Determination of critical micelle concentration of cetyltrimethylammonium bromide: Different procedures for analysis of experimental data

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Abstract
Conductivity of two micellar systems was measured in order to determine critical micelle concentration (CMC) of cetyltrimethylammonium bromide (CTAB). Those systems were: CTAB in water and CTAB in binary mixture acetonitrile (ACN)–water. Conductivity (κ)–– concentration (c) data were treated by four different methods: conventional method, differential methods (first and second derivative) and method of integration (methods A–D, respectively). As CTAB in water micellar system shows a sharp transition between premicellar and postmicellar part of the κ/c curve, any of the applied methods gives reliable CMC values and there is no statistically significant difference between them. However, for CTAB in ACN–water mixture micellar system the integration method for CMC determination is recommended due to a weak curvature of κ/c plot.

Keywords: acetonitrile–water mixture, cetyltrimethylammonium bromide, conductometry, critical micellar concentration.

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Surfactants, surface active agents or tenzides, are among the most important chemicals and most prominent components of many consumer products such as pharmaceuticals, foods, soaps, *etc*. Those amphiphilic molecules possess two parts: a polar or an apolar ″head″ (liophylic part), and a long chain hydrocarbon, *i.e.*, nonpolar ″tail″ (liophobic part), so that one of these two parts of the molecule always has a particular affinity for the molecules of the solvent (polar or nonpolar) [1,2].

Apart to the strong tendency to spontaneously accumulate at the boundary surfaces phase, surfactants molecules (monomers) in aqueous solution at relatively high concentration show a distinct tendency towards arranging themselves into organized thermodynamically stable molegular aggregates known as micelles. Those agregate structures in surfactant solutions are first to form over a narrow range of surfactant concentration called the critical micelle concentration (*CMC*). This property appears to be a fundamental micellar quantity to study the self-aggregation of amphiphilic molecules in solution. In order to obtain thermodynamic parameters of micellization process [3,4], the theoretically proposed models (the mass action model or the phase separation model) [5–7] use expressions in which, directly or indirectly, the knowledge of the *CMC* is absolutely necessary. Thus, obtaining precise value of the *CMC* has extraordinary scientific, as well as practical significance [1,8–12].

In the narrow concentration range over which micelles are formed, the surfactant solutions show an abrupt change of different physicochemical properties (specific conductivity, surface tension, light scattering, *etc.*). Significant methodological difference in the determination of the *CMC* can be found, depending on the used experimental technique, the way data are processed, as well as how they are plotted and then analysed [13,14]. The focus of this paper is on the conductometric method, commonly used electrochemical technique for CMC determination [15], because of its experimental simplicity and inexpensive instrumentation. Thus, for ionic surfactant, the *CMC* can be determined by measuring the specific conductivity (κ) of surfactant of certain concentration (c), and by constructing a graph $\kappa = f(c)$. The change of slope or discontinuity of κ/c dependence gives the *CMC**. Accord-

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*Related to the experimental determination of the *CMC*, several definitions of this surfactant property have been proposed. For example, according to Williams and co-works [16], *CMC* is surfactant concentration at which the micelle

ing to the simplest approach (Williams method) [16], the intersection of two straight lines obtained for surf-actant concentration, which are smaller (premicellar range) and higher (postmicellar range) related to *CMC* gives value of *CMC*. This "conventional procedure" can be used for accurate determination of *CMC*, if κ changes abruptly at the transition between premicellar and postmicellar regions, as it is often the case with aqueous surfactant solutions [18,19,11]. However, the addition of co-solvents in aqueous surfactant solution, often leads to an increase in the degree of ionization micelles (α), and consequently to a weak curvature in vicinity of *CMC*, making the precise determination of *CMC* difficult [4,20,21]. To solve this problem, analysis of the plots of differential conductivity (first or second order) *versus* surfactant concentration [5,22], or more sophisticated approaches such as the fitting of the experimental raw data to a simple nonlinear function obtained by the direct integration of a Boltzmann type sigmoidal function [23] were frequently used. Among those, some other fitting procedures to the experimental data were used to obtain precise value of *CMC* in systems with low aggregation numbers (*i.e.*, with high α), and slow variations of physical property/concentration curves (for example, the method based on deconvolution into Gaussians of the second derivative of κ–c data, followed by two consecutive numerical integrations [24], then the method which consists of the application of a combination of the Runge–Kutta numerical integrations method and the Levenberg––Marquardt least-squares fitting algorithm [17], or statistical method (the local polynomial regression method, based on a nonparametric estimation of the regression function [25]).

