cyanopyridinium in SDS micelles (but not in hexadecyltrimethylammonium bromide

(HTAB) micelles) [39]. The half-wave potential is also affected: -0.6 V in SDS and -1.30 V in HTAB. However, there are cases as the methylferrocene that remains electroactive although it dissolves in the hydrophobic core of the HTAB micelles where it is relatively inaccessible to water and oxygen [40].

The D value depends on both, the surfactant and the probe concentration. D is computed using the analytic concentration of the probe, which is only valid if all the probes in the micelles are discharged when the micelles reach the electrode [41]. The Ilkovič equation can be used to check this: if i_d is not linear with the probe concentration, the effective concentration of the probe $[P_{eff}]$ is reduced. If a Poisson distribution of probe molecules among micelles is assumed then:

$$[P_{eff}] = [P] \left(1 - \exp(-[P]/[M]) \right) / ([P]/[M]) \quad (12)$$

where $[P]$ and $[M]$ are the probe and the micelles concentrations (in micelle moles per litre), respectively. The diffusion current is proportional to $[P_{eff}]$ instead of $[P]$. If not all the probes are discharged at the electrode, i_d , and consequently D , will diminish when the probe concentration is augmented and the surfactant concentration remains constant. This inconvenient is usually avoided using probes that do not partition between micelles and water and with $[P]/[M] \leq 1$. This latter condition also ensures that the size and shape of micelles are not affected by the inclusion of the probe molecule in the micelle [31, 42]. This has been also verified in microemulsions [30]. However, in very concentrated systems with rod-like micelles, the presence of several probe molecules in the same micelle may modify its size and shape [43].

The electroactive probe may be directly added to the surfactant solution in an appropriate amount [44]. This procedure was used with Cd^{+2} in sodium dodecylsulphate [65], disodium n-dodecane phosphonate [28] and sodium hexadecanoate [21]. The cadmium ions adsorb at the anionic micelle Stern layer forming a water insoluble compound solubilized by micelles.

The first probe used was Cd^{+2} , with $n = 2$ [32], which is useful for anionic micelles.

Water insoluble anthraquinone dyes (1,4-diamineanthraquinone and 1,4,5,8 tetraamineanthraquinone) have been used to tag non-ionic micelles [45]. The reactions of both dyes are reversible with $n = 2$ and the diffusion coefficients determined by polarography are of the order of $3 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$. These values are consistent with those expected for non-ionic micelles. The half-wave potentials were not affected by changes in the concentrations of the probe or the surfactant.

Ferrocene and tetrahydrofulvene were used in HTAB, hexadecyltrimethylammonium chloride (HTAC) and SDS. In all cases the probe was associated with micelles [46]. Ferrocene solubility in 0.1 M NaCl aqueous solution is $5 \times 10^{-5} \text{ M}$ [47] and $D_{\text{ferrocene}}$ is $6.7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. Cu^{+2} [48], several Fe^{+2} complexes [49] and N-alkyl-p-cyanopyridinium [31] have been also employed.

For cationic micelles, 1-dodecyl-4-cyanopyridinium iodide ($C_{12}PI$) and 1-hexadecyl-4-pyridinium iodide ($C_{16}PI$) [31] can be used as probes. $C_{12}PI$ is partitioned between water and micelles, whilst $C_{16}PI$ is almost water insoluble ($4.55 \pm 0.1 \cdot 10^{-4} \text{ M}$ at 23°C) and dissolves completely in micelles. These probes are useless with an anionic surfactant (such as SDS) because they are not accessible to the electrode electrons. Another homologous, the $C_{18}PBr$ has a water solubility of $4.05 \pm 0.1 \cdot 10^{-5} \text{ M}$ and $E_{1/2} = -0.63 \text{ mV}$ ($n = 1$) and -1.05 mV ($n = 1$) [42].

If the probe does not partition between water and micelles, i_D is independent of the surfactant concentration. Otherwise, both i_D and $E_{1/2}$ change with surfactant concentration.

