

# What Affects the Degree of Micelle Ionization: Conductivity Study of Alkyltrimethylammonium Chlorides

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70<sup>th</sup> birthday

## Abstract

The critical micelle concentration, cmc, and the degree of micelle ionization,  $\beta$ , of decyltrimethylammonium chloride (DeTAC), dodecyltrimethylammonium chloride (DTAC) and tetradecyltrimethylammonium chloride (TTAC) in water, 0.01 M, and 0.1 M NaCl solution were determined from the electrical conductivity data in the temperature range from 278.15 to 328.15 K. It has been found that cmc is decreasing with increasing surfactant chain length and increasing concentration of added NaCl, whereas the temperature dependence of cmc shows the typical U-shaped form with a minimum around  $(306 \pm 3)$  K. Further,  $\beta$  is decreasing with lengthening the alkyl chain of surfactant and increasing with increasing temperature, but no distinct influence of added salt has been found actually. It can be concluded that the effect of electrolyte on micelle ionization is quite complex.

**Keywords:** Alkyltrimethylammonium chloride, electrical conductivity, micellization, NaCl, critical micelle concentration, degree of micelle ionization

## 1. Introduction

Despite much progress that has been made at investigations of micellar systems there are still some ambiguities in micellization properties, especially for surfactants in salt solutions. For ionic surfactants it has been confirmed that critical micelle concentration, cmc, is decreasing with increasing concentration of added salt due to the screened repulsion between charged head groups of surfactant monomers because of the condensed counterions, what leads to easier formation of the micelles.<sup>1,2</sup> Thus, the degree of micelle ionization,  $\beta$ , could be believed to decrease with electrolyte addition on account of the excess counterions in solution also.

The effect of electrolytes on micellar behaviour of sodium dodecylsulfate (SDS) has been investigated thoroughly by Dutkiewicz and Jakubowska by electrical conductivity technique.<sup>3</sup> The cmc values were found to decrease with increasing electrolyte concentration. As could be expected, they strongly depend on the nature of cation as well. Further, the reported results for  $\beta$  reveal not only the dependence of degree of micelle ionization on the

kind of electrolyte added, but show that there is no exact decrease in  $\beta$  with increasing electrolyte concentration. Moreover,  $\beta$  values actually increase or decrease or remain constant with increasing electrolyte concentration in solution indicating the very complex effect of added electrolyte on the degree of SDS micelle ionization. Jakubowska has been studying SDS and hexadecyltrimethylammonium bromide (CTAB) micellization by conductivity measurements together with electrospray ionization mass spectrometry (ESI-MS) also.<sup>4-6</sup> Her recent investigation showed that the effect of added electrolyte on micelle ionization depends on the kind of counterions (cosmotropic or chaotropic ions) and their polarizabilities.<sup>6</sup>

However, electrical conductivity measurement turned out as one of the most accurate techniques for determining the cmc of ionic surfactants which is usually appointed to an abrupt change in certain physical property over a very narrow concentration range. According to the Phillips, cmc is defined as a concentration corresponding to a maximum change in gradient of the solution property versus surfactant concentration curve,<sup>7</sup> but it can be graphically determined also. In order to determine precise cmc values from conductivity data, different fitting procedures to the experimental data have

been applied already.<sup>8–10</sup> In addition, the degree of micelle ionization can be estimated from experimental conductivity data as a ratio between slopes of electrical conductivity versus surfactant molality plot above and below the cmc.<sup>11–13</sup>

Conductometry has been already widely used for determining cmc and  $\beta$  of ionic surfactants in water as it can be read in ref.<sup>14</sup> and the references cited there. Nowadays, it has been also applied in the investigations of aggregation and micellization properties of ionic surfactants in salt solutions.<sup>3,6,14–16</sup> In our previous work we focused our attention on the influence of temperature and added NaCl on thermodynamics of dodecyltrimethylammonium chloride (DTAC) micellization process.<sup>1</sup> The possible influence of added electrolyte on  $\beta$  was not taken into account at that time and thus the degree of DTAC micelle ionization in water<sup>14</sup> was used in the calculations of Gibbs free energy of micellization,  $\Delta_M G^0$ . The proposed assumption can be treated as possible and correct because only minor influence of  $\beta$  on  $\Delta_M G^0$  was found.

Nevertheless, the question of true  $\beta$  of ionic surfactant in salt solution remained a challenge for us, which we have taken up in this work. Electrical conductivity of decyltrimethylammonium chloride (DeTAC), DTAC, and tetradecyltrimethylammonium chloride (TTAC) in 0.01 M and 0.1 M NaCl solution was measured in a temperature range between 278.15 and 328.15 K in steps of 10 K. Values of cmc and  $\beta$  were determined from conductivity versus surfactant molality plots graphically and by help of the integral Boltzman-type sigmoid equation proposed by Carpena et. al.<sup>8</sup> The obtained values were compared to the already published and re-evaluated data for DeTAC, DTAC, and TTAC in water also.<sup>14</sup> The influence of alkyl chain length, temperature, and salt on the micellization properties of alkyltrimethylammonium chloride (TAC) surfactants is discussed.

