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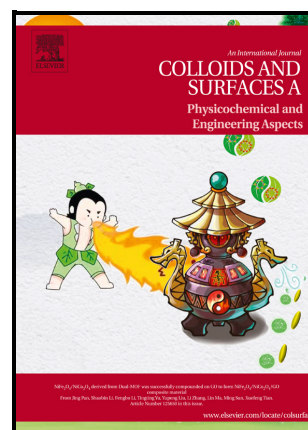
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# CRITICAL MICELLE CONCENTRATION DETERMINATION WITH NON-CONTACT RF DIELECTRIC IMPEDANCE METRY FOR SURFACTANTS IN SOLUTION

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## Abstract

Surfactants are a widely used family of polar molecules which possess both hydrophilic and lipophilic parts. Their polar conformation properties make them useful in a variety of applications, including emulsion stabilization, drug delivery, and detergency. In a colloidal solution, surfactant molecules self-aggregate to form micelles which can be used to reduce the surface tension of oil-water interfaces in emulsions. The Critical Micelle Concentration (CMC) is the point at which the surfactant undergoes self-aggregation, forming a separate phase that modifies the electrical and mechanical properties of the colloidal solution. From a kinematic perspective, it is related to the critical stage at which the droplets are stabilized by the surfactant molecules. The CMC can be estimated using a variety of techniques. Each method possesses its own inherent limitations, which can result in approximations, especially when dealing with mixtures of multiple surfactants and polymers. This article presents a novel contactless radiofrequency inductive technique for measuring the CMC of surfactants in complex fluids. This method is based on the monitoring of the dielectric properties of the complex medium. The effectiveness of the technique is validated using known surfactants according to literature and conventional methods. The capacity of this technique to provide consistent and accurate CMC values, even for complex solutions comprising multiple surfactants, is demonstrated.

## Keywords

CMC, surfactant, dielectric properties, radiofrequency impedancemetry.

## 1 Introduction

Surfactants are characterized by the presence of polar functional groups, which impart a dual hydrophilic and lipophilic nature. This unique chemical feature governs their preferential absorption at oil/water and air/solution interfaces. At the interface, the polar head group solvates into the continuous phase, while the apolar part permeates into the oil or air phase, thereby reducing surface tension, and even inducing self-aggregation in colloidal media. This ability makes them suitable for a variety of applications, including stabilization of emulsions, formation of polymeric micelles, drug-delivery control, and optimization of detergency product [1], [2], [3]. As the concentration of surfactants increases, they populate the interface until complete saturation is reached. At this point, a barrier of surfactants is formed, facilitating emulsion stabilization [4]. At the critical concentration, defined as the Critical Micelle Concentration (CMC), a new separate phase consisting of self-aggregated amphiphilic structures (micelles) occurs, and coexists with the saturated barrier, which is known as the Langmuir monolayer.

The shape of the micelles, which are typically spherical, is dictated by their electrical and steric interactions with the continuous phase and any extant droplets. These interactions give rise to an amphiphilic shell comprising both polar head groups (a hydrophilic shell) and a centripetal internal distribution of non-polar amphiphilic tail groups [5]. The structural behavior and stability of the micelles can be significantly altered by changes in temperature, pH, and the presence of electrolytes and polymers [6], [7], [8], [9]. Consequently, changes in global CMC occur [10]. To characterize surfactant micelle formation and to optimize the stability of novel micellar solutions [11] or droplet interactions in emulsions [12], CMC monitoring is a common and crucial approach.

Several methods have been proposed for the determination of CMC [13]. The prevailing methodologies are based on the surface tension [14] and conductivity measurements [15] and may involve the use of fluorescent probes [16], [17]. Although inaccurate values can be obtained as a function of surfactant concentration, surface tension and conductivity measurements are known to be the most expedient for high CMC values. However, at low surfactant concentrations these two techniques lack the sensitivity required to detect mesoscopic variations and may be affected by the presence of impurities. Fluorescent probe methods, such as those using fluorescein [18] or organic compounds [19], can provide accurate results, but may be affected by the presence of additional compounds that alter the CMC and the geometry of the micelles [20]. Beyond the aforementioned limitations, these techniques may not be universally applicable to all surfactants [21] and are unable to quantify the CMC values of complex fluids containing multiple surfactants. Alternative methods exist for measuring the CMC of a surfactant solution such as viscosity and density measurements [22], osmotic pressure [23], Micellar Electro Kinetic Chromatography (MEKC) [9], calorimetry [24], Dynamic Light Scattering (DLS) [24], centrifugation [25], or  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectroscopy [26]. Each of these methods possesses its own set of limitations, including the necessity for prior knowledge of the CMC, difficulties in setting up the measurement, and the requirement for ionic surfactants [27]. The CMC values obtained from these techniques can exhibit significant variability, and there is currently no known correlation between the results obtained from different methods [28]. This highlights the necessity for alternative or combined methods to accurately determine CMC values for a wide range of surfactants and mixed solutions in complex fluids. There are substantial inconsistencies in the measured values reported in the literature, even for common surfactants.

The polarizability of the head group layer in contact with water is strongly governed by its binding to carbon atoms, as evidenced by NMR or fluorescence measurements [29], [30], [31], [32]. Therefore, measuring the dielectric properties of the fluid is of interest. Initial determinations of the dielectric constant have permitted the calculation of the critical micellar concentration (CMC) through the utilization of a capacitive probe immersed in the fluid, and through the application of a Gaussian second derivative approximation fit to the measured permittivity within a frequency range between 200 kHz and 20 MHz [15]. Nevertheless, the high-frequency resistive effects of the contact surfaces between the probe and the complex fluid can introduce a significant bias.

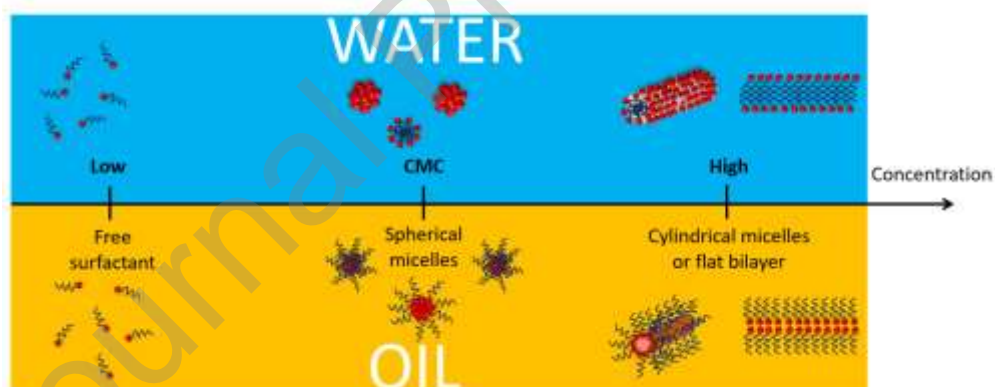
The objective of this article is to present an alternative inductive technique for an accurate measuring of the CMC through complex dielectric characteristics of a fluid [33], [34]. The physical principle of the technique regarding steric and electrical interactions is described in order to link the inductive measurements to the CMC deduced from a surfactant solution. The study was conducted in a variety of solvents, including water, thickened water, and oil, to examine the influence of chemical interactions and steric hindrance and to anticipate the potential applications of this technique in fields such as emulsion formulation in cosmetics. A

comparison of the results is done with a classic tensiometer. Finally, a protocol to determine the CMC value of mixtures is proposed and validated according to the theory.

