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# A Comparative Study of the Determination of the Critical Micelle Concentration by Conductivity and Dielectric Constant Measurements

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Conductivities and dielectric constant measurements in water at 25 °C have been made on the amphiphilic sodium *n*-dodecyl sulfate, *n*-dodecyltrimethylammonium bromide, and chlorpromazine hydrochloride. By using the conductivity/concentration data, critical micelle concentrations (cmc) have been determined by applying the Williams definition and two forms of the Phillips method. This first Phillips form consists of an approximation to Gaussians of the second derivative of the conductivity/concentration data followed by two consecutive integrations. The second form, which is proposed here, consists of the application of a combination of the Runge–Kutta numerical integrations method and the Levenberg–Marquardt least-squares fitting algorithm. The proposed method permits the determination of the cmc in systems with low aggregation numbers and with slow variations of physical property/concentration curves allowing the determination of the so-called second cmc. A comparative study with results obtained by dielectric constant measurements has been carried out. With this new technique, the cmc's (first and second) are directly obtained as singular points in the dielectric constant/concentration curves, and thus, this technique is an alternative to the determination of cmc's from conductivities.

## Introduction

The critical micelle concentration (cmc) represents a fundamental micellar quantity to study the self-aggregation of amphiphilic molecules in solution. To theoretically treat the micelles, we can use the mass action model<sup>1–5</sup> that regards the micelle as a chemical species, or the phase separation model<sup>6–9</sup> that considers micelles as a separate phase. To derive thermodynamic parameters of micellization, both models use expressions in which directly, or indirectly, the knowledge of the cmc is absolutely necessary. Thus, to obtain precise values of the cmc is of special scientific interest.

The cmc is the narrow concentration range over which amphiphilic or surfactant solutions show an abrupt change in a physical property such as electrical conductivity, surface tension, osmotic pressure, density, light scattering, or refractive index. To determine the cmc, several definitions have been proposed. Corrin<sup>10</sup> defines the cmc as the total surfactant concentration at which a small and constant number of surfactant molecules are in aggregated form. According to Williams et al.,<sup>11</sup> the cmc is the concentration of surfactant at which the concentra-

tion of micelles would become zero if the micellar concentration continued to change at the same rate as it does at a slightly higher concentration. The cmc can be determined by the intersection of the two straight lines of solution properties above and below the cmc, but the precision of the measurement depends on the width of the concentration range that shows the change in the physical properties. When this change is slow it is practically impossible to obtain a singular point. Phillips<sup>1</sup> defined the cmc as the concentration corresponding to the maximum change in a gradient in the solution property versus concentration ( $\phi - c_i$ ) curve

$$\left(\frac{d^3\phi}{dc_i^3}\right)_{c_i} = \text{cmc} = 0 \quad (1)$$

where

$$\phi = \alpha[S] + \beta[M] \quad (2)$$

$\alpha$  and  $\beta$  are constants of proportionality, and  $[S]$  and  $[M]$  are the concentrations of the monomeric surfactant and of the micelle, respectively.

Hall et al.<sup>12</sup> developed the idea of Phillips and gave another definition that places the cmc at the point where

$$\left[\frac{\partial(x_2 + x_m)}{\partial x_d}\right]_{T,p} = 0.5 \quad (3)$$

and

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$$x_d = x_2 + \bar{n}x \quad (4)$$

where  $x_2$  and  $x_m$  represent the mole fractions of nonmicellar and micellar surfactants, respectively, and  $\bar{n}$  is the mean aggregation number of micelles. Israelachvili et al.<sup>13</sup> defined the cmc as the concentration at which the analytical surfactant concentration in micelles equals the monomer concentration in bulk. The definition of Phillips is the most commonly used because it is centered in the area of major variation of physical properties and, thus, is more rigorous than that of Williams et al. We have applied the Phillips definition to obtain the cmc of both classical surfactants and drugs with amphiphilic structure.<sup>5,14–20</sup> In agreement with García-Mateos et al.,<sup>21</sup> the method was an approximation to Gaussians of the second derivative of the conductivity/concentration data, followed by two consecutive numerical integrations. In the case of drugs and surfactants with a low aggregation number we have had difficulties in obtaining precise cmc's due to the conductivity/concentration curves showing a very slow variation.

