

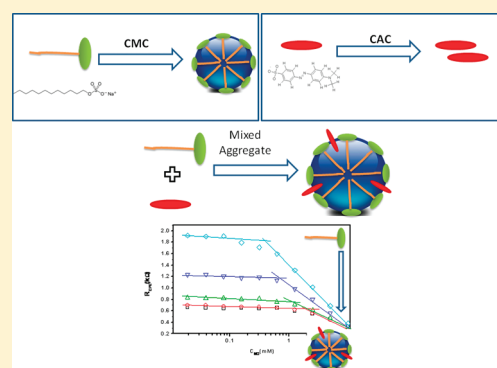
# Use of Electrical Impedance Spectroscopy as a Practical Method of Investigating the Formation of Aggregates in Aqueous Solutions of Dyes and Surfactants

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**ABSTRACT:** Molecular aggregation plays a key role in the physicochemical properties of dyes and surfactants. In this work, we show that electrical impedance spectroscopy (EIS) provides a practical method for the investigation of processes such as micellization in surfactants and dye dimerization. The electrical characterization of the structural phase transitions associated with aggregation events in these systems allows an accurate and direct determination of relevant parameters such as the corresponding critical concentrations for micelle formation and dimerization of these types of molecules, without the need of recurring to the use of auxiliary probe or reporter molecules. Because of its competitive advantages with respect to currently used methods (such as conductimetry and spectroscopic techniques), we argue that when implemented along the procedures described in this work, EIS becomes a simple and convenient technique for the characterization of aggregation processes in soft matter.



## 1. INTRODUCTION

Surfactants are molecules characterized by the simultaneous presence in their structure of a hydrophobic head and a hydrophilic tail that confer them an amphiphilic character.<sup>1</sup> In this manner, when diluted in small quantities in an aqueous solution, these molecules tend to migrate to the free air–water interface, reducing the surface tension of the liquid. When their relative concentration is further increased, free molecules become dispersed in the volume of the liquid subphase until a critical concentration is reached when they suddenly reorganize themselves to form globular aggregates. This typical aggregation process is commonly defined as micellization, and the corresponding concentration is named the critical micelle concentration (CMC), a temperature-dependent characteristic of the surfactant. In a polar medium, micelles are formed with the surfactant molecules radially oriented, their hydrophobic portion directed toward the core of the aggregate and the hydrophilic part exposed to the liquid and forming the outer part of the agglomerate; in the case of ionic surfactants, the counterions become distributed as an interfacial layer.<sup>2</sup> All physicochemical properties of a surfactant are deeply altered at the micellization concentration, so that the corresponding structural phase transition continues to be an important topic of interest. The thermodynamics of self-aggregation of amphiphilic molecules in a polar medium depends on a delicate balance between the interaction of the solvent molecules among themselves and with the surfactant's polar head<sup>3</sup> that favors the phase separation of the micelle into polar and apolar regions.

The use of amphiphilic molecules in biochemistry and pharmacology<sup>4</sup> has increased largely in the last years. Critical parameters such as the CMC are typically obtained by use of spectroscopic techniques (such as absorbance and fluorescence), which rely on the change of behavior of probe molecules (usually organic dyes)<sup>5</sup> or other techniques such as osmotic pressure, surface tension, and electrical conductivity.<sup>6</sup> However, one has to be careful to interpret the corresponding CMC results as the measured value seems to be dependent on the technique used for its determination.<sup>5a,7</sup> In fact, dye molecules, which have been widely used as reporters, also interact among themselves; the concentration for which dyes begin to form dimers in an aqueous solution is known as the (first) critical aggregate concentration (CAC). Hence, after the surfactant micelles are formed, the dye molecules used as probe in a reporter-based method of CMC determination are distributed into two different environments: one, where they are “free” and interact mostly with the solvent or tend to form dimers (when present in a concentration higher than the corresponding CAC), and another substantially distinct, inside the micelles, where their incorporation into the agglomerate structure is a mechanism competitive to the direct pairing between them.<sup>8</sup> As a consequence, properties such as fluorescence shifts at surfactant concentrations near the critical value can become more difficult to interpret.<sup>9</sup> Also, changes of the

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electrostatic forces within the micelles due to the presence of dye counterions can induce shifts in the critical value of the surfactant concentration at which the micelles are actually formed.<sup>10</sup>

