

Problems Associated with the Treatment of Conductivity–Concentration Data in Surfactant Solutions: Simulations and Experiments

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In this paper, we propose a new approach to analyze the conductivity–concentration data of ionic surfactant solutions, in the context of the determination of micellization parameters such as critical micelle concentration and degree of counterion dissociation. The method is based on the fit of the experimental raw data to a simple nonlinear function obtained by direct integration of a Boltzmann type sigmoidal function. The advantages of this procedure as compared to that most commonly used, namely, the intersection of the data regression lines above and below the critical micelle concentration and those employing the differentiation of the experimental data, are demonstrated by means of Monte Carlo simulations combined with nonlinear fits based on the Levenberg–Marquardt algorithm. The proposed method applied well to real systems that present a very gradual transition from the premicellar to the postmicellar region, in which the break of the conductivity–concentration plots is usually hard to determine.

Introduction

Because of their amphipathic structure, surfactants tend to form, in aqueous solutions, thermodynamically stable molecular aggregates called micelles. The micellar formation takes place above a certain surfactant concentration, the so-called critical micelle concentration (cmc), below which surfactant molecules are present as monomers.^{1–3}

It is widely recognized that the cmc is the most important parameter in studies dealing with micellization of surfactants. There are several and good reasons for that, but we will mention only a few. The first one is that the cmc value of a surfactant can be considered as a measure of stability of the micellar form relative to its monomeric form. Another important aspect is related to the thermodynamic studies of micellization. Note that a procedure extensively used to obtain thermodynamic information on the micellization process consists of analyzing the cmc values of the surfactant in a temperature range by using a determined model of micelle formation. In addition, in studies on mixed surfactant systems the cmc determination becomes decisive to test a determined thermodynamic model. This problem reaches a remarkable dimension because the composition of the micellar phase cannot be measured directly but is estimated by using a proper mixing model. For all these reasons, the availability of accurate methods providing precise values of cmc is essential in studies on micellization of surfactants.

The cmc value is usually determined from the abrupt change of a certain physical property over a very small concentration range. It is possible to distinguish between methods examining the behavior of a bulk solution property (such as surface tension, conductivity, light scattering, etc.) and those using some spectroscopic

property of a solubilized dye. In most cases, the choice of the method depends on the availability of various techniques or the personal preference of the worker. Usually, the cmc is obtained from empirical graphical procedures, and often one finds that it is difficult to determine the exact break point providing the cmc value. As a consequence, sometimes the cmc reported value depends, in some measure, on the good judgment of the researcher. A frequent problem arises when the conductance method is used in the cmc determination of surfactants with a small aggregation number. In these cases, it is very difficult to determine the break in the conductance–concentration curves and, consequently, the cmc is affected by a great uncertainty. To solve this problem, the preferred procedure is to plot differential conductance against concentration of surfactant. Manabe et al.⁴ have obtained cmc at the shoulder point of the first derivative versus concentration plots. Sugihara et al.^{5–7} used plots of the first derivative of specific conductivity versus the square root of the surfactant concentration, thus reducing the range of the independent variable where the variation of specific conductivity occurs. This same approach was also applied in a recent study on the effect of ethylene glycol addition on the micellization of tetradecyltrimethylammonium bromide (TTAB).⁸ García-Mateos et al.⁹ have proposed a method based on the approximation to Gaussians of the second derivative of the conductivity–concentration data, followed by two consecutive numerical integrations. Recently, Pérez-Rodríguez et al.¹⁰ have developed a new procedure consisting of the application

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of a Runge-Kutta numerical integration method and the Levenberg-Marquardt least-squares fitting algorithm.