## 2 Surfactant effects and interactions in solutions

### 2.1 Micelle formation due to surfactants

The inherent instability of oil-water mixtures can be primarily attributed to their high interfacial energy of interaction and thermodynamic disturbances. However, this instability can be mitigated through the addition of suitable surfactants, which possess a polar group that enables solubility in water, due to the amphiphile part (head or tail), and solubility in oil, due to the aliphatic second part. These molecules facilitate optimal interactions by occupying the interfaces, thereby reducing the interfacial energy which reaches a plateau (ideally close to zero). These reductions are observable at unmissable liquid-liquid interfaces and at air-liquid interfaces. When the bulk concentration of the added surfactant reaches a certain threshold, it no longer reaches the interface but instead remains in one of the bulk phases in the form of micelles. The nature of the created micelles is determined by the composition (hydrophilic and lipophilic groups presence), and the electric charge (ionic or nonionic head) of the surfactant. The evolution of surfactant aggregation in relation to its concentration in the solution is illustrated in Figure 1. As the concentration of surfactant molecules increases, its structural behavior evolves from interface interactions to the formation of disperse spherical micelles. Under specific conditions, surfactants may also form more sophisticated interpenetrated and multilayered structures.



**FIGURE 1 - EVOLUTION OF SURFACTANT MOLECULES STRUCTURATION IN CONTINUOUS PHASE (OIL OR WATER) REGARDING THE CONCENTRATION, FOCUS ON MICELLES AND NOT ON THE SATURATED LANGMUIR MONOLAYER**

At the microscopic scale, the structuration of micelles is governed by the equilibrium of electrical interactions. When the concentration of surfactants is sufficient, the interplay between Van-der-Waals attractive forces and Brownian movements is counterbalanced by repulsive forces, leading to the aggregation of surfactant molecules into micelles. The resulting distribution of electric charges at the interfaces of macromolecules can be modeled as a spherical double layer, as outlined in the Gouy-Chapman and Stern models. The first layer, being adsorbed in the micelle, is less susceptible to local mechanical or electrical solicitation. The second layer is more dispersed in the continuous phase. The application of a local electric field can deform the layer, given the viscosity of the continuous phase and the mobile electric charges nature. Therefore, the double layer structuration is linked to its polarizability. The relation between interfacial structure and polarizability is usually characterized by zeta potential. In the context of cosmetic emulsions, for instance, it has been observed that the

higher the zeta potential, the more the emulsion resists to thermodynamic evolution [35]. The zeta potential can be determined from induction currents monitoring [36]. This relation can be linked to the one existing between dielectric relaxation and mechanical relaxation [37].

## 2.2 Polarizability and dielectric loss factor for surfactants in solution

The double layer generates a significant variation in polarizability, while mobile electric charges enhance the conductivity of the continuous phase. Consequently, the apparent dielectric properties variations are contingent on both the polarizability distribution and the associated dispersion law [15], [38]. Historically, the dielectric relaxation process model was proposed by Debye. However, this model only applies to dipoles in viscous fluids. For more complex media, in which anomalous diffusion is observed, such as polymers, glass forming liquids, and disordered media, empirical models based on power laws have been proposed. The most used are the Cole-Cole, Cole-Davidson, and Havriliak-Negami ones [39], [40], [41]. The mathematical framework of the dielectric relaxation model is derived from fractional calculus formalism and Maxwell equations [42], [43], [44], [45], [46]. Here, we start from the Havriliak-Negami model which is the more generic. It is expressed by Eq (1) [47], with  $\epsilon_0$  the vacuum permittivity,  $\epsilon^*$  the complex permittivity at the considered frequency  $\omega$ ,  $\tau$  a relaxation characteristic time, and  $\alpha, \beta$  two dimensionless coefficients. In the following,  $j$  is the imaginary unit.

$$\frac{\epsilon^*}{\epsilon_0} = (1 + (j\omega\tau)^\alpha)^{-\beta} \quad (1)$$

It is assumed that  $\alpha$  and  $\beta$  are empirical parameters that are fitted to experimental data. Their physical significance is related to the structure and motion of atoms, clusters of atoms, and more generally to electric charges distribution [46], [48], [49]. Then, the relaxation time  $\tau$ , and both  $\alpha$  and  $\beta$  coefficients are representative of the medium structural characteristics. Specifically,  $\alpha$  is associated with the ionic polarizability, while  $\beta$  is related to the interfacial polarizability [50], [51].

The complex permittivity can be expressed as a function of two components:  $\epsilon'$  representing the relative dielectric constant, which is related to polarizability, and  $\epsilon''$  representing the electrical conductivity, which is linked to the dispersion. From an energetic perspective, the ability to store electrical energy is explained by  $\epsilon'$ , while the energy dissipation of the material is described by  $\epsilon''$  [52], [53], [54]. The relation between the complex permittivity parts, the frequency, the conductivity  $\sigma$  and the permittivity  $\epsilon$  is summarized in Eq (2) [52], [54], [55], [56].

$$\epsilon^* = \epsilon' - j\epsilon'' = \frac{\epsilon}{\epsilon_0} - j \frac{\sigma}{\epsilon_0 \omega} \quad (2)$$

The frequency  $\omega$  defines the variation rate of local electromagnetic sollicitation, and, consequently, the investigated spatiotemporal scale. To operate at the interfaces scale, a frequency around the hundreds of megahertz appears to be suitable, whereas low frequency is more appropriate for macroscopic characterization [57].