## 2. Experimental

### 2. 1. Materials

Decyltrimethylammonium chloride (DeTAC, > 0.98%), dodecyltrimethylammonium (DTAC, > 0.98%), and tetradecyltrimethylammonium chloride (TTAC, > 0.98%) were purchased from Anatrace, Inc. (Maumee, OH, USA) and stored in a refrigerator before use. All the compounds were used as received. Sodium chloride was obtained from Merck and kept in a desiccator before use.

Surfactant solutions were prepared by weighting surfactant and demineralised water distilled in a quartz bi-distillation apparatus (DESTAMAT Bi18E, Heraeus).

### 2. 2. Methods

#### 2. 2. 1. Electrical Conductivity Measurements

Electrical conductivity data were recorded with a PC-interfaced LCR Meter Agilent 4284 A connected to a

three-electrode measuring cell described elsewhere.<sup>17</sup> A conductivity cell with a cell constant,  $B = (2.2130 \pm 0.0003) \text{ cm}^{-1}$ , was calibrated with dilute potassium chloride solutions<sup>18</sup> and immersed in a high precision thermostat described previously.<sup>19</sup> For the experiments, where extremely low differences in electrical resistance at surfactant solution addition were expected, a conductivity cell with higher cell constant,  $B = (43.84 \pm 0.02) \text{ cm}^{-1}$ , was applied. This cell was not immersed in the thermostat bath, but was equipped with a double coat which enables the circulation of the thermostatic liquid. The monoethylene glycol bath was set to a defined temperature with reproducibility better than 0.005 K and stability during measurement of 0.003 K. The exact temperature was additionally checked with a calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) connected to a HP 3458 A multimeter.

After measuring a resistance of NaCl solution (0.01 M or 0.1 M) at the set temperature,  $R_{\text{NaCl}}$ , successive aliquots of a stock solution of DeTAC, DTAC, or TTAC in the same medium were added by a programmable syringe pump (Model 1250, J-KEM Scientific, MO, USA) and a resistance of the solution,  $R$ , was measured each time. A home-developed software package was used for temperature control and acquisition of conductance data. The measuring procedure including corrections and extrapolation of the sample resistance to infinite frequency has been described previously.<sup>19</sup> Corresponding conductivities,  $\kappa_{\text{overall}}$ , were obtained as  $\kappa_{\text{overall}} = B/R$ . NaCl solution was always treated as a solvent, therefore a corresponding electrical conductivity,  $\kappa_{\text{NaCl}} = B/R_{\text{NaCl}}$ , was subtracted from the overall measured electrical conductivities. Afterwards, a surfactant contribution to the measured conductivity was calculated as  $\kappa = \kappa_{\text{overall}} - \kappa_{\text{NaCl}}$ . Taking into account the sources of error (calibration, titration, measurements, impurities) the determined conductivities are accurate within 0.5%.

#### 2. 2. 2. Critical Micelle Concentration and Degree of Micelle Ionization

The plot of electrical conductivity,  $\kappa$ , versus surfactant molality,  $m$ , typically consists of a two distinct linear regions below and above the break (cmc) of experimental curve.<sup>20</sup> The cmc can be thus graphically determined as an intersection point between two straight lines corresponding to the well-defined parts of breaking curve.<sup>8,21–23</sup> This approach was found to produce accurate cmc values in a case of sharp transition, but is indeed less appropriate in cases where transition occurs gradually.<sup>8</sup>

The ratio between slopes of the mentioned fragments above and below the breaking point of experimental curve could be used as an estimate of degree of micelle ionization.<sup>11,13</sup> The initial increasing part of diagram with a slope  $p_1$  results from an increasing electrical conductivity of free surfactant ion,  $\lambda_{\text{S}^{\ominus}}$ , and corresponding counter-ions,  $\lambda_{\text{Cl}^{\ominus}}$ ,

due to an increasing concentration of surfactant,  $c_s$ , in solution (TAC is considered a strong 1:1 electrolyte):

$$\kappa = (\lambda_{s^+} + \lambda_{Cl^-})c_s = p_1 \cdot c_s \quad (1)$$

Above the breaking point, electrical conductivity increases slower with addition of surfactant obviously. According to the mass-action model it is assumed that the concentration of surfactant monomer ions above the critical micelle concentration remains equal to the cmc, thus only the micelle and corresponding counter-ion concentration increases with surfactant addition:

$$\kappa = (\lambda_{s^+} + \lambda_{Cl^-})\text{cmc} + \frac{c_s - \text{cmc}}{n} \lambda_{\text{mic}} + (c_s - \text{cmc})\beta \cdot \lambda_{Cl^-} \quad (2)$$

A postmicellar slope of electrical conductivity versus surfactant molality plot,  $p_2$ , can be thus expressed as

$$\frac{\kappa - (\lambda_{s^+} + \lambda_{Cl^-})\text{cmc}}{c_s - \text{cmc}} = \frac{1}{n} \lambda_{\text{mic}} + \beta \cdot \lambda_{Cl^-} = p_2 \quad (3)$$

In contrast to surfactant monomer, micelle is considered an associated electrolyte. Its ionic molar conductivity,  $\lambda_{\text{mic}}$ , is assumed to be proportional to the molar conductivity of free surfactant ion, taking an effective charge of the micelle,  $z = n \cdot \beta$  ( $n$  is the aggregation number of micelle), as a proportionality constant:

$$\lambda_{\text{mic}} = z \cdot \lambda_{s^+} = n \cdot \beta \cdot \lambda_{s^+} \quad (4)$$