To resolve this problem, two methods have been used. On one hand, to estimate the parameters we have employed the Runge–Kutta<sup>22</sup> numeral integrations method and the Levenberg–Marquardt<sup>23</sup> least-squares fitting algorithm instead of the method proposed by García-Mateos et al. This allows us to obtain the cmc with a smaller number of points and with greater precision than the Euler method.<sup>22</sup> On the other hand, we present the results obtained using the dielectric measurements as a new alternative technique to conductivity. The cmc's (first and second) are directly obtained as singular points in the dielectric constant/concentration curves, giving highly satisfactory results.

To compare the different methods, we have measured electrical conductivities and dielectric constants of two typical surfactants, the anionic sodium *n*-dodecyl sulfate (SDS) and the cationic *n*-dodecyl trimethylammonium bromide (DTAB), and a phenothiazine drug, chlorpromazine hydrochloride (CIPH). We have selected these systems because they have highly reliable cmc data. The surfactants have aggregation numbers of approximately 64 and 57 for SDS and DTAB respectively,<sup>24</sup> and their conductivity/concentration curves and dielectric constant/concentration curves show a clear break. The CIPH was chosen as a system of special difficulty because it presents two cmc's<sup>25–27</sup> and has a small aggregation number, 10.<sup>25,28</sup>

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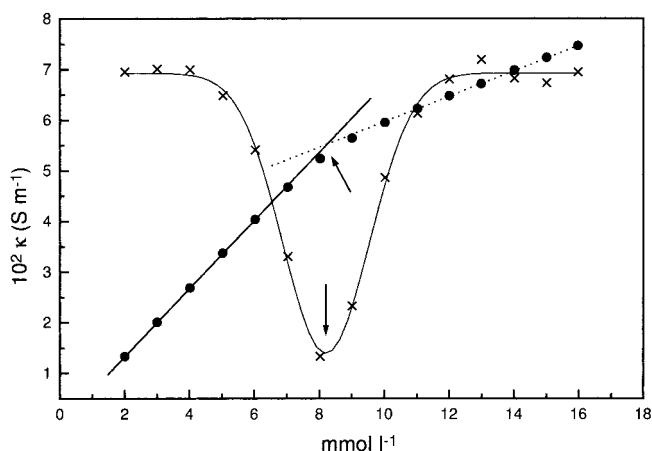
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**Figure 1.** Specific conductivity,  $\kappa$ , of sodium *n*-dodecyl sulfate in water as a function of molar concentration at 298.15 K and 200 kHz: (●) experimental points, (×) second derivative. The arrows denote the cmc's calculated by the Williams and the Phillips methods. Gaussian is the continuous line.

The Phillips treatment proposed here and the dielectric constant measurements predict the two cmc's and allow their determination.

## Experimental Section

Sodium dodecyl sulfate with a purity of >99% was obtained from Fluka (No. 71725), *n*-dodecyltrimethylammonium bromide with a purity of 97% was obtained from Lancaster MTM Research Ltd (No. 3676), and chlorpromazine hydrochloride was obtained from Sigma Chemical Co. (No. 8138). Solutions were made in double-distilled, deionized, and degassed water.

Conductivities and dielectric constants of colloid solutions were measured with an HP 4285A Precision LCR meter equipped with a HP E5050A colloid dielectric probe operating in a frequency range between 200 kHz and 20 MHz. The probe is especially designed to measure inductances and to avoid the polarization of the molecules which occurs when the probe is formed by a plain condenser. To obtain the highest precision, the probe was introduced in a cell especially designed by us. The cell is a cylinder with a diameter of 8 cm and a height of 5 cm with the probe entrance on the side. In this way, the probe head is always surrounded by at least 2 cm of solution. The cell with the probe was immersed in a Techne, model RB-12A thermostated bath equipped with a Tempunit TU-16A thermostat. Temperature control was achieved using an Anton Paar DT 100-30 thermometer, maintaining the temperature constantly within  $\pm 0.01$  K. To homogenize the solution, a Variomag 20P shaker was used.