Other probes are:

1-nitropyrene (PyNO₂): water solubility at 25°C: $(5.9 \pm 2) \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$, solubility in $2.78 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ TTAB: $(4.4 \pm 1) \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$. Half-wave potential in cationic surfactants $E_{1/2} = -0.61 \text{ mV}$ ($n = 4$) and -1.20 mV ($n = 2$), in anionic surfactants (SDS): $E_{1/2} = -0.26 \text{ mV}$ ($n = 1$), -0.68 mV ($n = 1$), -1.18 mV ($n = 2$).

1-pyrenecarboxylaldehyde (PyCHO):): water solubility at 25°C: $((3.4 \pm 0.5) \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$, solubility in TTAB $2.78 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$: $(6.75 \pm 1) \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. $E_{1/2} = -1.12 \text{ mV}$, $n = 1$ [42].

9-nitroanthracene (ANO₂): water insoluble. $E_{1/2} = -0.70 \text{ mV}$, $n = 1$

9-anthracenecarbonitrile (ACN): water insoluble. $E_{1/2} = -1.30 \text{ mV}$, $n = 1$ and -1.57 ($n = 1$) [42].

2,2'-dinitrobiphenyl: it undergoes a reduction in up to four steps in anionic, cationic or non-ionic surfactants. It is water insoluble but it seems that it is partitioned between the intermicellar solution and micelles, in a proportion of 77% in SDS, 95% in HTAB and 96% in Tween 80. In water-ethanol solution its diffusion coefficient is $1.1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ [50].

All these probes may be dissolved in organic solvents (ethanol, toluene or benzene). Then the solvent is evaporated and the surfactant solution is added and sonicated to allow the probe to be solubilised in micelles. In some cases the probe is added to the surfactant solution and then sonicated. Generally 2–4 hours of sonication is enough, but in some cases up to 10 hours were needed to ensure the correct solubilisation.

2.4.5. Surfactants whose counterion is electroactive

The measured diffusion coefficient is formed by the contributions of the counterions attached to the micelles, those released by the micelle ionization and those belonging to the dissociation of the unmicellised monomers. Adriamanampisoa and Mackay [51] performed voltammetric measurements on cadmium dodecylsulphate, and analysed the measured diffusion coefficient (D_{measured}) as:

$$D_{\text{measured}} = \left[1 - \beta - \beta(\text{CMC}/c)^2 + 2\beta (\text{CMC}/c) \right] D_x + \beta D_M (1 - \text{CMC}/c)^2 \quad (13)$$

where c is the total concentration; $\beta = 1 - \alpha = m/n$, the number of counterions (m) bounded to the micelle having an aggregation number n ; D_x and D_M are the diffusion coefficients of the unmicellised counterions and of the micelles, respectively. It is assumed in this equation that β and the concentration of unmicellised surfactant ions and counterions are constant above the CMC, what has been proved not to be generally true. Eq. (13) can be rearranged so that a plot of $(D_x - D_{\text{measured}})^{1/2}$ vs. c^{-1} must give a straight line:

$$(D_x - D_{\text{measured}})^{1/2} = -\beta^{1/2} \text{CMC} (D_x - D_M)^{1/2} c^{-1} + \beta^{1/2} (D_x - D_M)^{1/2} \quad (14)$$

Or it can be also rearranged to obtain a straight line whose intercept is D_x and the slope is $\beta(D_M - D_x)$ when plotting D_{measured} vs. $(1 - \text{CMC}/c)^2$:

$$D_{\text{measured}} = \beta (D_M - D_x)(1 - \text{CMC}/c)^2 + D_x \quad (15)$$

The authors found that the model failed at low supporting electrolyte concentration what was attributed to a significant contribution of the micelles to i_D . It is also possible that part of the cadmium attached to the micelles is not accessible to the electrode. Besides, the exchange between Na^+ and Cd^{+2} between the intermicellar solution and the micelle Stern layer may also affect the measured diffusion coefficient.

2.4.6. Electroactive surfactant ion

Saji et al. [52] deduced the following expression for the measured diffusion coefficient:

$$D_{\text{measured}} = [(\text{CMC}/c) - (\text{CMC}/c)^2] D_p + D_M(1 - \text{CMC}/c)^2 \quad (16)$$

where D_p is the diffusion coefficient of the monomeric electroactive surfactant ion.