Although the monitoring of the electrical characteristics of aqueous solutions of detergents has been previously used to investigate micelle characteristics,<sup>11</sup> electrical impedance spectroscopy (EIS) has only been sparsely used to examine surfactant aggregation.<sup>12</sup> Two different methods have been used to determine the CMC by considering the change in the slope of the variation of a given electrical parameter as a function of the surfactant concentration.<sup>13</sup> In the “conductance” technique, the specific conductance (defined as the ratio of the cell constant to the resistance of solution) is measured in a four-terminal cell for surfactant solutions of increasing concentrations,<sup>12b</sup> and this same approach has been applied to study the micellization process in microemulsions and miniemulsions.<sup>12c</sup> Alternatively, the self-assembly of amphiphilic molecules soluble in supercritical carbon dioxide has been investigated<sup>14</sup> by measuring how the static dielectric constant of the medium is affected by the structural reorganization of the surfactant at the CMC.

However, when a time-dependent electric field is applied upon a complex molecular system, there is a characteristic limiting frequency for which the internal degrees of motion are not anymore excited and the regions of the molecule that used to vibrate in phase cease to respond to the field; above this threshold frequency, a phase delay appears between the applied field and the response of the system. From the EIS point of view, reactive terms associated with changes in the charge distribution are now present, and a simultaneous increase in the AC conductivity is observed. When the CMC is reached and the dissolved surfactant molecules suddenly organize themselves by forming micelles, the characteristic frequency for which capacitive (i.e., reactive) terms begin to contribute to the electrical response of the system is decreased in a noticeable manner, an observation that can be considered as a dielectric signature of the structural phase transition. Reactive terms are associated with the imaginary part ( $Z''$ ) of the electrical response of the sample: in fact, at the critical micelle concentration, a well-defined transition must be observed for both dissipative ( $Z'$ ) and capacitive ( $Z''$ ) components of the impedance of the systems.

In the frequency domain, we can graphically represent the typical electrical response of a surfactant aqueous solution as the so-called RX diagram (or Nyquist plot), which is typically composed by a linear region at low frequencies associated with the diffusion and electrode polarization effects, plus a depressed arc that results from the composition of different semicircles, each one of them associated with a specific relaxation process. The relaxation times of different dissolved surfactants can be conveniently characterized by the so-called R-CPE equivalent circuit model (composed by a constant phase impedance element (CPE) in parallel with a resistor ( $R_{CPE}$ )),<sup>15</sup> chosen as to provide the same electrical response as the actual system. The CPE impedance is defined as

$$Z = \frac{1}{(j\omega)^\alpha C} \quad (1)$$

where  $j = \sqrt{-1}$ ,  $\alpha$  is a coefficient that measures the degree of distortion of the arc,  $C$  is a pseudo capacitance, and  $\omega = 2\pi f$ , where  $f$  is the frequency of the electrical field.<sup>16</sup>

In this work, we argue that electrical impedance spectroscopy can be used as a simple and convenient technique to investigate processes of molecular aggregation, such as those involved in

micelle formation in dissolved surfactants and in dimerization of organic dyes.<sup>17</sup> We will show that the CPE parameters correctly describe the corresponding structural transitions, assigning the deviation of the depressed arcs from true semicircles to the variation of the parameter  $\alpha$  (from 0 to 1, the upper limit in the case of an ideal capacitor).<sup>13</sup> One additional advantage of the EIS technique is that the use of foreign probe molecules is not required, as the noticeable electrical response comes directly from the structural reorganization (i.e., micelle or dimer formation) of the molecules of interest. Hence, as compared to alternative methods, such as use of fluorescent molecule “reporters”,<sup>5a,9,10</sup> the critical concentrations can be determined with no experimental error associated with the interaction between the probe and the dissolved molecules.