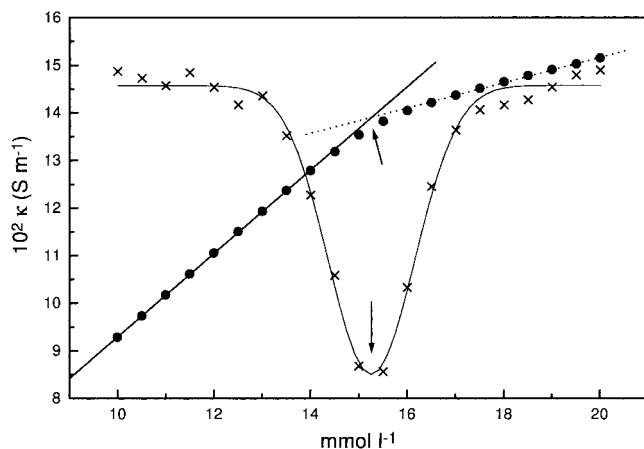
## Results and Discussion

By using the Williams method the cmc was obtained by the intersection of the fitting lines of the conductivity/concentration curves above and below the break point. For the criterion of the fit the best correlation coefficient was chosen. In Figures 1–3 results for SDS, DTAB, and CIPH are shown. The experiments were carried out at 200 kHz. Other frequencies did not give significantly different results for the cmc. The correlation coefficients were 0.9999 for the two lines of the SDS (cmc = 8.28 mmol L<sup>-1</sup>) and 0.9999 and 0.9996 for the lines above and below the cmc, respectively, in the case of DTAB (cmc = 15.3 mmol L<sup>-1</sup>). For CIPH, these coefficients were 0.9997 for the line above the second cmc, 0.9997 for the line above

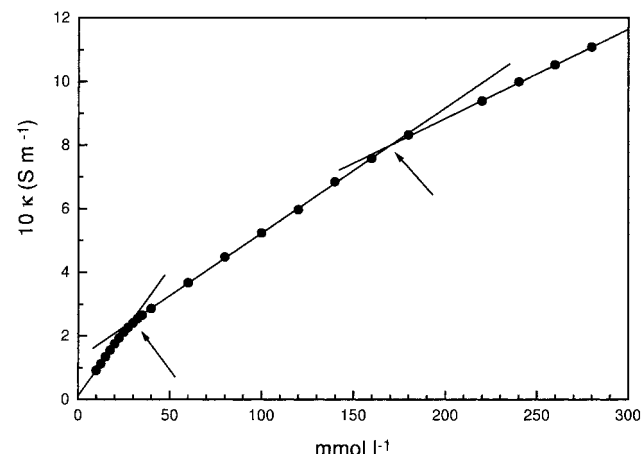
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**Figure 2.** Specific conductivity,  $\kappa$ , of *n*-dodecyl trimethylammonium bromide in water as a function of molar concentration at 298.15 K and 200 kHz: (●) experimental points, (×) second derivative. The arrows denote the cmc's calculated by the Williams and the Phillips methods. Gaussian is the continuous line.



**Figure 3.** Specific conductivity,  $\kappa$ , of chlorpromazine hydrochloride in water as a function of molar concentration at 298.15 K and 200 kHz: (●) experimental points. The arrows denote the cmc's calculated by the Williams method.

the first cmc, and 0.9993 for the line below the first cmc. The cmc's for the CIPH were  $\text{cmc}_1 = 27.7 \text{ mmol L}^{-1}$  and  $\text{cmc}_2 = 169.5 \text{ mmol L}^{-1}$ .

The Phillips method has been applied in two forms. The first, which is denoted "classical", consists of directly fitting the second derivative of the conductivity/concentration data to a Gaussian without additional treatment of the data. The second consists of an integration by the Runge–Kutta method and a least squares Levenberg–Marquardt fitting. The application of the Runge–Kutta method to our conductivity measurements is as follows:

The expression for the second derivative of the specific conductivity/concentration curve of an aggregate in solution is<sup>29</sup>

$$k'' = A \exp\left\{-\frac{(c_t - \text{cmc})^2}{2\sigma^2}\right\} \quad (5)$$

where  $c_t$  is the total concentration of the surfactant,  $\sigma$  is the standard deviation, and  $A$  is the width of the curve. This equation can be written as  $y'' = f(x)$ , where  $x$  is the surfactant concentration. By transforming this into a

system of two first order differential equations, we obtain  $y' = z$  and  $z' = f(x)$ .