At the interfaces scale, we can consider that the ionic displacement is negligible, and then  $\alpha$  equals one. From a mathematical point of view, this coefficient is mostly used to flatten the frequency response at low frequencies. Then, Eq (1) can be developed, according to complex formalism, as Eq (3).

$$\frac{\epsilon^*}{\epsilon_0} = (1 + \omega^2\tau^2)^{-\frac{\beta}{2}} \exp((-j\beta \arctan(\omega\tau)) \quad (3)$$

Eq (3) can be separated in its real and imaginary parts as shown in Eq (4).

$$\begin{aligned} \epsilon' &= (1 + \omega^2\tau^2)^{-\frac{\beta}{2}} \cos \\ \epsilon'' &= - (1 + \omega^2\tau^2)^{-\frac{\beta}{2}} \sin(\beta \arctan(\omega\tau)) \end{aligned} \quad (4)$$

Considering that  $\omega\tau$  should remain the same on frequency range investigated, the extraction of the dielectric structuration information can be achieved through the measurement of the dielectric loss factor, as delineated in Eq (5). The first line is derived from Eq (2), the second line is derived from Eq (4).

$$\left\{ \begin{array}{l} \tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\sigma}{\epsilon\omega} \\ \tan \delta = \frac{\epsilon''}{\epsilon'} = \tan(\beta \arctan \omega\tau) \end{array} \right. \quad (5)$$

The aggregation of surfactant molecules into micelles, and then the CMC point, can be investigated by monitoring the polarizability at mesoscopic scale, regardless of its ionic or non-ionic nature.

## 2.3 CMC of surfactants mixtures in solution

As previously explained, the Critical Micellar Concentration is defined as the concentration of surfactant that initiates micelle formation in solution. This value depends on various parameters, including temperature and the chemical nature of the surfactants. Consequently, predicting the CMC point remains a challenge [5], [58], [59].

However, in a more general context, mixtures are formulated with multiple surfactants to enhance their characteristics. According to the research conducted by Clint [60], it is possible to ascertain the CMC value of a mixture based on a mixture distribution model. Typically, the CMC value of a mixture falls between the CMC value of the individual surfactants. The expression for the mixture distribution model is given by Eq () which is derived from Lange and Beck [61]. In this equation, the CMC of the individual surfactants is denoted  $CMC_{S_1}$  and  $CMC_{S_2}$ , while the mixture one is designated as  $CMC_{mixture}$ .

$$\frac{1}{CMC_{mixture}} = \frac{x}{CMC_{S_1}} + \frac{(1-x)}{CMC_{S_2}} \quad (6)$$

The application of an appropriate characterization method is expected to facilitate the determination of the unknown CMC value of a surfactant, given the knowledge of the one of a reference substance.

## 3 Materials and Methods

### 3.1 Raw materials

To execute the previously designated tests, a variety of raw materials are used. Among the surfactants, Polysorbate 80® (Alfa Aesar) and Brij® O20 (INCI: Oleth-20, Sigma Aldrich) are employed. These materials have both been extensively documented with regard to their CMC values (respectively 13 mg.L<sup>-1</sup> to 15 mg.L<sup>-1</sup> and 25 mg.L<sup>-1</sup>) [14], [27], [62], [63], [64], [65], [66]. Additionally, their CMC values are sufficiently separated to allow for the observation of a

significant difference during the measurement process. The purity of Polysorbate 80® is  $\geq 95\%$ , while for Brij® O20 it is only mentioned to be  $\leq 100\%$  (quality level MQ200 of Sigma Aldrich).

The two surfactants are studied in demineralized water, in demineralized water containing a non-activated thickener called Carbopol® Easy To Dispersed (CETD® 2050, Lubrizol) and in isopropyl palmitate (Alfa Aesar®), a chemical oil. The demineralized water is obtained from an Aquadem Option R equipment from Veolia (resistivity at 18 M $\Omega$ .cm). In addition, mixtures of both surfactants are tested, either in a 50/50 w/w ratio or a 25/75 w/w ratio.

Based on reported values of CMC in water, a first screening experiment is done for all configuration with a concentration range of surfactant in solution between 5 mg.L<sup>-1</sup> and 35 mg.L<sup>-1</sup>s to ascertain the CMC based on the reported literature values. A second one is done, restraining this range to experimentally observed values. In this article, only this second experiment is presented. Consequently, the ranges for the different configurations are the following:

- Polysorbate 80 in water: [10 – 20] mg.L<sup>-1</sup>
- Brij®O20 in water: [10 – 35] mg.L<sup>-1</sup>
- Polysorbate 80 mixed with Brij®O20 in water: [10 – 35] mg.L<sup>-1</sup>
- Polysorbate 80 in thickened water: [5 – 25] mg.L<sup>-1</sup>
- Brij®O20 in thickened water: [20 – 30] mg.L<sup>-1</sup>
- Polysorbate 80 mixed with Brij®O20 in thickened water: [5 – 30] mg.L<sup>-1</sup>
- Polysorbate 80 in isopropyl palmitate: [10 – 30] mg.L<sup>-1</sup>
- Brij®O20 in isopropyl palmitate: [10 – 40] mg.L<sup>-1</sup>
- Polysorbate 80 mixed Brij®O20 with in isopropyl palmitate: [10 – 40] mg.L<sup>-1</sup>

The uncertainty on concentration is obtained from the type B uncertainty on the weight measurement. Given the number of compounds, the latter ranges between 0.6 mg.L<sup>-1</sup> and 1.00 mg.L<sup>-1</sup>. All products are stored at 25°C. The measurements are conducted at room temperature for the tensiometer, and at 25°C for the impedancemeter. All measurements are performed the week following the formulation.

### 3.2 Surface tension tensiometer

In this study, a Du Noüy K6 surface tension tensiometer from Krüss is employed, owing to its good reproducibility and sensitivity in CMC determination. The calibration of the instrument is made with water to ensure a measurement at 72 mN.m<sup>-1</sup>. A glass crystallizer containing the solution is positioned beneath the system and a platinum ring is maintained on the surface. Then, a crank arm is rotated to create a meniscus between the ring and the solution. The rupture of the meniscus results in the measurement of the force. The graphical determination of the CMC is then done by reading the concentration corresponding to the slope discontinuity.

### 3.3 RF impedancemeter

The SATIE laboratory developed a dedicated device to better comprehend the dielectric behavior of molecules depending on their conformation. This system is an inductive technic that utilizes radio frequency to measure the sample electrical impedance [52], [67]. A similar device with an alternative geometry was previously employed to characterize biological tissues [67], [68], [69] and to identify alterations of organic compounds, such as oil adulteration [70]. While other electromagnetic characterization techniques exist [70], [71], the device described in this article presents the advantages to be contactless and non-destructive. It operates at

high frequencies, enabling the probing of the mesoscopic scale, which encompasses the spatiotemporal dynamics of interfaces involving macromolecules dispersed in a solution or a multiphasic medium. Furthermore, the device is independent from the nature of the solvent and the surfactant.

The device is based on a monitoring one-wire loop copper coil coupled to a resonant bracelet composed of two copper cylinders separated by a 250  $\mu\text{m}$  CuFlon<sup>®</sup> layer. A harmonic electric current is set in the copper coil, which induces an electromagnetic field. At the frequency resonance of the bracelet, which depends on its geometry, the electromagnetic field is amplified. The presence of the sample within the resonant bracelet modifies the dielectric properties of the apparent medium sensed by the electromagnetic field, as displacement and eddy currents are generated in the sample. It is then possible to retrieve the sample dielectric properties (permittivity and conductivity) with a differential measurement [52], [54]. The experimental setup is illustrated in Figure 2.