## 2. EXPERIMENTAL SECTION

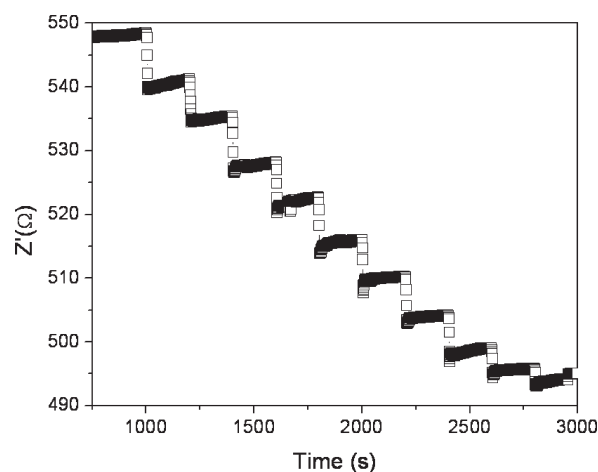
**CMC Determination.** The use of the EIS procedure for CMC determination of a specific surfactant at a given temperature consists of the simultaneous characterization of the real and imaginary parts of the total impedance of the corresponding aqueous solution.<sup>18</sup> We have implemented this by the introduction into a working solution of successive aliquots of a mother solution of the desired surfactant, assuring a stepwise increase in the surfactant concentration from a very diluted to a concentrated (i.e., with well-established micelles) limit.

The mother solutions were prepared after the prolonged stirring of a fixed amount of surfactant in ultrapure water obtained from a Nanopure system (Millipore, U.S.). The impedance measurements were performed at 25 °C using a SI 1260 gain/phase impedance analyzer and a SI 1296 dielectric interface (Solartron Instruments, UK) operating at the ( $10^0$ – $10^6$ ) Hz frequency range. A 100 mV excitation, with no external polarization, was applied to each solution analyzed through two ( $20 \times 11$ ) mm<sup>2</sup> parallel plates of steel, set 22 mm apart in the interior of a 20 mL beaker. The data analysis was performed by use of Z view, through the convenient adjust of data with the parameters of a R-CPE equivalent circuit model that characterize the dispersive processes and the electrical polarization. The surfactants (SDS, sodium dodecyl sulfate; DTAB, dodecyl trimethyl ammonium bromide; HDTMAB, hexadecyl-trimethylammonium bromide; LiDS, lithium dodecyl sulfate) were acquired from Aldrich and were used without further purification.

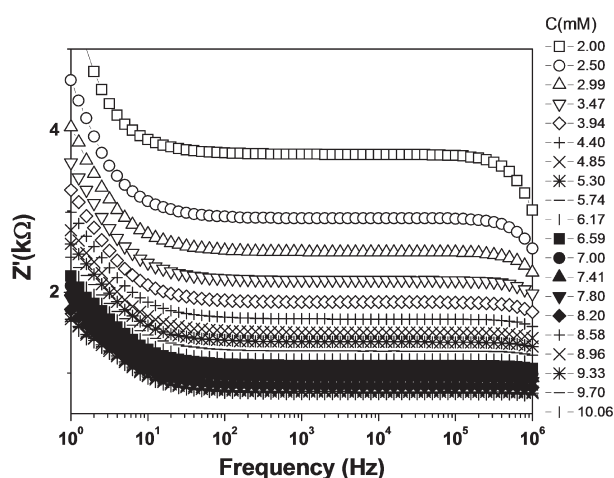
**CAC Determination.** Methyl orange has been appointed as an appropriate reporter molecule for the study of micelle formation in SDS aqueous solutions.<sup>5a</sup> So we have chosen this organic dye, which was purchased from Aldrich, in our investigation of existing interactions of probe molecules with surfactant micelles. The possible influence of dimers and oligomers on the micellization process was examined by a progressive and controlled increase in the concentration of methyl orange in a working solution of the chosen surfactant, where the same stabilization protocol described in the previous section was adopted. The EIS data were collected and analyzed as discussed above, so that changes in the dielectric response due to dye aggregation could be duly registered.

## 3. RESULTS AND DISCUSSION

**CMC Determination.** For both cases of CMC and CAC determination, we have to wait for the stabilization of the electrical response after the introduction of each additional



**Figure 1.** Electrical response ( $f = 1$  kHz) for successive insertions of aliquots from a SDS mother solution into a pure aqueous solution.