In the present paper, we analyze conductivity versus surfactant concentration data in the context of the determination of common micellization parameters of ionic surfactants, such as critical micelle concentration and degree of counterion dissociation. We focus our attention on the advantages of the methods based on the treatment of raw experimental data versus those based on any kind of handled data. We discuss in the following sections the general properties of the conductivity-concentration data, and we propose a fitting model, which improves the estimation of the parameters with respect to the traditional approach. The improvements are shown by means of Monte Carlo simulations combined with nonlinear fits based on the Levenberg-Marquardt method. At the same time, several sets of experimental data are presented and discussed to illustrate the convenience of the proposed approach.

Results and Discussion

General Properties of Conductivity versus Concentration Data. Because cmc can be considered a phase transition between two different regimes of the system, these plots present, in general, a linear behavior with different slopes at the beginning and the end of the concentration axis and a transition (often very smooth) between these two regimes for intermediate values of the concentration. The cmc must be a value in this intermediate concentration range. Usually, this singular point is determined by the intersection of the two straight lines in the conductivity-concentration plots above and below the cmc. In addition, the ratio between the slopes of the postmicellar region (S^M) to that of the premicellar region (S^I) is commonly assumed to be the degree of counterion dissociation of micelles (α).¹⁰⁻¹³ The described behavior for the conductivity-concentration plots of surfactant solutions encloses some approximations. First of all, Kohlrausch's law¹⁴ of the square root of concentration predicts a nonlinear relation between conductivity and concentration at a lower concentration range. This point has been previously discussed in the context of surfactant solutions.⁷ On the other hand, at a higher concentration range, that is, at concentrations much higher than cmc, one can also observe a lack of linearity in the conductivity-concentration plots. Therefore, to guarantee the linear behavior in both the pre- and postmicellar regions, it would be convenient to exclude the very low and very high concentration data. Often, when this method is applied to analyze the conductivity-concentration data, the procedure followed consists of selecting those experimental data reporting a better regression coefficient at each part of the curve.

The above-described method, the "conventional procedure" henceforth, is the one mainly used for the cmc determination and the evaluation of an approximate value of the degree of counterion dissociation (α).^{7,11-13} Of course, in the application of this method is usually assumed a linear behavior between conductivity and concentration, with different slopes above and below the break corresponding to the cmc. However, this procedure presents

difficulties when the conductivity-concentration plot exhibits a weak curvature, as will be discussed below.

Precisely the behavior described above has suggested many of the proposed approaches to obtain the cmc, which are based on differentiation of the conductivity data against the surfactant concentration. Note that if the conductivity-concentration curve can be considered to show two linear regimes above and below the cmc, as assumed by the conventional procedure, the corresponding first derivative plot behaves as a sigmoid: a curve that changes smoothly from an asymptotic constant value to another asymptotic constant value. The parameters of this curve allow fitting not only these two asymptotic values but also the "width" of the transition and its central point, which should correspond to the cmc value. Nevertheless, this procedure presents several drawbacks. The main one is that a numerical derivative, especially if the number of data available is not very large, always introduces numerical errors, which lead to unavoidable errors in the determination of the fitting parameters. In addition, these errors join the inherent experimental errors of the original conductivity versus concentration data, which are amplified in the numerical differentiation procedure: both type of errors lead to a sigmoidal-like derivative, but with a noisy behavior instead of a perfect and regular behavior.

Thus, it seems preferable to obtain cmc and other information of interest (such as the degree of counterion dissociation of micelles or the width of the transition, which indicates how abrupt or gradual is the micellization process) from the original data, without any processing which ultimately introduces spurious errors.

Here, we propose a fitting method dealing with the behavior of conductivity versus concentration plots, which allows direct fitting of these data, thus avoiding any numerical derivative. In addition, by means of Monte Carlo simulations, we will show that the errors in the estimation of the parameters of the proposed fitting model, and consequently in cmc and α , are clearly smaller than the errors in the estimation of the parameters by using the derivative of the original data.