2.4.7. Oxygen elimination

Oxygen interferes with the measurements. Generally, oxygen is eliminated by slowly bubbling nitrogen or argon at most by 12 minutes, and the bubbling is maintained while the measurement is performed [42]. Alternatively, when the foam formation is excessive, the sample may be placed in a two-neck flask and bubbled 1–2 minutes, then the flask is closed and the sample is left in an oxygen-free atmosphere. Once the foam is reduced, the procedure is repeated. Normally three cycles suffice to obtain a sample ready to measure.

2.4.8. Support electrolyte

Many studies on micellar or O/W microemulsions systems are performed with the addition of supporting electrolyte such as NaCl, KBr or KCl. This allows the suppression of the contribution of the aggregates tagged with the electroactive probe to the migration current while maintaining their diffusion current contribution.

In systems with ionic surfactants, provided the CMC is not very low, it is usually not necessary to add supporting electrolyte since the non-micellised surfactant ions and counterions act as supporting electrolyte. As the micelles are bigger than these ions and their concentration is low, their charge transport number is generally negligible. However, in some systems, the contribution of the micelles to the total conductivity of the system may be significant [9].

In order to study non-ionic micelles it is necessary to add supporting electrolyte which are usually adsorb on the micelles [53]. However, except in very high concentrations well above those needed to ensure conductivity, the non-ionic micelles are not affected by the swamping electrolyte.

When supporting electrolyte is added, it must be taken into account that it may affect the size and shape of micelles (especially ionic ones), the adsorption of the surfactant to the electrode surface and the electrostatic interactions among micelles [54].

2.5. The adsorption of surfactants on the electrode surface

At concentrations well below the CMC lone molecules adsorb. However, at a concentration called the critical hemimicellisation concentration (CHMC) the adsorption is by aggregates called hemimicelles (for SDS, CHMC \approx CMC/20) [55]. Above the CHMC the coverage of the electrode surface increases rapidly until it is saturated. Mono- and multi-layers may be formed, depending on the surfactant concentration and the applied potential to the electrode [54]. Since the studies on micelles are obviously above the CMC, the electrode surface is commonly covered by one or more surfactant layers. Anionic surfactants will desorb only at very negative potentials and the cationic ones at very positive potentials. Depending on the applied potential, the layer may re-orientate changing its density or reverse the orientation of their polar groups and chains. The adsorbed layer may affect the discharge of the electroactive species on the electrode [56]. The surfactant adsorbed layer may displace an absorbable electroactive species or may promote its incorporation to the adsorbed layer. If the surfactant is ionic, the layer may produce an additional electrostatic barrier against the electroactive ionic species. Ionic surfactants may also affect the structure of the electrode ionic double layer.

Adsorbed cationic surfactants usually extend the anodic range in aqueous solutions. The hydrophobic conducting film on the electrode inhibits water to reach the electrode surface [57, 58]

The presence of the adsorption layers does not seem to affect the reactions of electron transfer of the electroactive probes carried by aggregates [59].

The adsorbed layers may affect the potential but if they are thin their effect on the diffusion of the electroactive species to the electrode is negligible. However, it is convenient to check this in each case [54]. If the employed technique is not sensitive to the details about how the electrons are transferred in the electrode reaction, this does not affect the determined D value [54]. As examples, the Ilkovič and the Levich equations may be used for both reversible and irreversible reactions, whereas that of Randles-Sevcik must only be employed in reversible or quasi-reversible processes.

2.5.1. The half-wave potential

$E_{1/2}$ of the electroactive species is presumed to be different when the probe is attached to micelles and when it is dissolved in water. The availability of the electron coming from the electrode is modified by the surface potential of the micelles and the micro-environment of the probe in the micelle. If $E_{1/2,w}$ and $E_{1/2,M}$ are the half-wave potential values for the probe in water and in micelles, respectively, the experimentally measured half-wave potential, in case of a probe partition between water and micelles will be:

$$E_{1/2} = \frac{E_{1/2,w}}{1 + K C_M} + \frac{E_{1/2,w} K C_M}{1 + K C_M} \quad (17)$$

where C_M is the concentration of the micelles and K , the probe distribution constant between micelles and water. This equation assumes that the probe exchange between water and micelles is so fast, when compared with the electronic transference speed, that the reduction of the free and attached probes is seen as a unique wave in polarography. This situation is actually observed.