In this paper, for the application and comparison of well known methods (conventional, differentiation and integration), we analyzed the two micellar systems: an aqueous solution of a cationic surfactant, hexadecyltrimethylammonium bromide (hereinafter, cetyltrimethylammonium bromide, CTAB) and CTAB in a binary mixture of acetonitrile (ACN) and water. The *CMC* of CTAB in water at *t* = 25.0 °C, as well as the binary mixture ACN-water (20 vol.% at *t* = 20.0 °C, were determined by measuring specific conductivity. These micellar systems were chosen because in the case of an aqueous solution of CTAB, specific conductivity/concentration curve shows a clear break, while in the case of CTAB in the mixture ACN–water we found the

concentration would become zero if the micellar concentration continues to change at the same rate as it does at a slightly higher concentration [17]. On the other hand, Phillips [5] defined CMC as the surfactant concentration that corresponds to the maximum change in the gradient of a plot of the magnitude of the solution property (Φ) against concentration (*c*): $(\mathrm{d}^3\Phi/\mathrm{d}c^3)_{c=CMC} = 0$.

appearance of curvature around *CMC*, so that the singular point can not be easily determined. Therefore, to determine accurately the *CMC* value in the latter case, we used the procedure that is commonly used to obtain *CMC* of surfactants with small aggregation number [4,20,22,26] and which has recently been proposed by Carpena and co-workes [23]. The aim of this paper is to show how/whether values of *CMC* change/depend on the applied mathematical analysis of κ–c data, as well as to find the best procedure that has appeared recently in literature [23], for *CMC* determination in the particular case.

EXPERIMENTAL

Material

The cationic surfactant, cetyltrimethylammonium bromide (CTAB) was obtained from Merck (Germany) having purity ≥ 97% used without any pretreatment. Acetonitrile ACN (HPLC grade purity ≥ 99.9%) was obtained from Sigma–Aldrich (USA). Deionized water (ρ = 18 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA) was used for preparation of all solutions.

Fresh solutions of CTAB in CAN–water (20 vol.%) binary mixtures were prepared in the following way. The accurately weighed (Mettler electronic balance with a precession of 0.0001 g) mass of CTAB was quantitatively transferred into a 100 mL volumetric beaker, and dissolved in 90 mL of 20 vol.% ACN; that mixture was gently stirred with a glass rod in order to avoid the foam formation. Then, the solution was transferred in 100 mL volumetric flask and filled up to volume with 20 vol.% ACN.

Methods

The conductivity measurements were carried out using a digital conductivity meter HI8820N (Hanna instruments, Portugal) with the uncertainties ±0.5 μS cm^{-1}, and with the matching HI7684W probe that uses the 4-ring method. The conductivity meter was calibrated with different concentration of solutions of potassium chloride (Merck, purity > 99 %) prior to the experiment. The conductivity–concentration data were obtained from two micellar system (water solution of CTAB as well as CTAB in binary mixture of water and co-solvent (ACN)) at constant temperature (25.0 °C in the case of CTAB in water, and 20.0 °C in the case of CTAB in mixture ACN–water). A circulating water bath (Series U, MLW, Frietal, Germany) was used for maintaining the constant temperature within uncertainties of ±0.2 °C. The specific conductivity values of each set containing 18−21 different CTAB concentrations, at a fixed solvent composition (expressed as ACN vol.%), were measured while stirring after achieving temperature equilibrium at each dilution.

All measurements were conducted in glass vessel, $V \approx 100$ mL (Metrohm, model 876–20) wrapped in the water recirculation jacked connected to thermostat and equipped with the magnetic stirrer ((IKA–COM-BIMAG RET, Staufen, Germany).

Data analysis

For processing (fitting) all experimental data, *i.e.*, obtaining precise values of critical micelle concentration of the examined micellar systems, software package OriginPro 9.0 (OriginLab Corporation, US) was used.

Procedure

The 90 mL solution of CTAB of different concentrations was introduced into the glass vessel that was capped with openings through which thermometer and conductometric cell are always put in the same place. Then, CTAB solution was thermostated ($\sim$20 min) at the examined temperature (20.0 or 25.0 °C) along with stirring (300 rpm), and equilibrated until the conductivity value became constant. For each of the examined CTAB solution, the specific conductivity measurements were repeated three times.