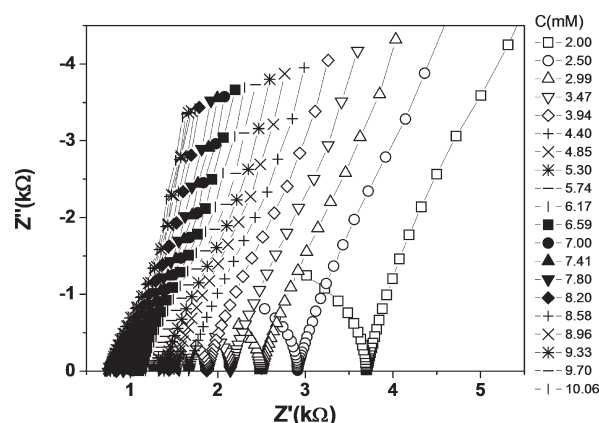


**Figure 2.** Real part of the impedance of SDS aqueous solutions at different concentrations.

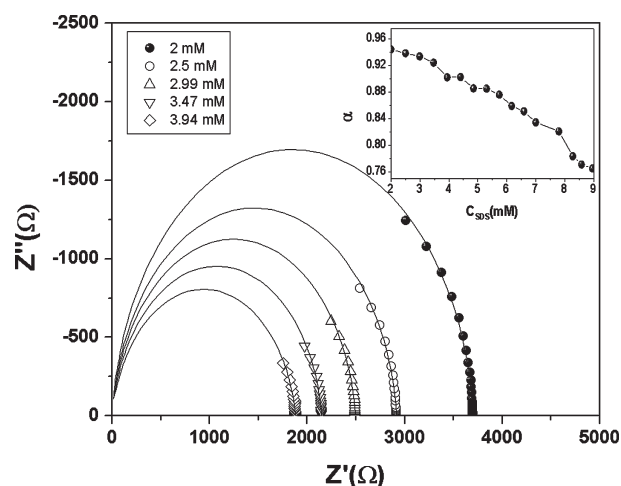
aliquot from the mother solution. After the complete dissolution of the added surfactant molecules in the working solution, a progressive and systematic reduction in the total impedance is observed (in Figure 1, we show the real part of the impedance at a frequency of 1 kHz of dissolved SDS at 25 °C). Note that this trend of progressive reduction in the value of impedance occurs in the complete range of analyzed frequencies, as can be seen in Figure 2.

The region of low frequency ( $f < 20$  Hz) in Figure 2 characterizes the electrode polarization, a phenomenon that is manifested in the plot of  $Z''$  versus  $Z'$  (Figure 3) as the almost linear branch at the far right. As expected, with the increase in the counterion concentration in the working solution, the radius of the Nyquist arc decreases and the relaxation frequency shifts to higher values, a trend that can be associated with the progressive reduction in the maximum value of  $Z''$  (see Figure 4, where the spreading factor  $\alpha$  (see eq 1) varies from 0.80, for high surfactant concentration, to 0.95, for very diluted solutions (2.0 mM SDS), as indicated in the inset of Figure 4).

At the same time, it is interesting to note that the 3-D map of  $1/Z''$  as a simultaneous function of both the frequency and



**Figure 3.** RX diagram of SDS aqueous solutions at different concentrations.

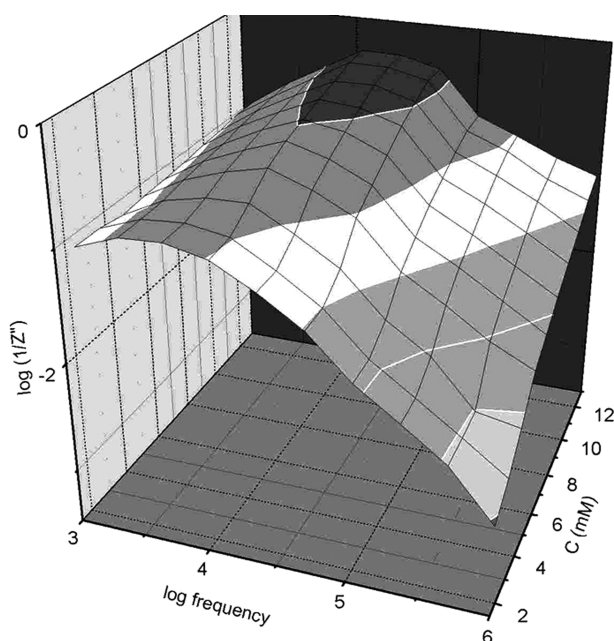


**Figure 4.** Nyquist plot of SDS aqueous solutions at different concentrations (symbols) and the fitting from R-CPE circuit model (continuous line). The variation of parameter  $\alpha$  as a function of concentration of SDS is indicated in the inset.