The general form of the Runge–Kutta method for a system of two equations is

$$z_{k+1} = z_k + \frac{1}{6}(\mu_{k1} + 2\mu_{k2} + 2\mu_{k3} + \mu_{k4}) \quad (6)$$

$$y_{k+1} = y_k + \frac{1}{6}(v_{k1} + 2v_{k2} + 2v_{k3} + v_{k4}) \quad (7)$$

where the parameters  $\mu_{ki}$  and  $v_{ki}$  are given for following expressions

$$\mu_{k1} = hf(x_k, z_k, y_k) \quad v_{k1} = hg(x_k, z_k, y_k) \quad (8)$$

$$\mu_{k2} = hf\left(x_k + \frac{h}{2}, z_k + \frac{\mu_{k1}}{2}, y_k + \frac{v_{k1}}{2}\right) \quad v_{k2} = hg\left(x_k + \frac{h}{2}, z_k + \frac{\mu_{k1}}{2}, y_k + \frac{v_{k1}}{2}\right) \quad (9)$$

$$\mu_{k3} = hf\left(x_k + \frac{h}{2}, z_k + \frac{\mu_{k2}}{2}, y_k + \frac{v_{k2}}{2}\right) \quad v_{k3} = hg\left(x_k + \frac{h}{2}, z_k + \frac{\mu_{k2}}{2}, y_k + \frac{v_{k2}}{2}\right) \quad (10)$$

$$\mu_{k4} = hf(x_k + h, z_k + \mu_{k3}, y_k + v_{k3}) \quad v_{k4} = hg(x_k + h, z_k + \mu_{k3}, y_k + v_{k3}) \quad (11)$$

$h$  being the integration step. By applying the method to our system, we obtain

$$f(x, y, z) = A \exp\left\{-\frac{(x - \text{cmc})^2}{2\sigma^2}\right\} \quad g(x, y, z) = z \quad (12)$$

and the parameter values are

$$\mu_{k1} = hA \exp\left\{-\frac{(x_k - \text{cmc})^2}{2\sigma^2}\right\} \quad v_{k1} = hz_k \quad (13)$$

$$\mu_{k2} = hA \exp\left\{-\frac{\left[\left(x_k + \frac{h}{2}\right) - \text{cmc}\right]^2}{2\sigma^2}\right\} \quad v_{k2} = h\left(z_k + \frac{\mu_{k1}}{2}\right) \quad (14)$$

$$\mu_{k3} = hA \exp\left\{-\frac{\left[\left(x_k + \frac{h}{2}\right) - \text{cmc}\right]^2}{2\sigma^2}\right\} \quad v_{k3} = h\left(z_k + \frac{\mu_{k2}}{2}\right) \quad (15)$$

$$\mu_{k4} = hA \exp\left\{-\frac{[(x_k + h) - \text{cmc}]^2}{2\sigma^2}\right\} \quad v_{k4} = h(z_k + \mu_{k3}) \quad (16)$$

These expressions can be simplified as a function of three parameters  $\alpha$ , and  $\beta$ , and  $\gamma$  in the form of

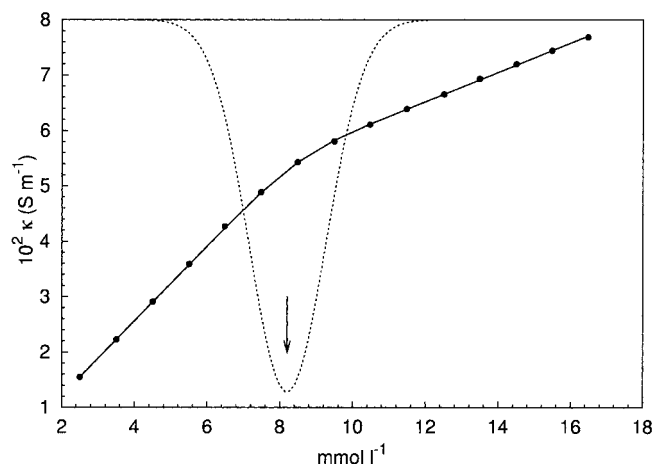
$$\alpha = hA \exp\left\{-\frac{(x_k - \text{cmc})^2}{2\sigma^2}\right\} \quad \beta = \exp\left\{h\text{cmc} - 2x_k - \left(\frac{h^2}{2}\right)\right\} \quad \gamma = \exp(2h\text{cmc} - 2x_k - h^2) \quad (17)$$