RESULTS AND DISSCUSION

For the analysis of experimental data obtained by measuring specific conductivity of certain surfactant concentrations, *i.e.*, the determination of *CMC* of the examined micellar systems, we used different methods (A, B, C and D, respectively) that are ″conventional procedure″ (Williams *et al.* method [16] methods of differentiation (either the first [22] or the second order [5]) as well as the method of integration (Carpena method) [22].

Conventional method − method A [16]. As the *CMC* is a "phase transition" between two different regimes of a surfactant solution, the plot of κ versus surfactant concentration is a curve which consists of two linear segments (premicellar and postmicellar) with different slopes; the intersection (singular point) of those straight lines below and the above *CMC* gives the value of *CMC*, while ratio of the slope of the postmicellar region (S_2) to that of the premicellar region (S_1) gives micelle ionization degree (α) [3,27–29].

The first derivative method − method B [22]. According to this method, one can analyze the dependence of the specific conductivity first derivative (dκ/dc) *versus* surfactant concentration, *c*. This derivative is of the sigmoidal type, and can be adequately described by using a Boltzmann type sigmoidal:

$$\frac{\mathrm{d}\kappa}{\mathrm{d}c} = A_2 + \frac{A_1 - A_2}{1 + e^{(c-c_0)/\Delta c}} \tag{1}$$

where A_1 (A_2) is the asymptotic value for small (large) values of surfactant concentration (horizontal asymptote), c_0, *i.e.*, *CMC* is center of sigmoidal curve (central point of the transition), and Δc is the width of the transition (fitting parameter, *i.e.*, the time constant, which is directly related to the independent variable range, where the sudden change of κ occurs).

The second derivative method − method C (Phillips method [5]). According to this method, one can analyze the dependence of the second derivative of specific conductivity (d$^2\kappa$/dc^2) *versus* surfactant concentration, *c*. This method consists of directly fitting the second derivative of the conductivity/concentration data to a Gaussian without additional treatment of the data. The equation to use in Origin program for fitting the curve is:

$$\left(\frac{\mathrm{d}^2\kappa}{\mathrm{d}c^2}\right) = \left(\frac{\mathrm{d}^2\kappa}{\mathrm{d}c^2}\right)_{c=0} + \frac{A}{w\sqrt{\pi/2}}\exp(\frac{-2(c-CMC)^2}{w^2}) \tag{2}$$

where $(\mathrm{d}^2\kappa/\mathrm{d}c^2)_{c=0}$, A and w are baseline offset, total area under the curve from the baseline and the width of the peak at half height, respectively. The minimum of the inverted Gaussian corresponds to points of maximum variation, and coincides with the *CMC*.

Method of integration − method D (Carpena´s method) [23]. This method is based on direct fitting of specific conductivity *versus* surfactant concentration data. If it is assumed that the dependence of the first derivative of specific conductivity *versus* surfactant concentration behaves as a sigmoid (Eq. (1)), then the original data should behave as the integral of the sigmoid. A direct integration of Eq. (1) yields:

$$\kappa = \kappa(0) + A_1 c + (A_2 - A_1)\Delta c \ln\left(\frac{1 + e^{(c-c_0)/\Delta c}}{1 + e^{-c_0/\Delta c}}\right) \tag{3}$$

where $\kappa(0)$ is the value of specific conductivity when surfactant concentration (*c*) is 0, A_1 and A_2 are the slopes obtained in the premicellar and postmicellar segments, c_0 (*CMC*) is the breakpoint of curve κ/c and Δc is a width of transition with c_0, *i.e.*, concentration range in which there is a change of κ (fast or slow) around *CMC*.

The above described mathematical procedures have both some advantages and drawbacks. Generally, if there is an appropriate curvature and the break point is clear, any method is suitable for determination of the *CMC*. On the other hand, a frequent problem arises from the conductivity method that it is usually difficult to determine the *CMC* for micellar systems in which the κ/c plot does not show a sharp transition from the premicellar to the postmicellar region. As the result, the obtained *CMC* will be affected to a greater uncertainty.

Table 1 shows the *CMC* and the degree of micelle ionization, α of CTAB in water obtained at 25.0 °C, from conductivity/concentration plots by using the above described different treatments of the experimental data (conventional, differentiation and integration).