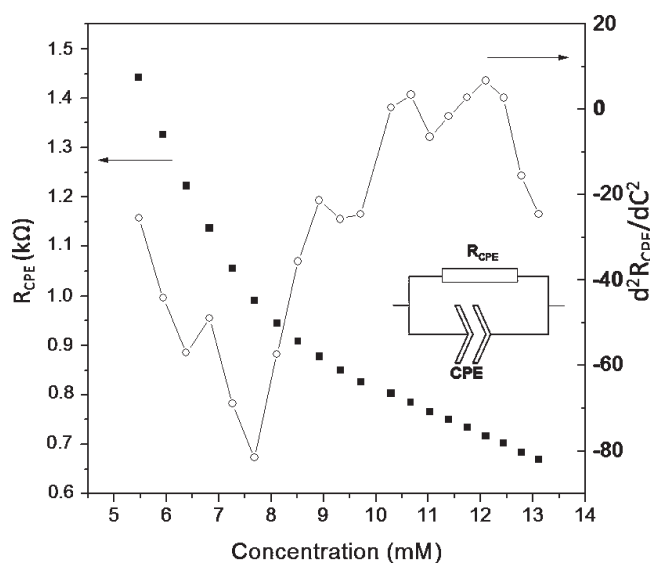
the surfactant concentration (Figure 5) reveals that a well-defined region of minimum in the modulus of imaginary part of impedance exists at intermediate frequencies ( $10^4$ – $10^5$  Hz) and surfactant concentrations above the typical CMC (8.08 mM in the case of SDS<sup>17,19</sup>). We call attention to the fact that, accordingly to the Kramers–Kronig relation,<sup>20</sup> changes in the real part of the impedance ( $Z'$ ) must be also reflected in the corresponding imaginary contribution ( $Z''$ ).

Therefore, the dielectric signature of aggregation processes can be found both in the real and in the imaginary parts of the impedance. The most convenient manner of separating the dispersive contribution from the total dielectric response is through the fitting of the experimental data by the electrical response of an equivalent R-CPE circuit model (the R-CPE model is shown as an inset in Figure 6). By including a distributed element, this model introduces a distribution of relaxation times associated with different aggregate sizes, allowing for the description of complex systems.

For the case of increasing concentrations of SDS, the results of equivalent resistance ( $R_{CPE}$ ) (Figure 6) reveal the existence of two linear limiting regions.

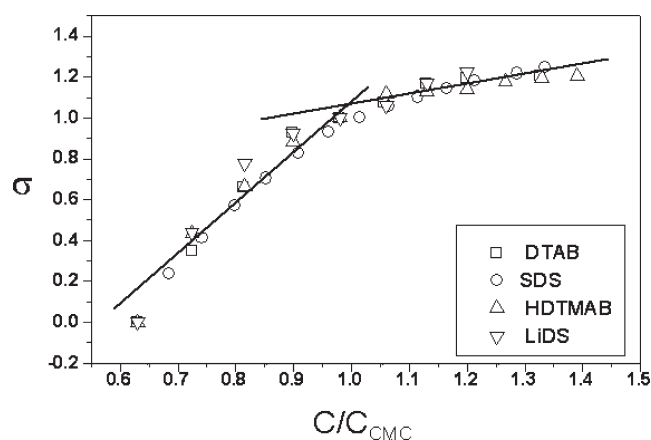


**Figure 5.** 3D map of inverse of  $Z''$  as a function of the frequency and SDS concentration.



**Figure 6.** Resistance of parallel circuit containing a resistor in parallel with a CPE and second derivative of curve as a function of surfactant concentration (the corresponding equivalent circuit is indicated in the inset).

In fact, the decrease in the impedance values should be fast at the beginning of the experiment, when the working solution still contains low surfactant concentrations. However, an abrupt transition in the slope of this curve is observed when the structural phase reorganization occurs, and a new linear region is obtained thereafter. The crossover of these two limiting behaviors (at 8.0 mM for the case of pure SDS) characterizes the CMC of the surfactant. This can be considered as a consequence of the Phillips criteria,<sup>21</sup> which establishes that at the critical concentration value of an independent variable  $\chi$ , a relevant physical



**Figure 7.** Normalized resistance of different ionic surfactant solutions as a function of the normalized concentration.