Taking into account Eqs. (1) and (4) it follows from the Eq. (3) that the degree of micelle ionization can be calculated as the ratio between the lower and the higher slope of electrical conductivity versus surfactant molality plot above and below the cmc:

$$\beta = \frac{p_2}{p_1} \quad (5)$$

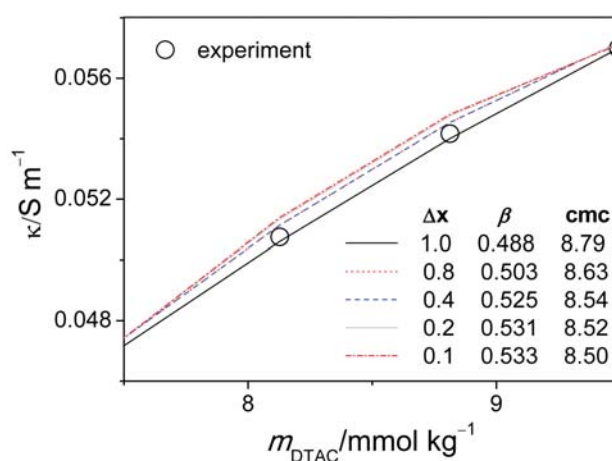
For detail information see ref.<sup>11</sup>. However, this procedure can be very subjective because it often depends on the number of experimental points taken for the linear fitting and slope determination.

In order to improve quality of the calculated cmc and  $\beta$  values, fitting of the equation

$$\kappa = a_1 \cdot c_s + (a_2 - a_1) \cdot \Delta x \cdot \ln \frac{1 + \exp((c_s - a_3) / \Delta x)}{1 + \exp(-c_s / \Delta x)} \quad (6)$$

to the experimental conductivity data was applied also. It is an integral form of the Boltzmann-type sigmoid equation proposed by Carpena et. al<sup>8</sup> and applied recently for surface active ionic liquids.<sup>10</sup> In Eq. (6),  $\kappa$  is the surfactant contribution to electrical conductivity and was calculated as previously described in chapter 2.2.1.,  $c_s$  is the surfactant concentration,  $a_1$ ,  $a_2$ , and  $a_3$  are fitting parameters and

$\Delta x$  is a width of transition with cmc being its central point. Although the initial guesses of fitting parameters have not been specified in the literature, they should be in part related to the physicochemical change being measured. In our case they were initially set to the values estimated graphically from the experimental diagrams as  $a_1 \approx p_1$  (premicellar slope),  $a_2 \approx p_2$  (postmicellar slope), and  $a_3 \approx \text{cmc}/\text{mmol kg}^{-1}$ . The width of transition,  $\Delta x = \Delta \text{cmc}/\text{mmol kg}^{-1}$  had to be chosen also. Whereas the initial guess values of  $a_1$ ,  $a_2$ , and  $a_3$  do not have any crucial influence on the result of fitting procedure, the same cannot be claimed for the set values of  $\Delta x$ . Actually, small  $\Delta x$  value means an abrupt transition, while higher values correspond to gradual transitions as it is presented on Figure 1 for the conductivity data of DTAC in 0.1 NaCl at 298.15 K.



**Figure 1.** The conductivity as a function of surfactant molality plot for DTAC in 0.1 M NaCl at 298.15 K. Only the area near cmc is shown actually. The lines represent fits according to the Eq. (6) for different transition widths,  $\Delta x$ , giving the corresponding values of  $\beta$  and cmc/mm $\text{mol kg}^{-1}$ .

In our evaluation,  $\Delta x$  was set to about 5% of the cmc value, assuming that micellization can be treated as an abrupt transition rather than a gradual process. Fitting to the data was carried out by help of a R software (R version 2.12.0), obtaining  $a_1$ ,  $a_2$ , and  $a_3$  as a result of the fitting procedure. The degree of micelle ionization was estimated from the ratio  $a_2/a_1$  and  $a_3$  was taken to be the cmc/mm $\text{mol kg}^{-1}$ . Uncertainties in the values of cmc and  $\beta$  are about  $\pm 1\%$  and  $\pm 5\%$ , respectively.

### 3. Results and Discussion

The typical dependence of solution's conductivity on surfactant molality is shown in Figure 2 for DTAC in water, 0.01 M, and 0.1 M NaCl at all the investigated temperatures. Identical diagrams for DeTAC and TTAC are available in the Supporting Informations (Figures S1 and S2). The solid lines represent fits according to the Eq. (6).