and the eqs 6 and 7 can be rewritten as

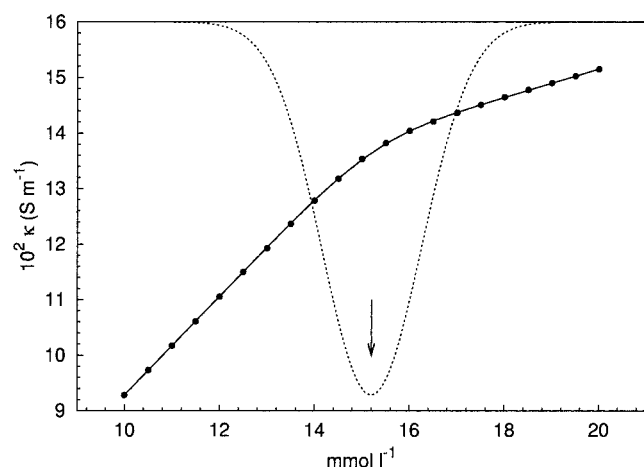
$$z_{k+1} = z_k + \alpha(1 + 4\beta + \gamma) \quad (18)$$

$$y_{k+1} = y_k + h[z_k + \alpha(1 + 2\gamma)] \quad (19)$$

with  $x_{k+1} = x_k + h$ .



**Figure 4.** Specific conductivity,  $\kappa$ , of sodium *n*-dodecyl sulfate in water as a function of molar concentration at 298.15 K and 200 kHz calculated by the proposed method: (•) experimental points. Continuous line is the fitting curve of these points. Dashed line corresponds to Gaussian, and the arrow denotes the cmc.

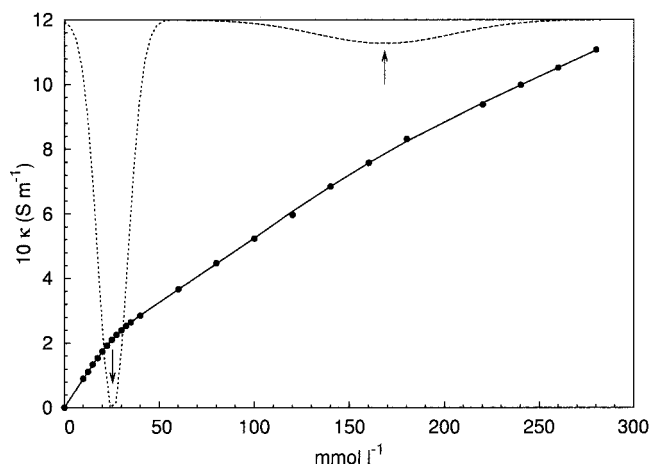


**Figure 5.** Specific conductivity,  $\kappa$ , of *n*-dodecyl trimethylammonium bromide in water as a function of molar concentration at 298.15 K and 200 kHz calculated by the proposed method: (•) experimental points. Continuous line is the fitting curve of these points. Dashed line corresponds to Gaussian, and the arrow denotes the cmc.

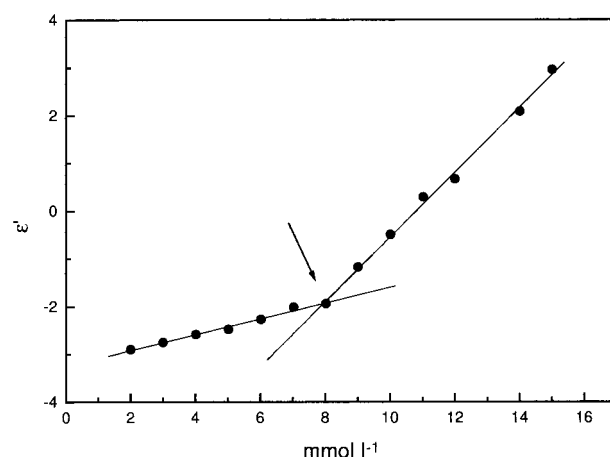
The Levenberg–Marquardt least-squares fitting algorithm for a nonlinear function consists of the combination of two classical methods to minimize  $\chi^2$ , the approximation to the minimum by a Taylor expansion and by a gradient approximation. The method is very appropriate for the points far from the minimum.