Treatment of Conductivity versus Concentration Data. We have qualitatively discussed before the general characteristics of the conductivity versus concentration plots and of the corresponding first derivative. This derivative is of the sigmoidal type and can be adequately described by using a Boltzmann type sigmoid, which has the following analytical expression:

$$f(x) = \frac{A_1 - A_2}{1 + e^{(x-x_0)/\Delta x}} + A_2 \quad (1)$$

The meaning of the four parameters in eq 1 is the following: A_1 (A_2) represents the asymptotic value for small (large) values of x , which from now on stands for the concentration values, x_0 represents the central point of the transition (it is direct to obtain that $f(x_0) = (A_1 + A_2)/2$), and Δx deals with the width of the transition.

Our proposal is simple: if the derivative of the original data behaves as a sigmoid, the original data should behave as the integral of the sigmoid. A direct integration of eq 1 yields

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln \left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right) \quad (2)$$

where $F(0)$ represents the value of $F(x)$ at $x = 0$. The function $F(x)$ has the desired properties of a model

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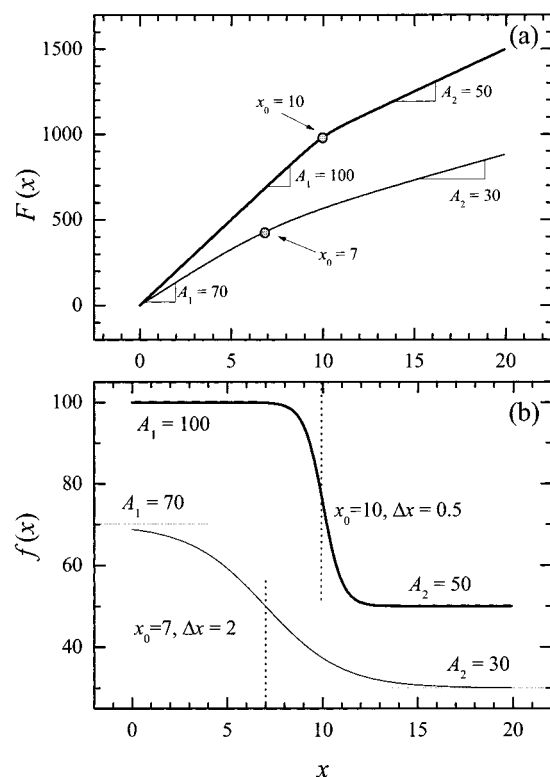


Figure 1. (a) Representative plots of conductivity, $F(x)$, vs surfactant concentration, x , for two different transition widths and (b) their corresponding first derivative, $f(x)$, plots.

describing the behavior of typical conductivity versus concentration plots. It presents two different linear regimes for large and small values of x and a transition between them whose position is controlled by x_0 and whose width is controlled by Δx . Note, in addition, that the degree of counterion dissociation (α), another interesting parameter in micellization of ionic surfactants, can be obtained from the A_2/A_1 ratio. In Figure 1, we plot the functions $f(x)$ and $F(x)$ for different values of the parameters.

As mentioned above, the so-called conventional procedure can present difficulties under certain circumstances. Figure 2 shows a typical case for the determination of the cmc by applying this approach. This figure illustrates two noteworthy aspects. On one hand, it is observed how the obtained cmc depends on the number of points chosen to perform the linear fits of the experimental data above and below the transition, and on the other, it is also apparent that this procedure does not report the real cmc. Moreover, these problems worsen when the transition occurs in a more gradual way. These are aspects often ignored that provide to the conventional approach a certain subjective character.

Testing the Method: A Monte Carlo Simulation.