Scattering of the experimental data for TTAC in 0.1 M NaCl prevented us from usage of the three-parameter fit according to the Eq. (6). Therefore, a two-parameter fit procedure was applied where  $a_3$  was fixed at the value of cmc obtained by isothermal titration calorimetry (ITC) previously.<sup>2</sup> In addition, the already published conductivity data for DeTAC, DTAC, and TTAC in water<sup>14</sup> was also re-evaluated by help of the Eq. (6). All the estimated cmc and  $\beta$  values are collected in Table 1 together with the

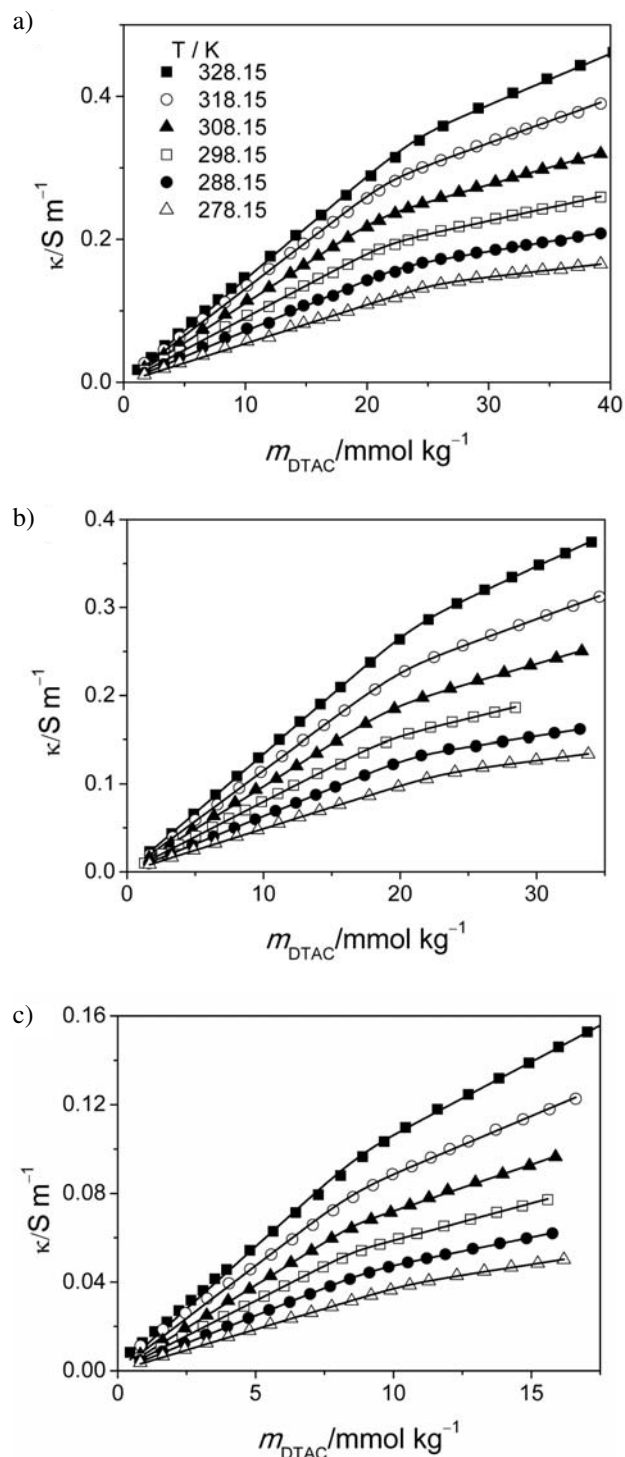
published data for DeTAC, DTAC, and TTAC in water<sup>14</sup> and cmc values obtained by ITC recently.<sup>1,2</sup> Evidently, the values of cmc and  $\beta$ , determined graphically and by help of the Eq. (6), are in reasonable agreement.

The cmc dependence on temperature exhibits a typical U-shaped form (Figure 3) reaching the minimum cmc at a temperature  $T^*$  for all the investigated systems. As already observed for homologous series of non-ionic and ionic surfactants,<sup>24</sup>  $T^*$  obviously decreases with increasing

**Table 1.** The critical micelle concentration, cmc, and the degree of micelle ionization,  $\beta$ , as obtained from the electrical conductivity experiments together with the already published cmc values from ITC experiments for DeTAC, DTAC, and TTAC in aqueous NaCl solutions at different temperatures. The values were obtained either by extrapolation of the conductivity plots (extr) or by fitting of the Eq. (6) to the experimental data (fit).<sup>a,b</sup>