Since i_D depends not only on the partition but on the size and shape of micelles, whereas $E_{1/2}$ is essentially only dependent on the partition, this later may be used to obtain the partition constant of the probe between micelles and intermicellar solution, on the supposition that K depends only slightly on the surfactant amount in the intermicellar solution.

2.5.2. Effect of probe partition between micelles and the intermicellar solution

If the electroactive probe is only solubilized by micelles, or its water solubility is extremely low, the measured diffusion coefficient is that of the micelle (D_M).

If the probe is distributed between micelles and intermicellar solution, the measured diffusion coefficient is higher, because $D_M < D_{P,W}$ ($D_{P,W}$ being the diffusion coefficient of the probe in water). This must be taken into account to obtain correct D_M values [31].

Eq. (17) applies when it is assumed that the interchange of probe molecules between micelles and intermicellar solution is fast in comparison with the electronic transference [60]:

$$D_{measured} = x_W D_{P,W} + x_M D_M \quad (18)$$

where $D_{measured}$ is the measured diffusion coefficient, x_W and x_M are the probe mole fraction in water and micelles, respectively. Supposing that the partition constant of the probe between water and micelles ($K = [P_w]/[P_M]$, $[P]$: probe concentration) is independent of the probe concentration, then:

$$D_{measured} = (D_M + K D_{P,W}) / (1 + K) \quad (19)$$

This assumption holds if the probe or micelles concentration is low, and the probe is preferentially solubilized in micelles.

If the exchange velocity between micelles and intermicellar solution is lower than the electron transfer process, then the equilibrium between probes in water and in micelles inside the electrode diffusion layer cannot be obtained and the equation to be used is [60]:

$$D_{measured} = (x_W D_{P,W}^Z + x_M D_M^Z)^{1/Z} \quad (20)$$

where $Z = 1/2$ for polarography and cyclic voltammetry, and $Z = 2/3$ for spinning disk voltammetry. For microelectrodes, $Z = 1$ [34, 35].

This situation is the most frequent [61]:

$$D_{measured}^{1/2} = \frac{i_D}{708.1 \text{ n m}^{2/3} \text{ t}^{1/6} \text{ c}} = \frac{D_M^{1/2} K C_M + D_{P,W}^{1/2}}{1 + K C_M} \quad (21)$$

where C_M is the micellised surfactant concentration (on a monomer basis). It is supposed that the diffusion of the probe dissolved in the intermicellar solution and that of micelles are independent. $D_{P,W}$ may be experimentally determined in absence of surfactant.

Provided that D_M is independent of the surfactant concentration (which is not generally true), a plot of $D_{measured}$ vs. the surfactant concentration allows the determination of K and D_M .

To determine the relation between the reduction time (t_{red}) and that of the diffusion (t_{dif}), the diffusion current i_D is plotted against the probe concentration $[P]$. If this plot is linear, $t_{\text{red}} \gg t_{\text{dif}}$ and Eq. (18) may be used. Otherwise, $t_{\text{red}} \ll t_{\text{dif}}$ and Eq. (20) must be used [42]. In some cases, linearity is only obtained for some $[P]/[M]$ ratios.

In the derivation of the preceding equations it has not been considered the possibility that probe molecules may be attached to different micelle loci. It has been also assumed that the partition constant is independent of the probe concentration, similarly to the partition of a solute between two immiscible liquids. However, in some cases it has been observed a dependence of the diffusion coefficient with $[P]$ for methylviologen and ferrocene [62]. This phenomenon has been studied as the equilibrium of multiple union sites. Eq. (21) is obtained when it is considered that the probe is strongly bounded to the micelle and that there are μ probe molecules per micelle:

$$D = D_{P.W} [1 + [M] K_M [P]^{\mu-1}] + D_M [M] K_M [P]^{\mu-1} / [1 + [M] K_M [P]^{\mu-1}] \quad (22)$$

where $K_M = \mu K'$, K' being the equilibrium constant for the union of the μ probe molecules to the micelle.