In this section, we will demonstrate that the method proposed here, based on the fit of the conductivity-concentration raw data to eq 2, is more adequate than both the conventional procedure and that based on differentiation (fitting the differential conductivity to eq 1). To get this, we have performed a Monte Carlo simulation, which is carried out in five steps:

(i) We generate artificial conductivity versus concentration data according to eq 2. To achieve this, we choose $x_0 = 1$ (a different value of x_0 only represents a translation in the x axis) and we set arbitrary values for the rest of the parameters, taking into account that high (low) values of Δx produce a gradual (abrupt) transition and that a

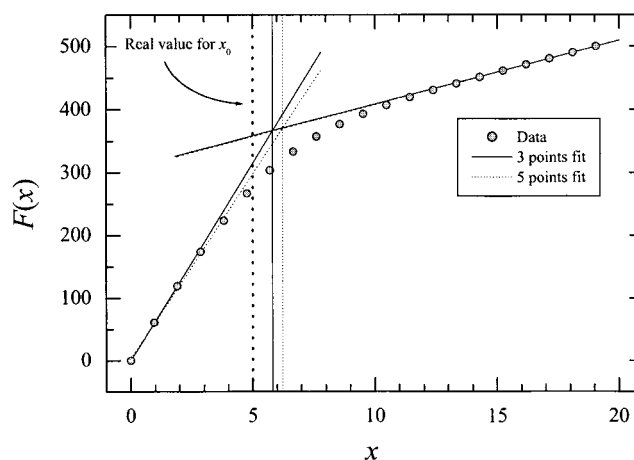


Figure 2. Determination of cmc, x_0 , by the conventional procedure in a typical conductivity-concentration plot. The circles correspond to data, in arbitrary units, generated by using the following parameters: $A_1 = 70$, $A_2 = 10$, $x_0 = 5$, and $\Delta x = 2$. The data show a shift in the evaluated cmc with an increase in the number of points chosen to perform the linear fits below and above the transition.

high (low) difference of the parameters A_1 and A_2 produces high (low) differences in the conductivity regime at both sides of the transition.

(ii) We introduce a random noise in the data to reproduce the experimental errors. This is done by adding a random number to each data. The random numbers are extracted with the same probability from the interval $[-W, W]$, and in this sense we say from now on that the noise has amplitude W .

(iii) We fit the resulting data to the model of eq 2 by using the Levenberg-Marquardt method.¹⁵ Note that we know the "real" value of the parameters, from which we generated the data prior to introducing the noise. Therefore, we can estimate the error in the parameters by comparing the original values and the values obtained in the fitting procedure. If we term as p and p_{fit} the original value and the value obtained in the fitting procedure for any of the parameters, we estimate the error in this parameter as $|p - p_{\text{fit}}|$.

(iv) We numerically differentiate the data generated in step ii, which simulate real experimental data, and we obtain a sigmoidlike curve.

(v) We fit this derivative to the model of eq 1 by using the Levenberg-Marquardt method to obtain the parameters of the model. Again, as we did in step iii, we can estimate the errors in these parameters by comparing the values obtained in the fitting procedure and the original values of the parameters used to generate the data in step i.

The five steps described above are repeated 10 000 times for each value of the noise amplitude W , and then a reliable average error in any of the parameters as a function of W can be obtained for both the model of eq 1 and the model of eq 2. The results for these errors, in the case of a gradual transition, for a set of initial parameters ($A_1 = 1$, $A_2 = 0.6$, $x_0 = 1$, $\Delta x = 0.3$) are shown in Figure 3. These results clearly show that our method determines all the parameters with errors smaller than those obtained with the differential conductivity method. We have also studied the case of an abrupt transition (data not shown), finding, on one hand, that the parameters provided by both

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Table 1. Critical Micelle Concentration (cmc) and Degree of Counterion Dissociation (α) for SDS, DTAB, TTAB, and CTAB at 25 °C, from Conductivity–Concentration Plots by Using Three Different Treatments of the Experimental Data

system	conventional		integration		differentiation	
	cmc (mM)	$\alpha = S^M/S^{1a}$	cmc (mM)	$\alpha = A_2/A_1$	cmc (mM)	$\alpha = A_2/A_1$
SDS	8.27	0.369	8.28	0.368	8.29	0.369
DTAB	15.2	0.251	15.2	0.248	15.2	0.251
TTAB	3.78	0.227	3.75	0.230	3.73	0.231
CTAB	0.96	0.243	0.97	0.241	0.96	0.250

^a Data obtained from the ratio between the slopes of the postmicellar region (S^M) to that of the premicellar region (S^1).