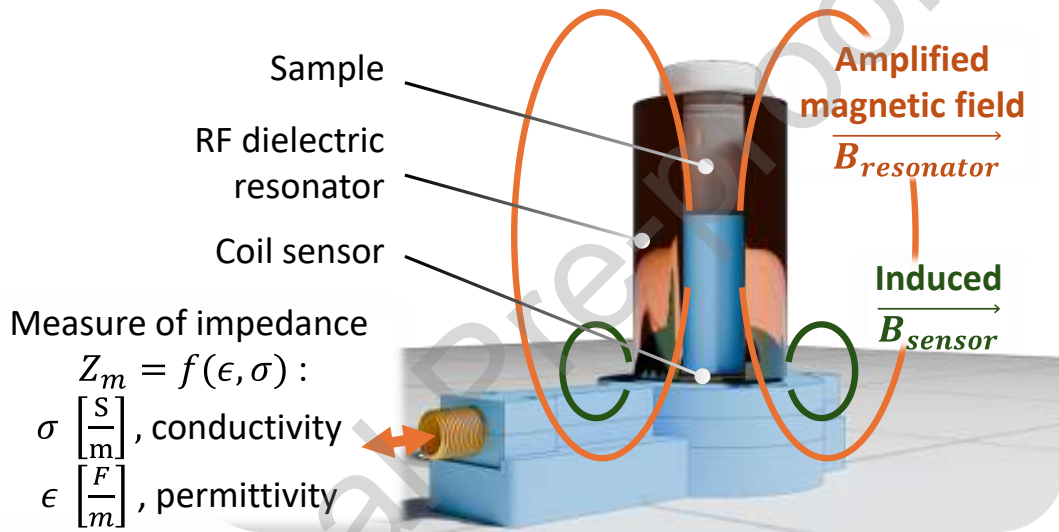


FIGURE 2 - EXPERIMENTAL SET-UP OF THE RF IMPEDANCEMETER

To retrieve the dielectric properties of the sample, the device utilizes the extraction of the electrical impedance [54]. The material impedance  $Z_m$  can be expressed as Eq (6), with  $V$  the investigated volume,  $\vec{B}$  the magnetic induction and  $I$  the associated current. The values of these three quantities are contingent on the geometry of the experimental set-up, the environment, and the dielectric properties of the apparent medium. The resultant values of  $V$ ,  $\vec{B}$ , and  $I$ , can be combined in an experimental constant, which is hypothesized to remain constant over the experiment duration.

$$Z_m(\omega) = \omega^2 \int_V (\sigma + j\omega\epsilon) \left| \frac{\vec{B}}{I} \right|^2 dv \Rightarrow \tan(\delta) = \frac{\text{Im}(Z_m(\omega))}{\text{Re}(Z_m(\omega))} \quad (7)$$

It is then conceivable to extract the apparent complex permittivity. To circumvent computation errors arising from the extraction of the experimental constant, it is advisable to calculate the ratio between the imaginary and real parts, which is equivalent to what is obtained in Eq (5). Consequently, the ratio  $\sigma/\epsilon\omega$  is indicative of interfacial polarization and, more broadly, of electrical charges structuration.

The experimental setup involves an inductive RF resonator operating at a frequency of 139 MHz, with a quality factor ranging from 700 to 1000. At this frequency, the measured values are an indicator of the ionic scale at the interface between the surfactant and water. The

dimensions of this resonator are 60 mm in height and 30 mm in diameter. The glass vial containing the emulsion is 37 mm in height and has a diameter of 20 mm. It is filled with a deposit of 6.2 g of solution, which represents 6 mL in volume. It is placed inside the resonator without direct contact.

The monitoring coil is probed with an HP® 4195A network analyzer. All experiments are performed in a thermo-regulated chamber (Binder® KT53) for a controlled atmosphere at 25 °C, with a thermal stabilization time of at least 10 min, which has been found to be the time to get an emulsion at thermal plateau in preliminary tests. A calibration is necessary to evaluate the equivalent impedance and the induced resistance of the system. Each measurement is made of 160 acquisition points with a reference (empty detector) and a data frame (sample in the resonator). Uncertainty is computed over the 160 points.

## 4 Results and discussion

The CMC is typically determined using a tensiometer by solubilizing the surfactant in water varying concentrations. Beyond the CMC, the surface tension remains constant regardless of concentration. In other media, this procedure is biased because of the viscosity of the continuous phase, or the interactions with other macromolecules. To evaluate the limits of both techniques, in this study, the CMC is also measured in water containing a non-activated thickening agent and in oil.

### 4.1 In water solvent

Measurements of the interfacial tension obtained with the tensiometer are presented in Figure 3 for both surfactants in water solution.

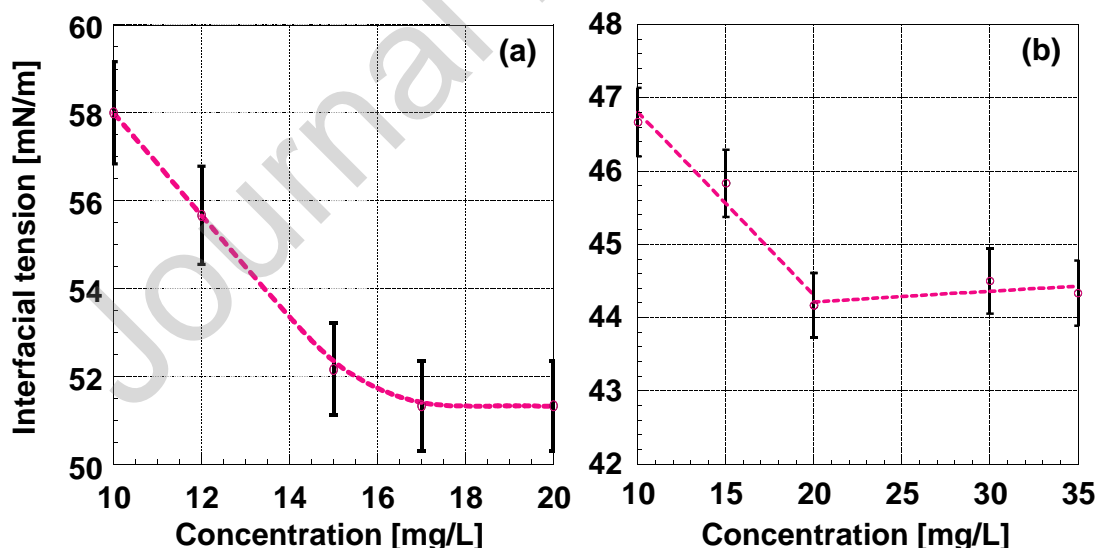


FIGURE 3 - CMC RESULTS WITH TENSIO METER FOR (A) POLYSORBATE 80 AND (B) BRIJ®O20 IN WATER

Running a Monte-Carlo approach, based on the estimation of the breakpoint in piecewise linear fits, we can estimate the slope discontinuity reading and its uncertainty. Given  $N = 1000$  random points for each interfacial tension in a range considering 2% of relative error, we get the following. For Polysorbate 80, the slope discontinuity indicates that the estimated CMC point is obtained at  $15.1 \text{ mg}\cdot\text{L}^{-1}$  with a standard deviation of  $1.6 \text{ mg}\cdot\text{L}^{-1}$ , while it is seen

above  $21.4 \text{ mg}\cdot\text{L}^{-1}$  for the Brij®O20 with a standard deviation of  $4.9 \text{ mg}\cdot\text{L}^{-1}$ . Considering the uncertainty, these values align with literature.