The dependence of the specific conductivity, κ on the concentration of CTAB, c_{CTAB} at t = 25.0 °C is presented in Fig. 1a. With c_{CTAB} increasing, κ also increases linearly. After a certain concentration of CTAB, κ further increases linearly, but the slope of the straight line decreases; concentration at which an abrupt change of κ occurs, represents *CMC*. As a point that corresponds to the *CMC* on κ/c plot divides graph on the two linear parts (premicellar and postmicellar) the

value of *CMC* is determined as the intersection point [16,17,20] of two lines that correspond to the κ values in those segments. The data points were fitted by the least square method and the equations of lines in premicellar and postmicellar segment are obtained: κ = 3.0 ($\pm$0.81) + 123.8 ($\pm$1.45)c_{CTAB} (r^2 = 0.9995, p < 0.001) and κ = 72.4 ($\pm$0.66) +47.3 ($\pm$0.49)c_{CTAB} (r^2 = 0.9996, p < < 0.001). By solving these equations for c, we obtained the value of the intersection points (*CMC*, method A), which was 0.907$\pm$0.04 mM. Likewise, the degree of counterion dissociation was determined from the ratio of the slopes of lines in both premicellar (S_1) and postmicellar (S_2) region, $\alpha = S_2/S_1$, and the obtained value is 0.38$\pm$0.01.

Table 1. Critical micelle concentration (CMC) and degree of counterion dissociation (α) for examined micellar systems obtained by different treatments of the experimental data

| Micellar system | Conventional (method A) | | Differentiation | | | Integration (method D) | |
| | | | First order (method B) | | Second order (method C) | | |
	CMC / mM	$\alpha(S_2/S_1)$[a]	CMC / mM	$\alpha(A_2/A_1)$[b]	CMC / mM	CMC / mM	$\alpha(A_2/A_1)$[b]
CTAB in water	0.907	0.38	0.900	0.37	0.907	0.911	0.39
CTAB in ACN−water	3.706	0.74	3.556	0.76	−	3.699	0.75

[a]Data obtained from the ratio between the slopes of line in the postmicellar region (S_2) to that in the premicellar region (S_1); [b]data obtained from the ratio between the slopes of line in the postmicellar region (A_2) to that in the premicellar region (A_1) (see Eqs. (1) and (3))
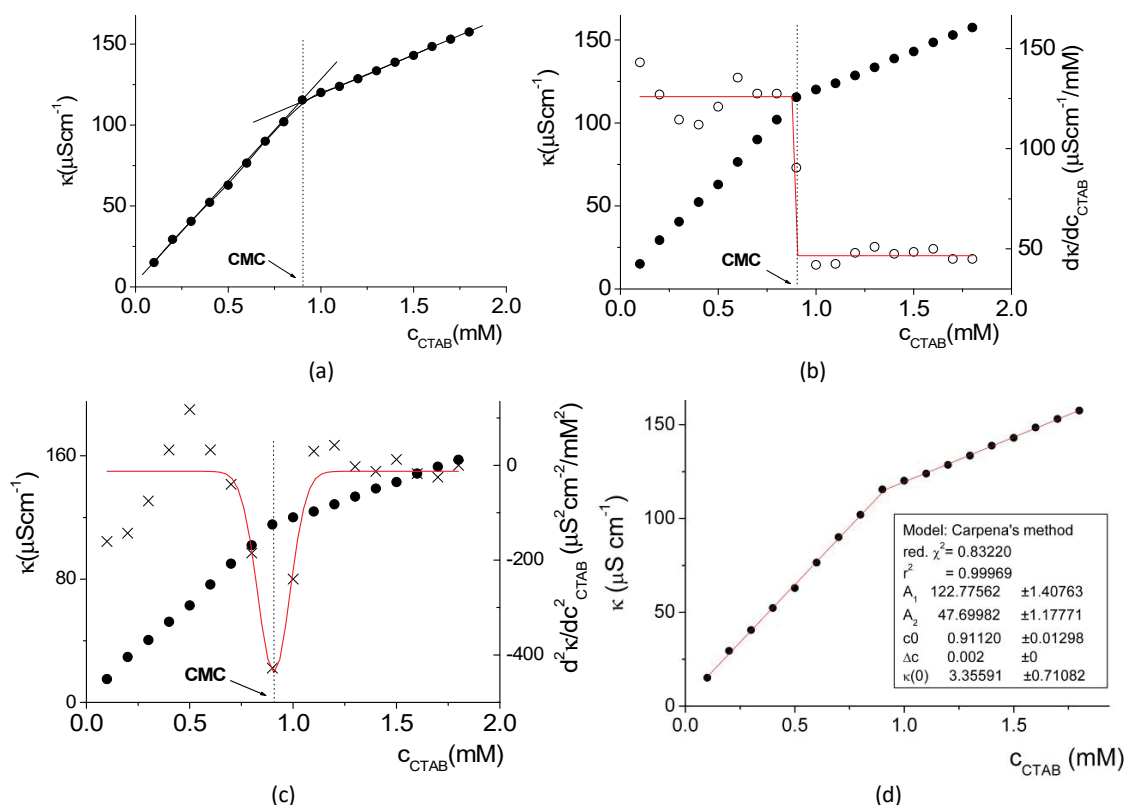