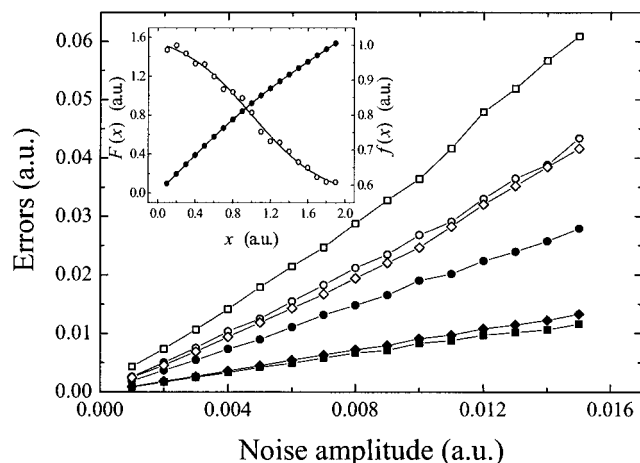


Figure 3. Errors in cmc (circles), transition width (squares), and degree of counterion dissociation (diamonds) as a function of the noise amplitude, for the fitting procedure according to eq 1 (open symbols) and eq 2 (filled symbols). The data have been generated with parameters $A_1 = 1$, $A_2 = 0.6$, $x_0 = 1$, and $\Delta x = 0.3$. Inset: plot of a representative example of conductivity–concentration data, $F(x)$ (filled circles), generated for the same parameters as before and noise amplitude = 0.006, and the corresponding first derivative $f(x)$ (open circles). The lines correspond to the best fittings to eqs 2 and 1, respectively.

methods are very similar and, on the other, that the errors in both approaches are much smaller than in the case of a gradual transition.

In some sense, these results are logical: the use of a model to fit the original data usually gives better results than the use of a model to fit data obtained by processing the original data through a numerical differentiation, which introduces unavoidable numerical errors.

Applying the Method to Experimental Data. To test the proposed method, we have selected several sets of real conductivity data obtained in our laboratory for a few cases. First of all, we present the case of various single surfactant systems, whose cmc's can be determined without difficulties and, in fact, for which reliable cmc values are available in the literature. Figure 4 shows representative conductivity versus concentration plots obtained for sodium dodecyl sulfate (SDS) and TTAB in water at 25.0 °C. In these cases, it can be observed that the method based on the fit of the first derivative to eq 1 is worse than that of the conductivity raw data according to eq 2. However, it must be pointed out that both methods provide similar results for the cmc and degree of the counterion dissociation (α) values. In addition, the conventional procedure also provides reliable values of both cmc and α . In fact, we have observed that when there is an appropriate curvature and the break point can be easily determined, any method provides good results. This fact can be seen in Table 1, where we present the results obtained for four single surfactants, for which cmc's are known enough.

In addition, we have also examined more complex systems in which the micellization process is less coop-