	Water			0.01 M NaCl			0.1 M NaCl			
	conductivity		ITC	conductivity		ITC	conductivity		ITC	
	T	$\beta$	cmc	$\beta$	cmc	cmc	$\beta$	cmc	cmc	
DeTAC										
extr	278.15	0.460 <sup>c</sup>	107.4 <sup>c</sup>	106 <sup>e</sup>	0.328	96.7	98 <sup>e</sup>	0.392	86.5	87 <sup>e</sup>
fit		0.457	99.1		0.416	91.2		0.442	83.2	
extr	288.15	0.491 <sup>c</sup>	97.7 <sup>c</sup>	95 <sup>e</sup>	0.426	93.1	92 <sup>e</sup>	0.419	78.0	75 <sup>e</sup>
fit		0.468	92.3		0.479	93.2		0.467	78.5	
extr	298.15	0.526 <sup>c</sup>	94.7 <sup>c</sup>	92 <sup>e</sup>	0.477	88.4	91 <sup>e</sup>	0.552	71.2	68 <sup>e</sup>
fit		0.502	86.4		0.515	87.4		0.565	67.0	
extr	308.15	0.570 <sup>c</sup>	86.8 <sup>c</sup>	82 <sup>e</sup>	0.564	83.7	80 <sup>e</sup>	0.550	67.6	59 <sup>e</sup>
fit		0.542	82.7		0.563	84.6		0.577	66.0	
extr	318.15	0.601 <sup>c</sup>	89.0 <sup>c</sup>	88 <sup>e</sup>	0.493	88.9	80 <sup>e</sup>	0.611	70.1	67 <sup>e</sup>
fit		0.577	80.9		0.511	88.3		0.643	68.7	
extr	328.15	0.563	98.3	102 <sup>e</sup>	0.577	90.8	85 <sup>e</sup>	0.652	72.1	70 <sup>e</sup>
fit		0.580	90.8		0.610	87.1		0.676	72.2	
DTAC										
extr	278.15	0.373 <sup>c</sup>	26.0 <sup>c</sup>	26.66 <sup>d</sup>	0.401	23.3	23.78 <sup>d</sup>	0.509	11.0	10.92 <sup>d</sup>
fit		0.356	25.6		0.407	23.0		0.522	10.5	
extr	288.15	0.398 <sup>c</sup>	23.6 <sup>c</sup>	24.83 <sup>d</sup>	0.398	20.5	20.94 <sup>d</sup>	0.513	9.38	9.13 <sup>d</sup>
fit		0.386	22.8		0.376	20.9		0.506	9.11	
extr	298.15	0.424 <sup>c</sup>	22.2 <sup>c</sup>	22.60 <sup>d</sup>	0.458	19.5	19.35 <sup>d</sup>	0.524	8.83	8.37 <sup>d</sup>
fit		0.409	21.5		0.476	18.9		0.523	8.55	
extr	308.15	0.451 <sup>c</sup>	21.9 <sup>c</sup>	21.80 <sup>d</sup>	0.470	19.5	18.53 <sup>d</sup>	0.538	8.89	8.62 <sup>d</sup>
fit		0.436	21.2		0.467	19.3		0.538	8.56	
extr	318.15	0.486 <sup>c</sup>	22.7 <sup>c</sup>	23.01 <sup>d</sup>	0.497	20.2	19.78 <sup>d</sup>	0.584	9.47	8.75 <sup>d</sup>
fit		0.471	21.7		0.495	20.0		0.553	8.57	
extr	328.15	0.486	24.5		0.521	21.5		0.613	9.75	
fit		0.498	23.8		0.539	21.1		0.587	8.77	
TTAC										
extr	278.15	0.328 <sup>c</sup>	6.45 <sup>c</sup>	6.2 <sup>e</sup>	0.355	3.70	3.58 <sup>e</sup>	0.338	0.92	0.85 <sup>e</sup>
fit		0.316	6.39		0.357	3.67		0.380	0.85 <sup>f</sup>	
extr	288.15	0.352 <sup>c</sup>	5.80 <sup>c</sup>	5.4 <sup>e</sup>	0.396	3.31	3.14 <sup>e</sup>	0.529	0.85	0.78 <sup>e</sup>
fit		0.336	5.79		0.402	3.31		0.495	0.78 <sup>f</sup>	
extr	298.15	0.377 <sup>c</sup>	5.63 <sup>c</sup>	4.9 <sup>e</sup>	0.391	3.12	2.91 <sup>e</sup>	0.510	0.82	0.80 <sup>e</sup>
fit		0.364	5.54		0.397	3.14		0.325	0.80 <sup>f</sup>	
extr	308.15	0.410 <sup>c</sup>	5.66 <sup>c</sup>	5.5 <sup>e</sup>	0.419	3.12	3.15 <sup>e</sup>	0.490	0.89	0.61 <sup>e</sup>
fit		0.396	5.56		0.443	3.15		0.516	0.61 <sup>f</sup>	
extr	318.15	0.443 <sup>c</sup>	5.96 <sup>c</sup>	5.6 <sup>e</sup>	0.456	3.38	3.23 <sup>e</sup>	0.503	0.77	0.65 <sup>e</sup>
fit		0.430	5.80		0.470	3.45		0.422	0.65 <sup>f</sup>	
extr	328.15	0.429	6.87	6.4 <sup>e</sup>	0.455	3.68	3.71 <sup>e</sup>	0.483	0.77	0.76 <sup>e</sup>
fit		0.483	7.16		0.470	3.78		0.413	0.76 <sup>f</sup>	

<sup>a</sup>Units: T, K; cmc, mmol kg<sup>-1</sup>; <sup>b</sup>uncertainties: cmc  $\pm$  1 %;  $\beta$   $\pm$  5%; <sup>c</sup>ref.<sup>14</sup>; <sup>d</sup>ref.<sup>1</sup>; <sup>e</sup>ref.<sup>2</sup>; <sup>f</sup>the cmc value from ITC was fixed during the fitting procedure (see the explanation in text).



**Figure 2.** The temperature dependent electrical conductivity versus molality plots for DTAC in a) water, b) 0.01 M NaCl, and c) 0.1 M NaCl. The solid lines represent fits according to the Eq. (6).

hydrophobicity of the amphiphile. The values of  $T^* = (310 \pm 2)$ ,  $(306 \pm 1)$ , and  $(303 \pm 3)$  K were determined through fitting of the second-order polynomial to the  $\ln X_{\text{cmc}} = f(T)$  plot for DeTAC, DTAC, and TTAC, respectively.<sup>14,25</sup> The

corresponding coefficients of fitted polynomials are given in Table S1 in the Supporting Informations.