quantity  $\varphi$  must obey the relationship:

$$\left. \frac{d^3\varphi}{d\chi^3} \right|_{\chi_{\text{CMC}}} = 0 \quad (2)$$

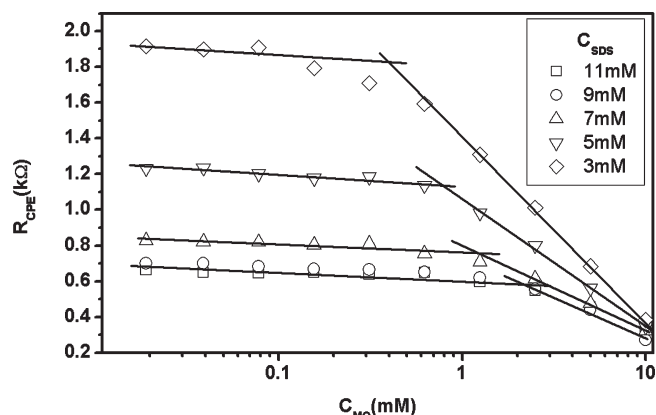
In the present case,  $\varphi \equiv R_{\text{CPE}}$ , and, consequently, the extreme in its second derivative characterizes the experimental value of the CMC.

We have applied this procedure to different cationic (HDTMAB and DTAB) and anionic (SDS and LiDS) surfactants, and the same general trend in the dielectric response is observed, as indicated in Figure 7. For this, we have defined a normalized resistance  $\sigma = (R_0 - R_{\text{CPE}})/(R_0 - R_{\text{CMC}})$ , where  $R_0$  is the resistance determined after applying the R-CPE equivalent circuit model to a working solution with low surfactant concentration,  $R_{\text{CMC}}$  is the fitted resistance at the CMC condition, and  $R_{\text{CPE}}$  is the resistance at different concentrations of the surfactant.

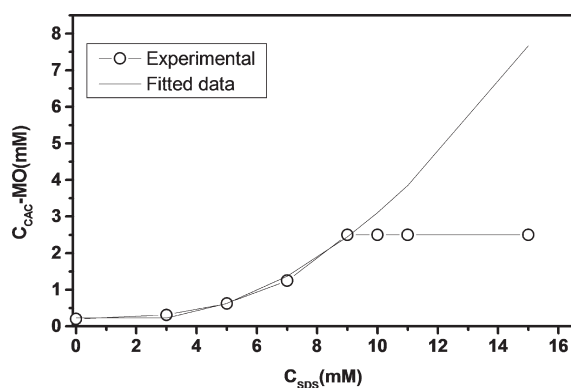
The fact that the dielectric response of different ionic surfactants follows a single “universal” curve can be taken as strong evidence that the EIS technique provides sufficient physical information about the system of interest to correctly describe the structural phase transition occurring at the CMC.

**Advantages of Not Using a Probe Molecule.** We have seen that contrary to what is usual in optical and spectroscopic methods of determination of the CMC value, in using the EIS technique there is no need to resort to the presence of a foreign probe molecule. If, for instance, dye molecules are introduced in the working solution,<sup>22</sup> a compromise must be reached between the minimum concentration required for obtaining a good signal-to-noise ratio and the need to avoid additional aggregation processes associated either with dye self-interaction (i.e., formation of dimers and oligomers) or with the interaction of the probe molecules with the surfactant. Both effects contribute to a higher degree of uncertainty in the measured value of the CMC of the system. It is important to note that, as when compared to the DC conductivity technique, measurements in frequency domain present another advantage: in the former method, the counterion concentration is necessarily high due to the simultaneous presence of dissolved dye and surfactant molecules, so that, at a low resistance limit, the sensitivity of DC conductivity is considerably reduced.<sup>23</sup> In the EIS technique, otherwise, even when the conductivity of the examined solution is very high, one can





**Figure 8.** Resistance of R-CPE equivalent circuit model from solutions containing SDS and methyl orange.

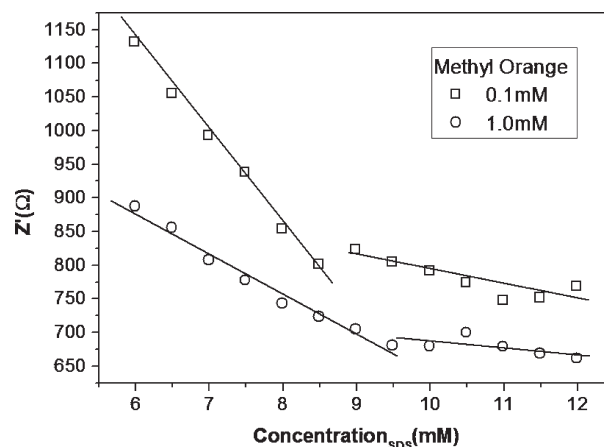


**Figure 9.** Critical aggregation concentration of methyl orange in aqueous solution as a function of SDS concentration. The lines characterize the fitted data to the absence of SDS micelles.

obtain a noticeable response from the dipolar components by choosing an appropriate high frequency limit of operation.