(a)

(b)

(c)

(d)

Figure 1. Graphical presentation of different methods of CMC determination for CTAB in water micellar system at 25.0 °C by: a) Williams method, b) first derivative method (solid line corresponds to a Boltzmann-type sigmoid), c) Phillips method (solid line corresponds to Gaussian) and d) Carpena method (solid line corresponds to integrated form of sigmoid of Boltzmann type); result of the fitting shown in the box. Experimental points, the first and the second derivative are denoted as ●, ○ and ✕, respectively. The arrows denote CMC values.

In addition, the *CMC* was determined using the first derivative method (method B). Figure 1b shows plot of dκ/d*c*, as a function of the surfactant concentration. The data were fitted to a sigmoidal curve of Boltzmann type (Eq. (1)), and the obtained value of both *CMC* and α was 0.900 mM and 0.37, respectively. Figure 1c shows the application of the Phillips' method (method C) for the determination of *CMC*. Crosses denote the values of d$^2\kappa$/d*c*^{2}, and a solid line corresponds to the Gaussian function (Eq. (2)). Value of *CMC* determined by this method was 0.907 mM.

Apart from the above-described procedures for determination of C*MC*, the recently proposed method (the method D [23]) was used. The solid lines (Figure 1d) correspond to the Carpena fitting, where the obtained value of *CMC* is 0.911±0.013 mM. The values of both the *CMC* and α obtained by this approach (method D) as well as by previously described methods A–C are all listed in Table 1. Fitting parameters of κ–*c* data to Eq. (3) are shown in Figure 1d. Besides the most significant fit parameters, the Figure 1d includes the regression-square (r^2) and reduced shi-square (red. χ^2) coefficients.

Obviously, between the values of *CMC* obtained by methods A–D there is no significant difference (*RSD* = = 0.5%), so that in the case of CTAB in water, for determination of *CMC* one can use any of the given procedures. Moreover, since conductivity shows the abrupt change in going from the premicellar surfactant concentration range to the postmicellar surfactant concentration range, then Williams method allows one to calculate a reliable value for the *CMC* (for α also). This value has been confirmed by derivative method as well as the method of integration. Also, *CMC*s obtained from conductivity measurements are consistent with previously published results which show that the values of *CMC* at *t* = 25.0 °C lie in the range 0.88–1.02 mM [20,23,24,30–33,10,34,11,13].

In our previous papers [26], we reported the effect of co-solvent, propylene-glycol on the micellization of CTAB at different temperatures. In the present paper our study is extended to the micellar system CTAB in mixture acetonitrile–water at *t* = 20.0 °C. Although the *CMC* values for CTAB in this mixture at different temperatures were already obtained [35,36], to our knowledge there were no previous studies on the influence of ACN on CTAB micellization at *t* = 20.0 °C.