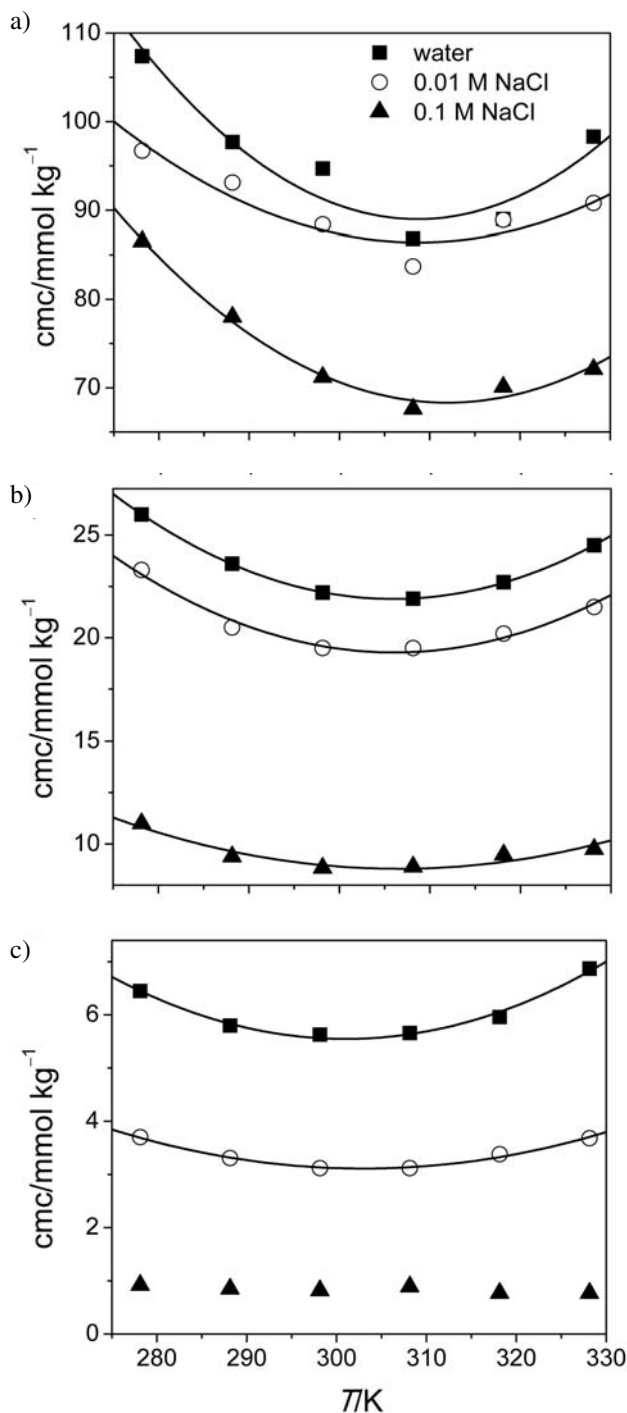
In general,  $\beta$  slightly lowers with increasing alkyl chain of the cationic TAC surfactants, what has been also observed for alkyltrimethylammonium bromides (TAB)<sup>26,27</sup> and sodium perfluoroalkyl carboxylates.<sup>28</sup> The formation of denser micelles with higher aggregation number is assumed for surfactants with longer alkyl chain what results in the increased charge density of the micelle surface and causes the increased condensation of counterions. Consequently there are less repulsive electrostatic forces between the cationic head groups, what lowers the cmc also. This is indeed consistent with the lowest cmc observed for TTAC and our assumption of denser aggregate formation in case of longer alkyl chain surfactants published recently.<sup>2</sup> There are also other articles reporting higher  $n$  of the micelles formed by alkyltrimethylammonium monomers with longer alkyl chain.<sup>26,29–31</sup>

Further,  $\beta$  increases slightly with increasing temperature in all the investigated systems. Similar trend has been observed for SDS,<sup>11,15,20</sup> sodium perfluoroalkyl carboxylates,<sup>28</sup> surface active ionic liquids,<sup>10</sup> and alkyltrimethylammonium surfactants<sup>8,14,32–36</sup> in water and salt solutions. Presumably, micelles with lower  $n$  are formed at higher temperature<sup>29,32,34,37</sup> what leads to lower charge density of the micelle surface and consequent higher  $\beta$  values.

In fact, no exact trend could be observed for  $\beta$  dependence on salt concentration for DeTAC, nevertheless slightly higher degree of micelle ionization can be noticed for DTAC and TTAC in 0.1 M NaCl in comparison to pure water and lower salt concentration. Similar has been already found for SDS<sup>3,15,20</sup> and CTAB<sup>6</sup> in aqueous salt solutions, but some contradictory data are reported in the literature for alkyltrimethylammonium surfactants.<sup>14,34,38</sup> As it has been concluded for SDS and CTAB, increase or decrease in  $\beta$  obviously depends on the type and concentration range of electrolyte added, what can explain the differences between literature data.<sup>3</sup> The increased  $\beta$  at higher salt concentration for DTAC and TTAC could be assigned to the increased charge screening in a diffuse layer around the micelles at higher ionic strength.<sup>3,20</sup>