3. Electrochemical study of the adsorption of surfactants on solid interfaces

Surfactant monolayers on a solid substrate have the potential to modify both the chemical and electrochemical behaviour of the interface between the solid and electrolyte [63]. These films have many applications in areas such as flotation, oil recovery, detergency [64], and templating of metallic nanoparticles [65, 66]. In this respect, nanoparticle (NP) synthesis in microemulsions has been a hot topic since the early 1980s, when the first colloidal solutions of platinum, palladium and rhodium metal nanoparticles were prepared [67]. Since then, a huge variety of nanoparticles has been synthesized in water in oil, and water in supercritical fluid solutions.

Coming back to the formation of surfactant monolayers at solid surfaces, this is also a subject of intensive research, with topics ranging from the influence of the surfactant's molecular structure [68, 69], to the hydrophilicity-hydrophobicity of the substrate surface [70], and the ionic strength and the nature of the counter ion [71]. The charging of the solid surface also has a significant impact on the surface assembly of non-ionic and ionic surfactants [72]. The electrical state of a surface plays a key role in determining the morphology of surfactants at solid interfaces and, unlike other shape determining factors such as the surfactant packing parameter [73], the electrical parameter can readily be adjusted *in situ*, providing a tuneable means to control films of soft condensed matter [74]. It is for this reason that electrochemistry provides the ideal set of tools to study the effect of charge on the behaviour of adsorbed surfactant molecules. By choosing a conductive substrate (such as gold), one has the unique opportunity to investigate the influence of charge density and hence the electrostatic field on the surface aggregation of surfactant molecules [75–80].

3.1. Differential capacitance measurements

The differential capacitance is defined as the derivative of the double layer's charge (q) with respect to the electric field (E) at a constant chemical potential (μ) (see Eq. (23))

$$C_d = \left(\frac{dq}{dE} \right)_{\mu} \quad (23)$$

In the electrical double layer, the capacitance depends upon the area of the electrode (A), the thickness of the double layer (d) the relative permittivity of the solution (ϵ_r), and the permittivity in a vacuum, (ϵ_0):

$$C_d = \frac{\epsilon_r \epsilon_0 A}{d} \quad (24)$$

In practice, the differential capacitance is measured using an electrochemical cell with a lock-in amplifier (LIA) that produces a sinusoidal voltage that is superimposed on the static electric potential, and analyses the oscillating current response. Since a LIA can measure signals with different phase shifts separately, using Eq. (25), one can obtain the C_d value from the real and imaginary current components [81]:

$$C_d = \frac{I_{\text{Im}}}{2\pi f V_{\text{ac}}} \left\{ 1 + \left(\frac{I_{\text{Re}}}{I_{\text{Im}}} \right)^2 \right\} \quad (25)$$

where f is the frequency of the alternating current, V_{ac} is the amplitude of the sinusoidal voltage and the real current (I_{Re}) and the 'imaginary' current (I_{Im}) are the currents measured in-phase and out-of-phase with the voltage, respectively.

Measurements of C_d therefore provide information on the permittivity of the layer adsorbed at the interface as well as the thickness of such a layer

3.2. Chronocoulometry measurements

Chronocoulometry (CC) allows the measurement of the change in charge density, σ_M , as a function of the potential. If the molecule of interest either does not conduct or is insoluble, then the measurements must be performed in an electrolyte solution. A measurement wherein current is measured with respect to time is called a current transient. At a certain potential, (E_{des}), all of the molecules will have been desorbed from the surface. The surface charge at this potential is the surface charge of the bare electrode (σ_M). After stepping the potential by ΔE to a potential of interest (E_i), where the molecules are adsorbed and waiting for equilibrium to be established, the relative surface charge of the electrical double layer can be measured by subsequently desorbing the molecules and integrating the current that flows during the desorption step. This process is repeated for a sequence of potentials E_i . A plot of charge density as a function of applied potential can be produced as a result.

In a plot of σ_M vs E the difference in area between the base electrolyte curve and the molecule of interest curve is equal to the surface pressure at that potential. This is because a surface pressure is equal to the difference between the surface energies of a system with and without the surface-bound molecule [82].