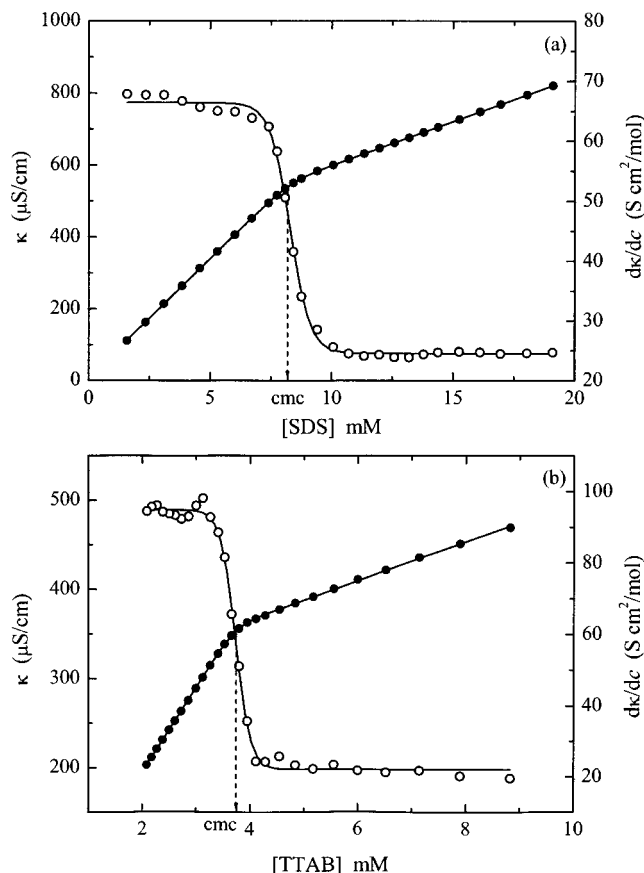
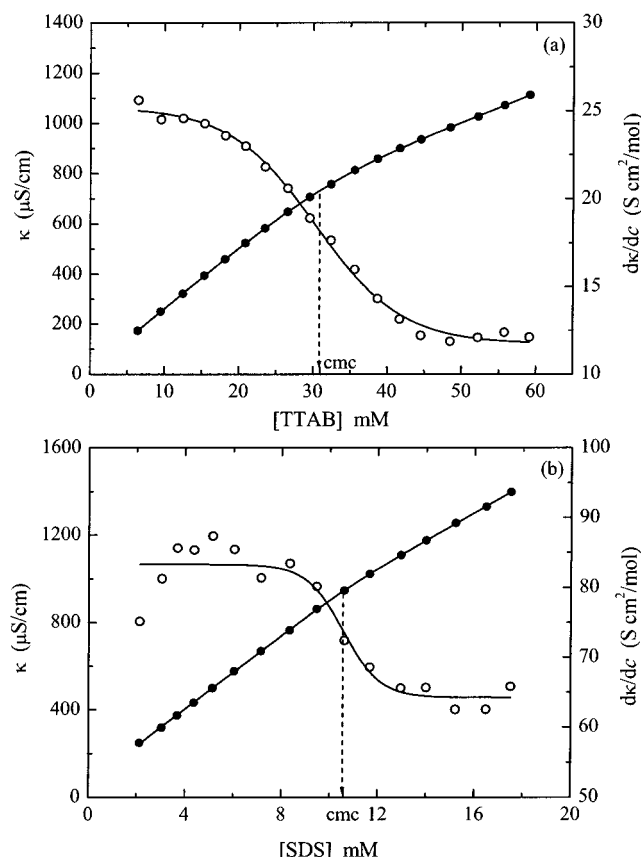


Figure 4. Experimental data of conductivity vs concentration, $F(x)$, and their corresponding first derivative, $f(x)$, for (a) SDS and (b) TTAB, at 25 °C. The lines are the best fits of data to eqs 1 and 2, respectively.

erative, that is, takes place in a more gradual way. We have selected two sets of data previously obtained in our laboratory: micellization of TTAB in an ethylene glycol–water mixed solvent (60 wt %) at different temperatures⁸ and of SDS in the presence of increasing urea concentrations.¹⁶ Figure 5 shows two representative examples of these systems: (a) TTAB in an ethylene glycol–water mixture (60 wt % EG) at 45 °C and (b) SDS in urea (6 M) at 25 °C. As can be seen in both cases, as the conductivity versus concentration curves show a weak curvature, it is hard to obtain the cmc precise value by applying the conventional method, and often the cmc values depend on the number of points selected to fit the lines above and below the break point, as discussed above. Nevertheless, fitting the experimental data to eq 2 we obtain, in an objective way, parameters providing both the cmc and the degree of counterion dissociation values. Moreover, Figure 5 also shows the distortion caused by the differentiation process of the conductivity data, which will produce in general a greater uncertainty in the determi-