A test with a mixture of surfactants is also conducted with the tensiometer. Indeed, surfactants are often mixed in pairs during formulation to improve characteristics due to synergistic effects. Moreover, as with the HLB method, it could be possible to determine the CMC of an unknown CMC by mixing it with a “reference” surfactant. However, regardless of the ratio (50/50 or 25/75), it was not possible to obtain an exploitable result with the tensiometer. This may be due to the saturation of the surface of the liquid with amphiphilic molecules, resulting in an invariable surface tension [14]. Measurements with tensiometer are also only possible in water. When another solvent with a higher viscosity is used, the only measurable value is the surface tension of the solvent itself.

The use of the inductive technique allows us to determine the CMC through the modification in the electromagnetic properties of the surfactant. This modification is monitored using the loss factor  $\frac{\sigma}{\epsilon\omega}$ , wherein  $\sigma$  denotes the conductivity,  $\epsilon$  denotes the permittivity and  $\omega$  denotes the frequency. Results are presented for Polysorbate 80 and Brij®O20 in Figure 4.

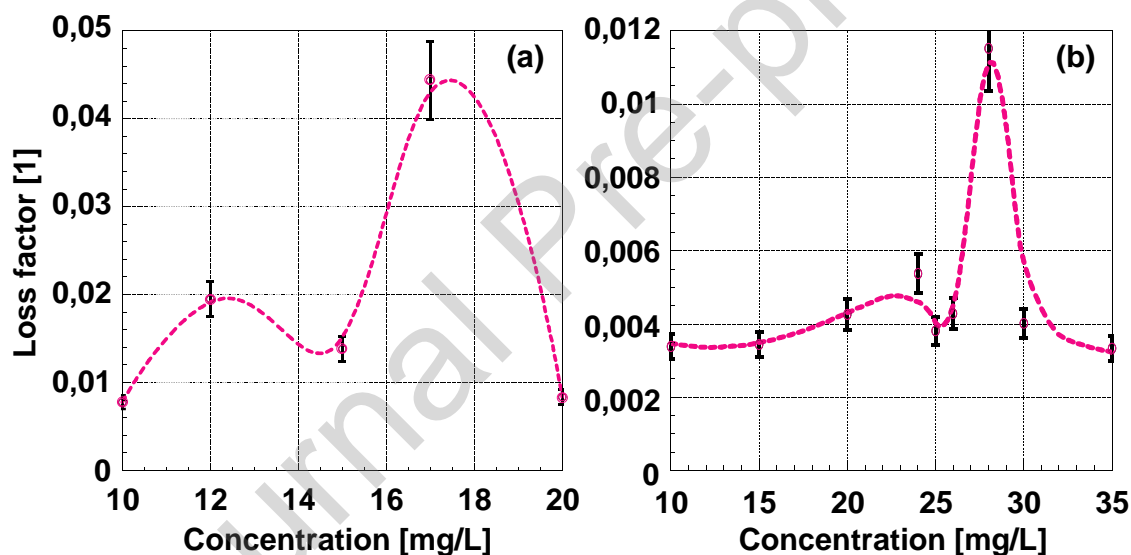


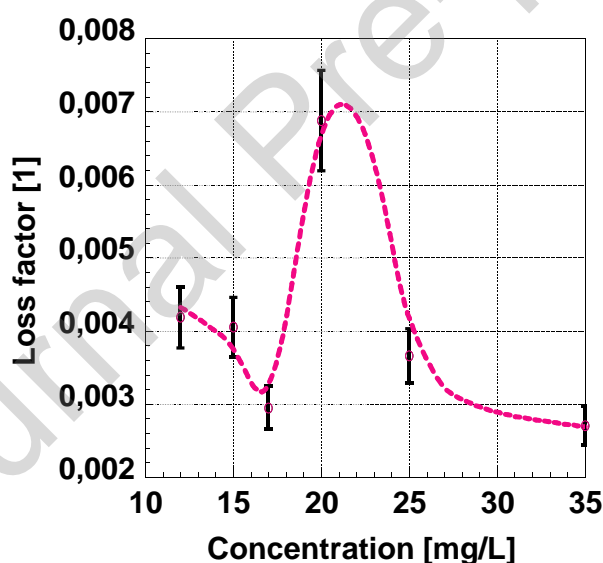
FIGURE 4 - CMC RESULTS WITH IMPEDANCEMETRY FOR (A) POLYSORBATE 80 AND (B) BRIJ®O20 IN WATER

Because the chosen surfactants are non-ionic, the increase of their concentration should not impact the conductivity which, then, remains constant. The observed changes in the dielectric factor can only be correlated to a change of conformation of the polar molecules. Prior to the formation of micelles, the surfactant molecules are free in the solvent. Under an electromagnetic field, they can be easily polarized at the mesoscopic scale. When the micelles are formed, the orientation of surfactant poles induce a minimal polarizability due to the annulation of the global dipole moment at the micelle scale. This phenomenon results in an increase in the loss factor which reaches a maximum. Consequently, the CMC represents a change of polarizability. The local minimum that precedes the CMC peak can be associated with the statistical initiation of self-aggregation of surfactant into micelles, which minimize the charges displacement.