## 4. Conclusions

The micellization behaviour of alkyltrimethylammonium chlorides, DeTAC, DTAC, and TTAC, in water, 0.01 M, and 0.1 M NaCl was investigated by electrical conductivity measurements in the temperature range between 278.15 and 328.15 K. From the experimental data the critical micelle concentration, cmc, and the degree of micelle ionization,  $\beta$ , were determined for all the investigated systems. Evidently, cmc is decreasing with increasing alkyl chain length of TAC and increasing concentration of added salt for all the studied surfactants, whereas



**Figure 3.** The cmc dependence on temperature for a) DeTAC, b) DTAC, and c) TTAC in water, 0.01 M NaCl, and 0.1 M NaCl. The solid lines represent polynomial fits through the experimental points for each investigated system.

the temperature dependence of cmc shows the typical U-shaped form with a minimum around  $(306 \pm 3)$  K.  $\beta$  is decreasing with alkyl chain length also, it increases with increasing temperature, but no distinct influence of NaCl addition on  $\beta$  could be observed actually.

The latter dependence turned out to be quite unpredictable, which is obviously a direct consequence of interplay between the micelle surface charge density and the screening of repulsive forces by excess counterions in the solution. Therefore, it can be misleading to predict the trend of  $\beta$  values prior to any further calculations relating to  $\beta$ . But still, our presumption in ref.<sup>14</sup> seems to be suitable, since  $\Delta_M G^0$  is only slightly dependent on  $\beta$ . However, the present work contributes essentially to understanding of ionic surfactant micellization process.

Namely, the electrical conductivity is an overall quantity therefore the contributions of all possible conducting species in solution have to be taken into account. In order to determine the size and the effective charge of micelles in water without salt addition, the applied strategy was successful to interpret the electrical conductivity measurements by help of the mean spherical approximation (MSA).<sup>36</sup> The contribution of micelles to the solution's conductivity in presence of added salt is indeed hidden by the overwhelming contribution of smaller and faster ions, making the previous procedure inaccurate. Therefore an adequate description of the conductivity of micelles in salt solutions still remains a challenge for our future work.

## 5. Acknowledgement

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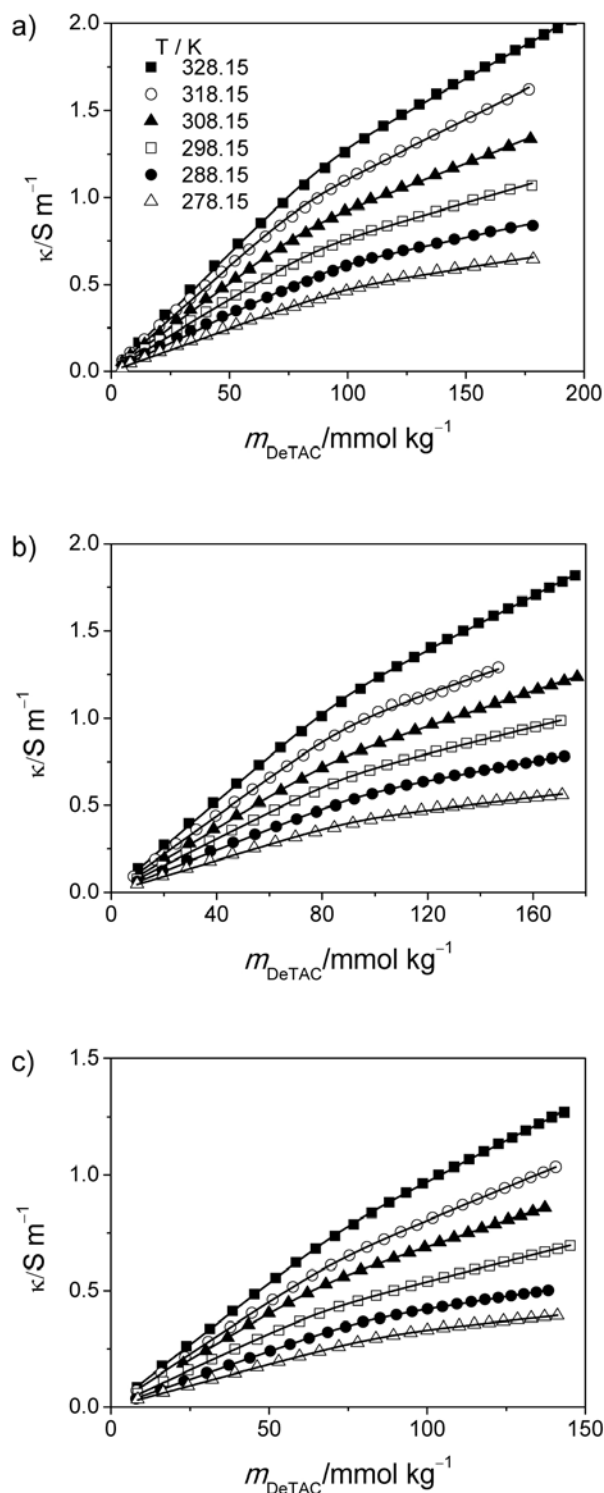
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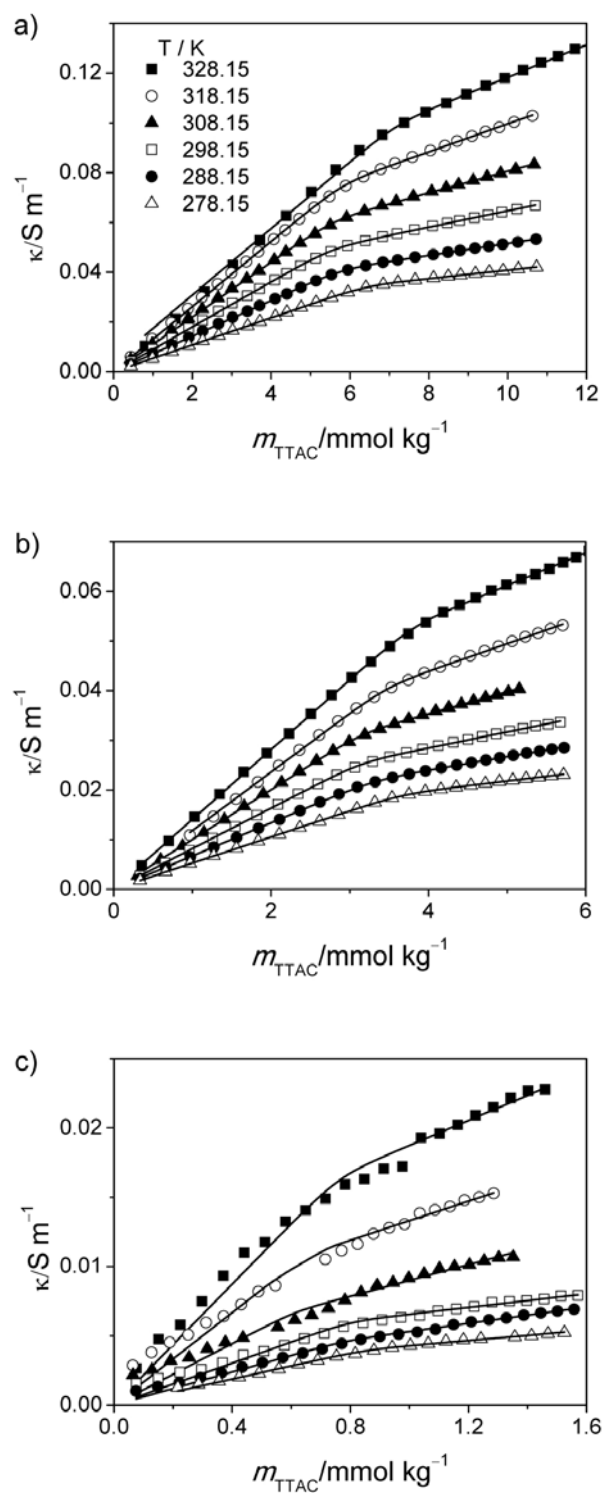
## Povzetek