In Figures 1 and 2 the results obtained by applying the Phillips method in its “classical” form are shown. The dashed line corresponds to the second derivative of conductivity/concentration curve, and the arrow denotes the cmc. The obtained values were 8.21 mmol L<sup>-1</sup> and 15.3 mmol L<sup>-1</sup> for SDS and DTAB, respectively. In the case of CIPH, it was not possible to get either the first or the second derivative due to the small curvature of the curves. The deviations of consecutive points are equal to or larger than the deviation due to the curve, thus making it impossible to obtain acceptable results.

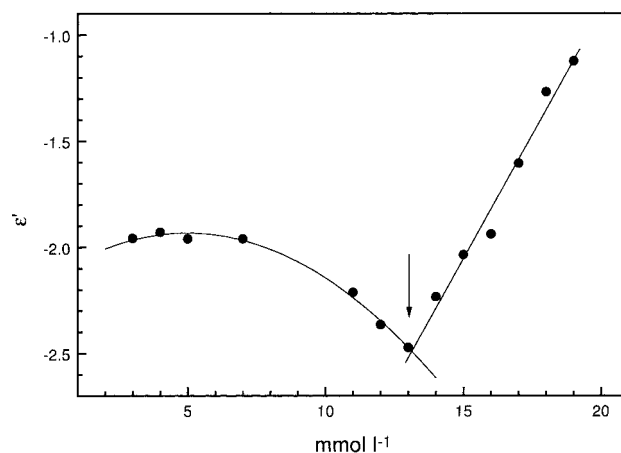
In Figures 4, 5, and 6, the results of applying the Phillips method in the form proposed in this work are shown. The minimum corresponds to points of maximum variation and coincides with the cmc. The corresponding values were 8.22 mmol L<sup>-1</sup> for SDS, 15.2 mmol L<sup>-1</sup> for DTBA,



**Figure 6.** Specific conductivity,  $\kappa$ , of chlorpromazine hydrochloride in water as a function of molar concentration at 298.15 K and 200 kHz calculated by the proposed method: (•) experimental points. Continuous line is the fitting curve of these points. Dashed line corresponds to Gaussian, and the arrows denote the two cmc.



**Figure 7.** Dielectric constant difference of sodium *n*-dodecyl sulfate and water,  $\epsilon' = \epsilon - \epsilon_0$ , as a function of molar concentration at 298.15 K and 200 kHz. The arrow denotes the cmc.

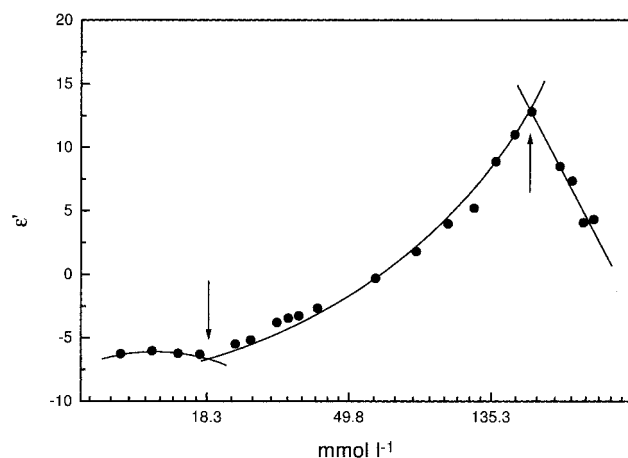


**Figure 8.** Dielectric constant difference of *n*-dodecyl trimethylammonium bromide and water,  $\epsilon' = \epsilon - \epsilon_0$ , as a function of molar concentration at 298.15 K and 200 kHz. The arrow denotes the cmc.

and 25.5 mmol L<sup>-1</sup> and 168.4 mmol L<sup>-1</sup> for the first and second cmc's, respectively, of the CIPH.