For Polysorbate 80, a maximum is observed at  $17.36 \text{ mg}\cdot\text{L}^{-1}$ , while the Brij®O20 possesses an optimum at  $28 \text{ mg}\cdot\text{L}^{-1}$ . Using the previous Monte-Carlo method on the maximum

extraction, the standard deviation reaches  $0.02 \text{ mg.L}^{-1}$  and  $0.01 \text{ mg.L}^{-1}$ , respectively. These values are close to the literature, even if they are slightly different from the ones obtained with the tensiometer, especially for Brij®O20 [72]. The difference of results is due to the measurement principles. The tensiometry is a macroscopic measurement resorting to an apparent quantity resulting from the surfactant structuration (the surface tension of the continuous phase). On the contrary, the impedancemetry measures the mesoscopic polarization of the electrical charges distribution. Here, the smaller values seen in tensiometry can also be explained by the presence of impurities, especially for the Brij®O20: the presence of impurities can lower the macroscopic surface tension while it does not have any effect on the polarizability of the electric charges distribution. The smaller uncertainties obtained with impedancemetry can be explained by, at least, two elements. Firstly, tensiometry is a manual mechanical technique which is strongly dependent on the operator (applied force, dilution preparation and container cleanliness). Secondly, the device is cleaned manually after each measurement and any residual compound can lead to discrepancies in the surface tension. In impedancemetry, the main sources of uncertainty include greasy residuals on the vials, dilution preparation, and numerical errors during signal processing. Here, it is clear that the uncertainty is drastically smaller in impedancemetry.

Results of the second experiment with Polysorbate 80 and Brij®O20 mixed at 50/50 w/w ratio are presented in Figure 5.



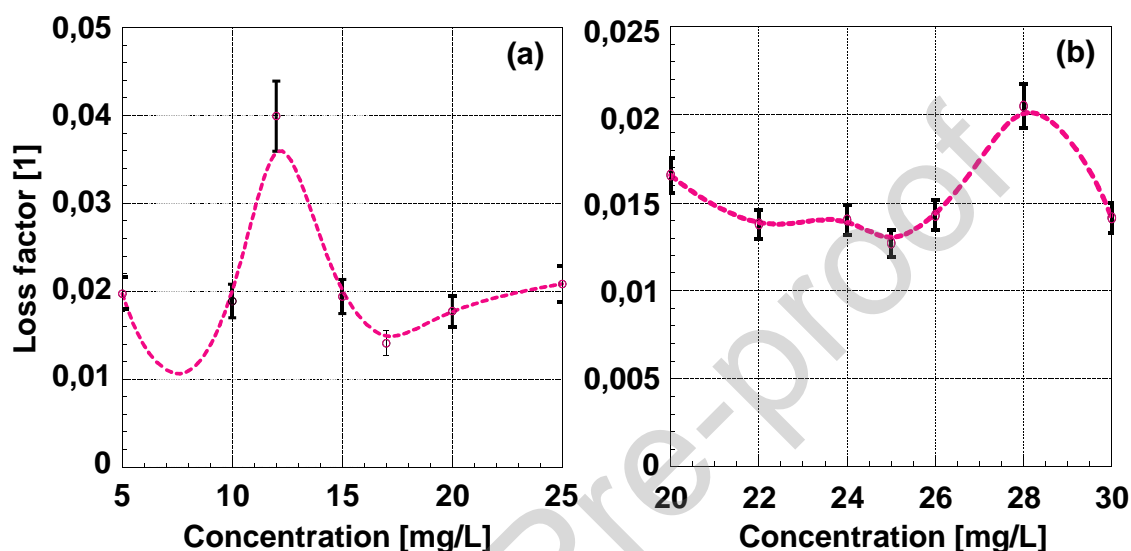
**FIGURE 5 - CMC RESULTS WITH IMPEDANCEMETRY FOR POLYSORBATE 80 AND BRIJ®O20 MIXTURE IN WATER (50/50 w/w)**

A maximum is observed at  $19.96 \text{ mg.L}^{-1}$  with a standard deviation of  $0.03 \text{ mg.L}^{-1}$ . Using Eq 6), with a Polysorbate 80 mole fraction of 0.659, we retrieve the same mixture CMC. It could be then possible to calculate the CMC of either Polysorbate 80 or Brij®O20, thanks to the CMC of the mixture.

It is important to determine whether the CMC can be identified through the application of the same methodology in a more sterically hindered environment, such as water containing a non-activated thickening agent. This type of characterization is of particular interest as it serves to define the reliability of the method for the development of more complex galenic forms, including, for instance, emulsion that are frequently formulated in cosmetics.

## 4.2 In water solvent with thickening agent

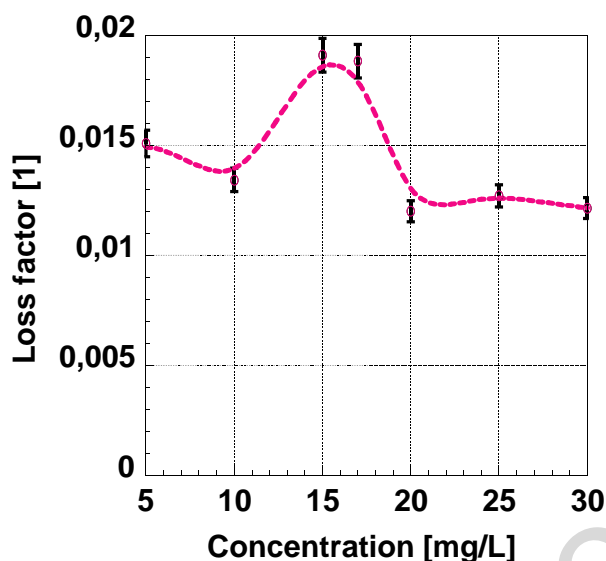
In this section, the tensiometer is not employed due to its incompatibility with complex aqueous media. The incorporation of polymeric structures elevates the macroscopic interfacial tension, thereby introducing bias in the CMC measurement. The objective is to demonstrate the ability of the RF impedancemeter to overcome this issue. As previously, the two individual CMC of Polysorbate 80 and Brij®O20 are presented in Figure 6 but in solvent supplemented with non-activated Carbopol® CEDT 2050.



**FIGURE 6 - CMC RESULTS WITH IMPEDANCEMETRY FOR (A) POLYSORBATE 80 AND (B) BRIJ®O20 IN WATER WITH NON-ACTIVATED CARBOPOL® CEDT 2050**

For Polysorbate 80, a maximum is observed at  $11.98 \text{ mg.L}^{-1}$  with a standard deviation of  $0.03 \text{ mg.L}^{-1}$ , which is slightly offset from the value observed in pure water, potentially due to steric effects. For Brij®O20, a maximum is observed at  $27.67 \text{ mg.L}^{-1}$  with a standard deviation of  $1.98 \text{ mg.L}^{-1}$ , also slightly offset from the value in pure water. The solvent being similar to water, except with an addition of steric effects, the CMC remains close to the one obtained with water.

To substantiate the utilization of the impedancemetry technique combined with Eq 6), the measurements of the mixture in thickened water are given in Figure 7.