Iz eksperimentalnih podatkov električne prevodnosti raztopin deciltrimetilamonijevega klorida (DeTAC), dodeciltrimetilamonijevega klorida (DTAC) in tetradeciltrimetilamonijevega klorida (TTAC) v vodi, 0.01 M in 0.1 M NaCl v temperaturnem območju med 278.15 in 328.15 K smo določili kritično micelno koncentracijo, cmc, in stopnjo ionizacije micel,  $\beta$ . Izkazalo se je, da se cmc zmanjšuje tako z daljšanjem alkilne verige surfaktanta kot s koncentracijo dodane soli. V vseh primerih cmc z naraščajočo temperaturo najprej pada, doseže minimum pri  $(306 \pm 3)$  K in potem narašča. Medtem ko  $\beta$  v vseh primerih pada s povečevanjem dolžine alkilne verige surfaktanta in narašča z višanjem temperature, nismo opazili sistematične odvisnosti  $\beta$  od koncentracije NaCl, kar kaže na kompleksnost vpliva elektrolita na proces micelizacije.

## Supporting information



**Figure S1:** The temperature dependent electrical conductivity versus molality plots for DeTAC in a) water, b) 0.01 M NaCl, and c) 0.1 M NaCl. The solid lines represent fits according to the Eq. (6).



**Figure S2:** The temperature dependent electrical conductivity versus molality plots for TTAC in a) water, b) 0.01 M NaCl, and c) 0.1 M NaCl. The solid lines represent fits according to the Eq. (6).



**Table S1:** The coefficients of fitted polynomials  $\ln X_{\text{cmc}} = A + BT + CT^2$  for DeTAC, DTAC, and TTAC in water, 0.01 M NaCl, and 0.1 M NaCl.<sup>a</sup>

	DeTAC			DTAC			TTAC		
	A	B	C	A	B	C	A	B	C
Water	13.85	-0.131	$2.13 \cdot 10^{-4}$	13.07	-0.137	$2.24 \cdot 10^{-4}$	16.16	-0.168	$2.80 \cdot 10^{-4}$
0.01 M NaCl	6.162	-0.082	$1.32 \cdot 10^{-4}$	13.64	-0.141	$2.31 \cdot 10^{-4}$	15.43	-0.166	$2.75 \cdot 10^{-4}$
0.1 M NaCl	13.57	-0.130	$2.08 \cdot 10^{-4}$	15.32	-0.157	$2.56 \cdot 10^{-4}$			

<sup>a</sup> Units:  $T/K$ ;  $B/K^{-1}$ ;  $C/K^{-2}$