In Figure 2a the results of *CMC* determination for CTAB in mixture ACN–water (20 vol.%) at *t* = 20.0 °C obtained by the conventional method (method A) and the first derivative method (method B) are shown. The solid line corresponds to the first derivative of the conductivity/concentration curve, and the arrows denote the values of *CMC* obtained by the method A (*CMC*$_1$) as well as the method B (*CMC*$_2$). Again, according to

method A, the data points were fitted by the least square method and the equations of lines in premicellar and postmicellar segment are obtained: κ = = −8.5 (±1.10) + 80.5 (±.53) c_{CTAB} (r^2 = 0.9997, *p* < 0.001) and κ = 67.8 (±7.41) + 59.9 (±1.61)c_{CTAB} (r^2 = 0.9978, *p* < < 0.001). Obtained value of critical micellar concentration was 3.706 ± 0.789 mM (*CMC*$_1$). On the other hand, this value obtained by method B was 3.556 mM (*CMC*$_2$). Moreover, due to a small curvature of the curve, in this micellar system it was not possible to get the second derivative (the method C).
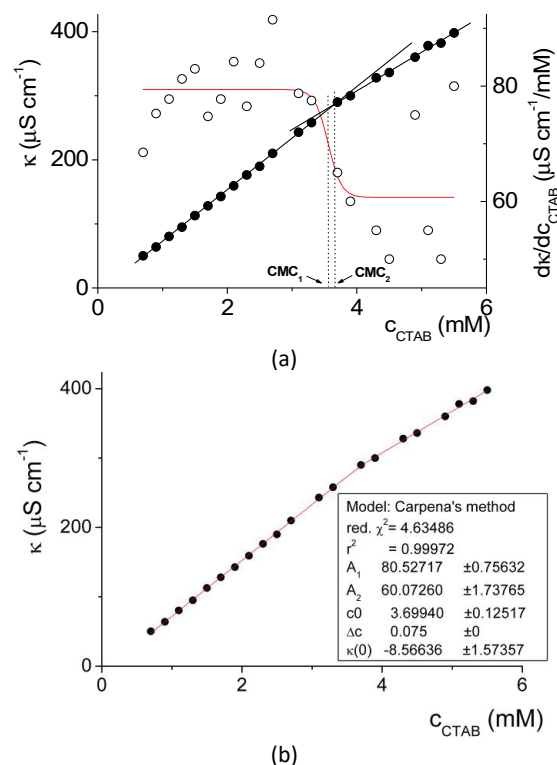

Figure 2. Graphical presentation of different methods of CMC determination for CTAB in CAN–water (20 vol.%) micellar system at 20.0 °C: a) Williams method as well as the first derivative method (solid line corresponds to a Boltzmann type sigmoid) and b) Carpena method (solid line corresponds to integrated form of sigmoid of Boltzmann type); result of the fitting shown in the box. Experimental points and the first derivative are denoted as ● and ○, respectively. The arrows denote CMC values.

In comparison to the previous examined micellar system (an aqueous solution of CTAB), in this case, the change κ with the CTAB concentration in the transition region (*i.e.*, the region between the two linear segments, premicellar and postmicellar) is gradual, thus, for the precise determination of *CMC*, the integration method (the method D) was used. The solid line (Figure 2b) represents fit according to the Eq. (3).

Data fitting was carried out by making use of initial values of κ(0), A_1, A_2, c_0 and Δc to calculate an approximate value of conductivity (Eq. (3)). The values of κ(0),

A_1, A_2 and c_0 were estimated graphically from the experimental plot by the method A. Once chosen, values of these parameters were not changed during fitting sessions as they didn't have a significant influence on the *CMC*, while this was not the case with Δc [20]. Initial values of Δc were chosen from a certain range shown in Figure 3a and changed for an each fitting session. It was noticed that low Δc starting values give lower reduced chi-square coefficient values (red. χ^2). Figure 3a shows that for the discussed micellar system there is a certain region of Δc initial values for which red. χ^2 obtained from these fitting sessions are constant. The final set of fitted parameters values was chosen according to this region. Namely, we took final set of fitted parameters values when red. χ^2 stopped decreasing and became constant as best-fit parameters. The dependence of C*MC* values obtained by a four-parameter fit procedure for different Δc is shown in Figure 3b. The most significant fitting parameters ($\kappa(0)$, A_1, A_2, c_0 and Δc), including the regression-square (r^2) and reduced chi-square (red. χ^2) coefficients are all summarized in Figure 2b. Obtained value of *CMC* was 3.699±0.125 mM. As we expected, uncertainty (expressed as *RSD*) in the *CMC* value obtained by method D, related to methods A, is much lower, and it is ±3.0%. The values of both the *CMC* and α for CTAB in the mixture CAN–water obtained by methods A, B and D are all listed in Table 1.
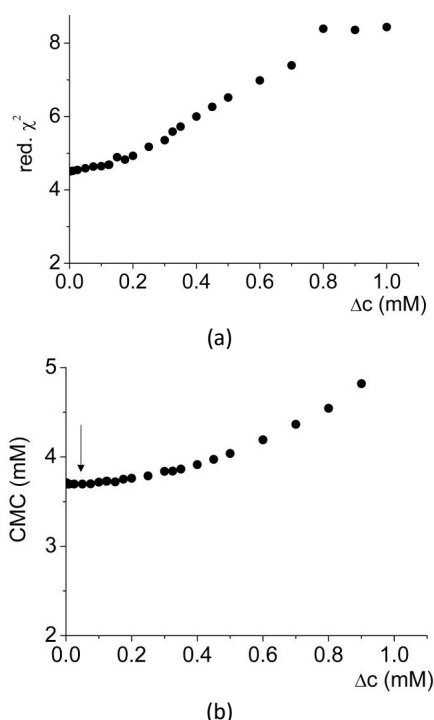