If the potential of zero charge (pzc) of the electrode is known (often measured by differential capacitance in a weak electrolyte solution such as 5 mM KPF₆), the measured surface charge ($\Delta\sigma_M$) at that potential can be used to calculate the absolute surface charge at the desorption potential by means of:

$$\Delta\sigma_M(pzc) = \sigma_M(pzc) - \sigma_M(E_{des}) = -\sigma_M(E_{des}) \quad (26)$$

Thus, the absolute surface charge at the potential of interest ($\sigma_M(E_i)$) can be calculated as:

$$\Delta\sigma_M(E_i) = \sigma_M(E_i) - \sigma_M(E_{des}) \quad (27)$$

When $E_i < E_{des}$, only the base electrolyte should contribute to $\Delta\sigma_M$, and the data should therefore resemble a curve of the base electrolyte alone.

By means of numerical integration one can obtain the area between the CC curve and that of the base electrolyte; that area is the surface pressure (π), usually in $\text{mN} \cdot \text{m}^{-1}$, when the surfactant adsorbs on the electrode's surface. The surface pressure is closely related to the excess free energy of the system (G^F) thus giving information on how much stable (or unstable) is the surface by having the surfactant adsorbed.

3.3. Electrochemical impedance spectroscopy

The classical electrochemical techniques use measurements of currents, electrochemical potentials, and charges as a function of time, which can in turn be related to the electrochemical potential. In contrast to this, electrochemical impedance spectroscopy (EIS) presents the signal as a function of the frequency at a constant potential. This can pose a problem to electrochemists, since we are used to thinking in terms of time, not frequencies. Another issue with EIS is that it requires a certain amount of knowledge in mathematics, in particular of Laplace and Fourier transforms, along with complex numbers. The following section is meant as a brief introduction to EIS along with its applications in systems with adsorption, such as the adsorption of surfactants on electrochemical interfaces.

The general definition of impedance is given by Eq. (28) as follows:

$$\hat{Z}(s) = \frac{L[E(t)]}{L[i(t)]} = \frac{\bar{E}(s)}{\bar{i}(s)} \quad (28)$$

where $\hat{Z}(s)$ is the operational impedance, and has units of resistance (Ω), L denotes the Laplace transform, s is the frequency, E the electrochemical potential and i the current density. The parameter s can be complex of the form $s = \sigma + j\omega$, or real $s = \sigma$, as in the classical Laplace transform. The impedance of each electrical circuit element is detailed in **Table 1** [83]. For each electrical component one can write the corresponding impedance and then, by applying

Element	Operational impedance	Ac impedance
R	R	R
C	$1/(sC)$	$1/(j\omega C)$
L	sL	$j\omega L$

Table 1. Impedance of linear electrical elements in an electrical circuit [83].

Kirchhoff's laws, calculate the total impedance of the electrical circuit. In the case of *ac* impedance, i.e. when the potential perturbation is sinusoidal, one uses the Fourier transform (*FT*), as shown in Eq. (29):

$$\widehat{Z}(j\omega) = \frac{F[E(t)]}{F[i(t)]} = \frac{\overline{E}(j\omega)}{\overline{i}(j\omega)} \quad (29)$$

Where the parameter s in this case imaginary and of the form $s = j\omega$. For further information about *FT* or *LT*, the reader is referred to any of the complex variable calculus books that cover in detail these transforms. Another quantity usually employed is the admittance, which is the inverse of the impedance:

$$\widehat{Y}(s) = \frac{1}{\widehat{Z}(s)} \quad (30)$$

Regarding applications with surfactants in electrochemistry, EIS has been widely used for the study of the inhibition of corrosion by surfactant coatings [84, 85], the investigation of ionic surfactant selective electrodes [86], the effect of anionic and cationic surfactants in the performance of batteries [87] and the study of electrochemical reactions in surfactant films [89], such as the study of O_2 reduction by haemoglobin in a film of didodecyldimethylammonium bromide [88], among other applications. By analysing the experimental EIS data and creating an equivalent electrical circuit for the reactions being studied, one can get a unique insight on the mechanism for those reactions.

The electrochemical techniques briefly described in this chapter can provide an insight on the mechanics of the adsorption of surfactants on solid electrochemical interfaces, as well as those of surfactant aggregates in solution. Electrochemistry possesses the advantage that by simply tuning the electrode potential one can create different conditions for the study of these systems, thus providing a powerful tool for the probing of surfactant systems.

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