With the aim of measuring the mutual interaction between components of a typical dye-surfactant system, we implemented the procedure described in the CMC Determination section by progressively increasing the concentration of methyl orange in a different aqueous SDS solution. We have chosen to work with five values of the surfactant concentration (three below and two above the presumed CMC value) and analyzed how the existence of SDS micelles in the working solution would affect relevant aggregation parameters of the dye, such as its CAC (Figure 8).

It is well established in the literature that the dimerization of methyl orange in pure dye aqueous solutions occurs at 0.2 mM.<sup>24</sup> The results in Figure 8 indicate that for any increase in the surfactant concentration, there will be a corresponding increase in the critical aggregation concentration of methyl orange. The most important aspect to be considered from these results is that the presence of surfactant molecules induces an increase in the MO concentration where dimer formation begins to occur. In the EIS procedure, this variation can be identified with the change in the slope of the limiting (i.e., low and high concentrations) resistance values as the concentration of the dye is varied. When the critical surfactant concentration is reached, the  $R_{CPE}$  values become much less sensitive to the surfactant concentration, while a noticeable increase in the value of the dye CAC is observed, a



**Figure 10.** Critical micelle concentration of SDS in the presence of a fixed concentration of methyl orange.

further evidence that, once formed, the micelles act as effective promoters of the solubility of the dye molecules, favoring their incorporation into the larger aggregate and retarding the onset of the dimerization.

The situation is more easily understood by examining Figures 9 and 10; in the former, we show the measured values of the  $C_{CAC}$  of methyl orange as a function of the SDS concentration of the working solution. As discussed before, the CAC of methyl orange increases monotonically with the increase in the SDS concentration, until saturation is observed at a surfactant concentration of the order of 9.0 mM. This value, which can be considered as the apparent CMC of SDS in presence of the MO probe molecules, is higher than its actual value measured in the absence of a foreign species (see above and ref 19). Even at concentrations below its CAC, the presence of dye molecules affects the measured value of a surfactant's CMC, as shown in Figure 10. As one can note from the corresponding variation of the  $R_{CPE}$  values for SDS aqueous solutions of different concentrations, the estimated CMC is shifted from its actual value of 8.0 mM (in the absence of probe molecules, see Figure 6) to 8.5 [9.5] mM when MO molecules are also present at a concentration of 0.1 [1.0] mM. Taking the results of both Figures 9 and 10 into consideration, we come to the conclusion that use of probe molecules can lead to overestimated values of the critical parameters, because the interaction between the molecules of the probe and the surfactant affects both processes of micelle formation in the surfactant and dimerization of the dye.

#### 4. SUMMARY AND CONCLUSIONS

The EIS represents a convenient technique for characterizing aggregation processes in colloidal solutions, because the application of an external potential in the form of sinusoidal signal can be correlated to the measured intensity and phase delay of the electrical current obtained as a response. In this manner, relevant information about the examined samples can be gathered not only from the observed charge transport but also from the measured charge polarization that results from the forced spatial reorientation of the microscopic electric dipoles. The use of distributed elements such as the CPE in the R-CPE equivalent circuit model introduces an additional advantage on the conventional technique of measurement of conductivity to determine the CMC and dimerization processes in organic dyes: by

conveniently separating the contribution of the loss and reactive (such as electrode polarization) terms, the EIS technique allows one to consider the ionic transport in the frequency domain as a fundamental parameter in the measurement of aggregation processes in the nanoscale, which involve an increase in the spatial localization of carriers.

By application of this model to the cases of micelle formation in surfactants and of dimer aggregation in dye aqueous solutions, we have been able to examine not only how the presence of probe molecules influences the measured values of CMC, but also how surfactant molecules affect the measured values of CAC in mixed dye–surfactant systems. The unavoidable interaction between these different molecules is a strong argument in favor of using methods that directly assess changes in the microscopic organization of both surfactant or dye aqueous solutions. In that regard, due to the simultaneous consideration of both loss and reactive contributions, EIS appears as a simple and competitive method for studying microscopic aggregation processes in soft matter. In the methodology here presented, EIS can be easily implemented by use of a two-terminal cell while (due to the range of operating frequencies) demanding only a modest time of measurement.

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