In Figures 7, 8, and 9, the results obtained for SDS, DTAB, and CIPH by dielectric constant measurements





**Figure 9.** Dielectric constant difference of chlorpromazine hydrochloride and water,  $\epsilon' = \epsilon - \epsilon_0$ , as a function of molar concentration at 298.15 K and 200 kHz. The arrows denote the cmc's.

are shown. In the case of SDS and DTAB, an abrupt change in the dielectric constant/concentration curves can be observed. The cmc values were 7.91 mmol L<sup>-1</sup> for SDS and 13.01 mmol L<sup>-1</sup> for DTAB, and they are lower than the values obtained when applying the Williams and Phillips methods to the conductivity data. From the observation of these curves, interesting features can be found. Below the cmc, the behavior is linear for SDS and nonlinear for DTAB. Above the cmc, the two systems behave linearly with positive slopes. These results are different from those obtained by conductivity measurements, where above and below the cmc the relationship was linear. A possible explanation of this fact could be the presence of dimers and trimers in the DTAB as has been suggested.<sup>30</sup> Indeed, when the measurement frequency was changed, a tendency toward negative slopes was found, although the intersection of the lines always gave the same cmc.

Inspection of Figure 9 reveals two singular points, corresponding to the concentrations of 17.7 mmol L<sup>-1</sup> and 180 mmol L<sup>-1</sup>, respectively. We can identify these concentrations as the first and second cmc.

The values obtained by the different methods are shown in Table 1. In general, the results coincide. For the CIPH, which shows a low transition in the conductivity/concentration curve, it was impossible to apply the Phillips method in its classical form. These values are compared with those in the references. Anianson et al.,<sup>31</sup> Lianos et al.,<sup>32</sup> and Chang et al.<sup>33</sup> give the value of 8.2 mmol L<sup>-1</sup> for

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**Table 1.** Critical Micelle Concentrations<sup>a</sup> of Sodium *n*-Dodecyl Sulfate (SDS), *n*-Dodecyltrimethylammonium Bromide (DTAB), and Chlorpromazine Hydrochloride (CIPH) at 298.15 K and 200 KHz Determined by Different Techniques

|      | conductivity    |                           |                          | dielectric constant |
|------|-----------------|---------------------------|--------------------------|---------------------|
|      | Williams method | Phillips classical method | Phillips proposed method |                     |
| SDS  | 8.28            | 8.21                      | 8.22                     | 7.91                |
| DTAB | 15.3            | 15.3                      | 15.2                     | 13.01               |
| CIPH | 27.7            |                           | 25.5                     | 17.7                |
|      | 169.5           |                           | 168.4                    | 180                 |

<sup>a</sup> All values expressed as mmol L<sup>-1</sup>.

SDS. Williams et al.<sup>11</sup> and Pérez-Villar et al.<sup>34</sup> give the value of 8.1 mmol L<sup>-1</sup> for the same surfactant. For DTAB, Evans et al.<sup>35</sup> give a value of 15.4 mmol L<sup>-1</sup> and Levère et al.<sup>36</sup> of 15 mmol L<sup>-1</sup>. In the case of CIPH, Attwood et al.<sup>37</sup> give a value of 21 mmol kg<sup>-1</sup> for the cmc obtained at 303 K by osmometry, and Attwood et al. in other works<sup>25,26</sup> give a value of 24 mmol kg<sup>-1</sup> obtained at 298.15 K by light scattering for the first cmc and a value of 170 mmol kg<sup>-1</sup> for the second cmc determined by ultrasound at 25 °C.

In conclusion, the problem of nonuniqueness that the Williams method creates is clearly resolved by nonlinear methods. At the same time, these methods are more sensitive and cannot be universally applied. The Phillips definition is not useful for very slow transitions because it is not possible to make a precise calculation. The method proposed here resolves the problem of the arbitrary solution. Additional treatment of the data is not necessary.

The use of dielectric constant measurements constitutes a simplification of the Phillips method and directly permits the determination of the cmc. As we can see, this method is an alternative to the conductivity measurements and allows us directly to obtain the first and second cmc as singular points in the dielectric constant/concentration curves.

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