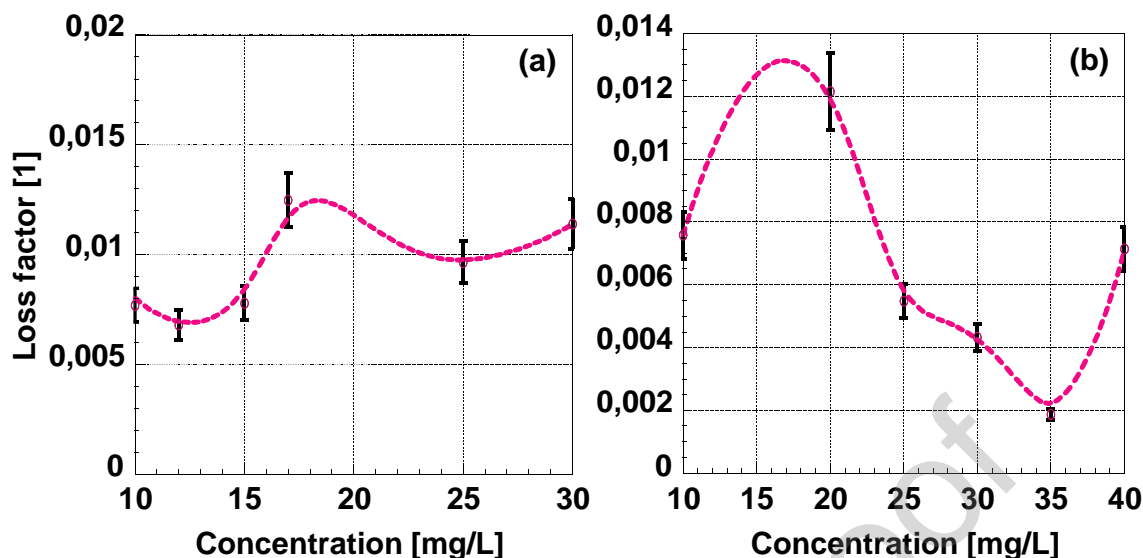
**FIGURE 7 - CMC RESULTS WITH IMPEDANCEMETRY FOR POLYSORBATE 80 AND BRIJ®O20 MIXTURE IN WATER WITH NON-ACTIVATED CARBOPOL® CETD 2050 (50/50 w/w)**

For the mixture, the maximum is noticed at  $15.83 \text{ mg.L}^{-1}$  with a standard deviation of  $1.39 \text{ mg.L}^{-1}$ . Using Eq (6), with a mole fraction of 0.571 for Polysorbate 80, it is possible to retrieve the CMC value of the mixture. The mixture model proposed by Clint applies even in more sterically hindered environments.

Two categories of surfactants are distinguished: water soluble and oil soluble. In the context of emulsion formulation, it is usual to mix those two kinds of surfactants to achieve optimal emulsion stabilization. Moreover, surfactants are frequently incorporated into the oil phase of emulsion during formulation. Consequently, it is of interest to observe the behavior of surfactants in oil and to evaluate the limitations of our inductive technique.

### 4.3 In isopropyl palmitate oil

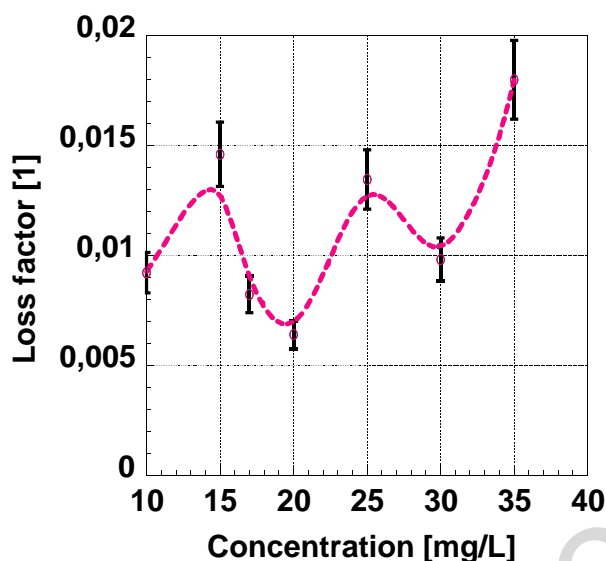
As in the previous section, the ensuing results concern exclusively the RF impedancemetry technique. The oil used for the solubilization of the surfactant is isopropyl palmitate. Such as previously, the initial step involves the measurement of both surfactants individually, and the results are presented in Figure 8.



**FIGURE 8 - CMC RESULTS WITH IMPEDANCEMETRY FOR (A) POLYSORBATE 80 AND (B) BRIJ®020 IN ISOPROPYL PALMITATE OIL**

The oil permittivity and conductivity are low; therefore, the addition of surfactants increases the polarity and decreases the ratio  $\frac{\sigma}{\epsilon\omega}$ . This results in minimizing the polar interactions between oil and surfactant molecules. Consequently, the performance of surfactants is maximized, especially at the CMC, which increases the ratio due to micelles formation. In oil, it is then possible to identify the CMC with the minimum value of the loss factor.

Significant minima are observed. For Polysorbate 80 it is approximately  $12.30 \text{ mg.L}^{-1}$  with a standard deviation of  $1.43 \text{ mg.L}^{-1}$ , while Brij®O20 exhibits a value around  $35.29 \text{ mg.L}^{-1}$  with a standard deviation of  $0.07 \text{ mg.L}^{-1}$ . There are no obvious reasons for the surfactant to have the same CMC value in oil and water. For Polysorbate 80, in oil, and in water CMC values are equivalent. This may be explained by the dual functionality of Polysorbate 80, which serves as both a dispersing and a wetting agent. In contrast, Brij®O20 exhibits substantial discrepancy its values in water and in oil, attributable to its key role as a dispersing agent. Results for the mixture of the two surfactants, with a 25/75 w/w ratio, are presented in Figure 9.



**FIGURE 9 - CMC RESULTS WITH IMPEDANCEMETRY FOR POLYSORBATE 80 AND BRIJ@O20 MIXTURE IN ISOPROPYL PALMITATE OIL (25/75 W/W)**

For this mixture, two minima are noticed at  $19.31 \text{ mg.L}^{-1}$  and  $29.89 \text{ mg.L}^{-1}$  with standard deviations of  $0.74 \text{ mg.L}^{-1}$  and  $0.49 \text{ mg.L}^{-1}$  respectively. These minima can be interpreted in various ways, such as, for instance, evolutions in geometry of micelles [73]. Here, we assume that the first minimum corresponds to the mixture CMC, and the second minimum corresponds to the CMC of Brij@O20. It is noteworthy that the quantity of Brij@O20 is significantly higher than that of Polysorbate 80. In addition, the Brij@O20 is a hydrophilic surfactant. Consequently, Brij@O20 may form micelles independently to lower its interactions with the oil phase, in addition to the micelles formed in conjunction with Polysorbate 80. Using Eq (6) with a mole fraction for Polysorbate 80 between 0.3 and 0.4, the calculated mixture CMC is around  $20 \text{ mg.L}^{-1}$ , given the uncertainties. The second CMC value aligns with the Brij@O20 one ( $30 \text{ mg.L}^{-1}$  Vs.  $35 \text{ mg.L}^{-1}$ ). The mixture distribution model can be still employed to determine the CMC of raw materials, even if we reach its limitations.