(a)

(b)

Figure 3. Initial values of the width of transition (Δc) influence on: a) reduced chi-square (red. χ^2) coefficient and b) the critical micelar concentration (CMC). These are obtained by fitting the raw experimental data for CTAB solution in mixture CAN–water (20 vol.%) at 20.0 °C to Eq. (3). The arrow denotes chosen (optimal) Δc.

CONCLUSION

In this paper, the *CMC* values of different micellar systems (CTAB in water, and CTAB in binary mixture ACN–water) were determined from conductivity measurements at t = 25.0 °C (CTAB in water) and t = 20.0 °C (CTAB in binary mixture ACN–water). Those values were calculated from experimental data by various procedures (conventional, the first and second derivative as well as integration), with a view to determine whether the value of the *CMC* change depending on the applied method or not, as well as finding out the optimal method for determining the *CMC* in the particular case. Thus, if there is an appropriate curvature and the break point is clear, any method is suitable for determination of the *CMC* (case of CTAB in water). The *CMC*s obtained by those methods were in a good agreement with each other. This means that the use of conventional method (Williams) is appropriate, and gives reliability to the *CMC* for CTAB in water. However, in the case of CTAB in the mixture ACN–water, the specific conductivity–concentration plot does not show a sharp transition from the premicellar and postmicellar region, but it rather exhibits a curvature. Therefore, for the precise determination of the *CMC*, the method of integration was considered, whereby calculated values of the *CMC* depend critically on the initial value of Δc (*i.e.*, the width of transition) in the process of fitting the experimental data.

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IZVOD

ODREĐIVANJE KRITIČNE MICELARNE KONCENTRACIJE CETILTRIMETILAMONIJUM BROMIDA: RAZLIČITE PROCEDURE ANALIZE EKSPERIMENTALNIH PODATAKA

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Korišćene su različite matematičke procedure za analizu eksperimentalnih podataka s ciljem određivanja kritične micelarne koncentracije (*CMC*) katjonskog surfaktanta, heksadeciltrimetilamonijum-bromida (cetiltrimetilamonijum-bromida, CTAB) u vodi, kao i binarnoj smeši vode i korastvarača (acetonitril, ACN). Provodljivost ovih micelarnih sistema merena je na *t* = 25.0 °C (CTAB u vodi) i *t* = 20.0 °C (CTAB u smeši ACN–voda). Na osnovu podataka specifična provodljivost (κ)–koncentracija surfaktanta (*c*), vrednosti *CMC* su određene primenom: klasične metode, metoda diferenciranja (prvog i drugog izvoda) i metodom integracije (metode A, B, C i D, redom). U slučaju vodenog rastvora CTAB, prelaz između predmicelarnog i postmicelarnog dela krive $\kappa = f(c)$ je oštar, tako da se *CMC* određuje kao tačka preseka dve linije koje odgovaraju ovim, dobro definisanim delovima krive (metod A). Pored toga, vrednost *CMC* ovog micelarnog sistema određena je metodama B, C i D, pri čemu između dobijenih vrednosti *CMC* ne postoje statistički značajne razlike. Međutim, u odnosu na čistu vodu, dodatak ACN rezultuje u manjoj promeni specifične provodljivosti s koncentracijom CTAB u uskoj oblasti koncentracija između dva linearna dela krive κ/c, što može dovesti do nepreciznog određivanja *CMC*. Zbog toga je, za precizno određivanje *CMC* u ovom micelarnom sistemu, predložen metod integraljenja (metod D).