Table 2. Critical Micelle Concentration (cmc) and Degree of Counterion Dissociation (α) for TTAB in EG–Water Mixtures (60 wt %) at Different Temperatures and for SDS in Increasing Urea Concentrations at 25 °C, as Obtained by Three Different Treatment of the Conductivity-concentration Data

system		conventional	$\alpha = S^M/S^I$	integration	$\alpha = A_2/A_1$	differentiation	$\alpha = A_2/A_1$
		cmc (mM)		cmc (mM)		cmc (mM)	
TTAB + EG 60 wt % ^a	25 °C	22.78	0.378	21.73	0.350	21.66	0.354
	30 °C	25.02	0.411	24.04	0.381	23.77	0.374
	35 °C	27.10	0.429	26.23	0.393	25.79	0.381
	40 °C	29.91	0.471	29.53	0.424	28.70	0.411
	45 °C	31.17	0.512	30.89	0.466	30.37	0.465
SDS ^b $T = 25$ °C	water	8.27	0.369	8.28	0.368	8.29	0.369
	urea, 2 M	8.54	0.508	8.61	0.493	8.59	0.497
	urea, 4 M	9.66	0.677	9.77	0.657	9.73	0.662
	urea, 6 M	10.54	0.763	10.58	0.749	10.56	0.770

^a Data from ref 8. ^b Data from ref 16.**Figure 5.** Experimental data of conductivity vs concentration, $F(x)$, and their corresponding first derivative, $f(x)$, for (a) TTAB in a 60% EG–water mixed solvent at 45 °C and (b) SDS in a 6 M urea solution, at 25 °C. The lines are the best fits of data to eqs 1 and 2, respectively.

nation of the micellization parameters. Table 2 lists the cmc and α values obtained by the three approaches. In the case of the TTAB–EG system, a monotonic increase of the cmc is observed as the temperature increases as a result of the disruption of the water structure surrounding the hydrophobic group of the surfactant, thereby inhibiting the micellization process. This fact is reflected by a more weak curvature in the conductivity–concentration plots. For this reason, increasing differences between the results obtained by the conventional procedure and those obtained by the other two approaches, as the temperature increases, are observed.

Similar conclusions can be extracted from the data of the SDS–urea system. In this case, urea is acting to break the water structure, producing an analogous effect to that commented above for the temperature increase. As the concentration of urea increases, the micellization process is impeded and a higher bulk concentration of surfactant is needed for micelle formation, hence increasing the cmc. At the same time, the size (aggregation number) of the micelles is decreasing, which is reflected by a weak curvature in the conductivity–concentration plots. This fact explains the differences observed (see Table 2) between the values reported by the conventional method in relation to those obtained by the integration and differentiation approaches. Although the differences observed between the cmc values obtained by these two last procedures are not significant, the α values show considerable differences, in particular at high urea concentrations.

Conclusions

In this work, we have shown by means of conductivity data generated by Monte Carlo simulations that the fitting model we propose is more adequate for the analysis of this type of data than both the conventional method and the differential conductivity method, especially in the cases where the transition occurs in a gradual way. On one hand, the conventional method presents clear undesired properties, such as its dependence on the researcher criterion and the lack of a systematic procedure of application. On the other hand, although the differential conductivity method is objective and systematic, we have demonstrated by Monte Carlo simulations that the errors in the fitting parameters provided by our method are smaller than in the differential conductivity method, which in addition needs a preprocessing of the experimental data. This manipulation of the original experimental data is an added source of errors. The application of our proposed method to experimental data of both single and more complex surfactant systems provides accurate and reliable values of the cmc and degree of counterion dissociation.

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