## 5 Conclusions

In this article, surfactants interactions in solution were discussed to introduce the possibility to measure the Critical Micelle Concentration of surfactants, resorting to polarizability information at the mesoscopic scale. It has been demonstrated that this information is associated with interfacial properties and with structuration of the electric charge distribution. A contactless device, comprising a resonant sensor, was employed to evaluate the electric impedance of the samples studied. This method enabled the retrieval of the loss factor, which is the ratio between conductivity and polarizability at mesoscopic scale. Measurements were conducted at frequencies in the hundreds of megahertz.

The study highlights the experimental potential of such a contactless device. It demonstrates the efficacy of the device in determining the CMC of surfactants in various media, including water, thickened water with steric polymers, and oil. The CMC of a mixture in these environments can also be measured, and the results align with existing literature and Clint's mixture distribution model. Furthermore, the device presents the ability to determine functional properties of surfactants, such as wetting and dispersing properties, regarding its behavior in water and oil.

In other tests ran alongside this study, it was seen that the presence of impurities in solvents could create micelles with different geometrical shapes. Those differences are due to interactions with the polymer. The proposed method could be then considered as sufficiently precise to assess the level of purity of a raw material.

Among others, a notable benefit of this technique is its independence from the use of fluorescent markers or dyes. In addition, the ability to work in oil, or steric-hindered environments, as the RF impedancemetry is not sensitive to the viscosity of the continuous phase, is a strong advantage. However, the mesoscopic measurement technique is not without limitations. One drawback lies in the multiple variations appearing on curves, witnessing local phenomena that are not yet fully understood. In addition, the determination of low soluble surfactant may be subject to bias. To improve the understanding about results in impedancemetry, it could be interesting to work with pure raw materials to reduce uncertainty of explanations regarding potential interactions with other compounds. Coupling other mesoscopic or microscopic measurements, such as ultrasonic microrheology or microscopy could help too. Finally, the extraction model of the polarizability information is to be optimized and refined to enhance its accuracy. Still, for a first approximation of these values, the contactless and non-destructive technique is reliable.

Further studies should be conducted in more complex environments such as cosmetic emulsions, which are mixtures of different solvents and surfactants, agri-food products, and even pharmaceuticals. The presented device has the potential to facilitate a better comprehension of the behavior of these mixtures, and not only surfactant molecules. It could be useful for, among others: quality control regarding raw material purity, thermodynamic stability evaluation, and active product delivery monitoring.

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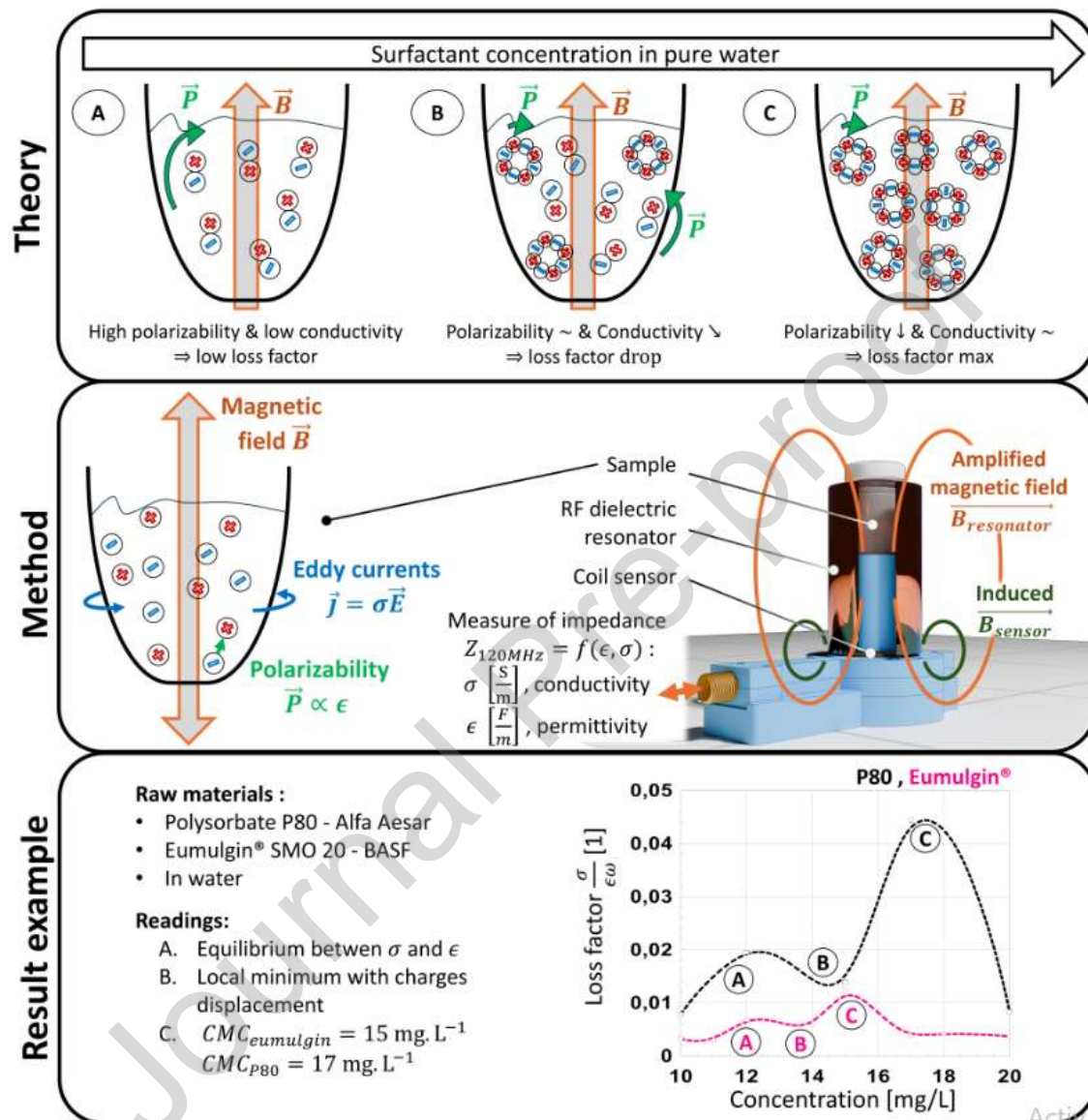
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# HIGHLIGHTS

- New contactless technique for the evaluation of CMC values in complex environments.
- Identification of a link between mesoscopic polarizability and macroscopic CMC.
- Identification of different phases of micelle formation in solution.
- Verification of Clint's mixture model for multiple surfactants in solution.

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