A New Method for Simultaneous Estimation of Micellization Parameters from Conductometric Data

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Abstract: A simple method for determination of the counterion binding parameter (α) and aggregation number (N) from conductivity data is proposed. The method is based on fitting the values of the first derivative of conductivity (κ) versus total surfactant concentration (c_t) function according to the equation derived from the mass action model (MAM) by using different conductivity models. Sodium dodecylsulphate (SDS) and dodecyltrimethylammonium bromide (DTAB) were chosen for validation of the proposed method. It was shown that the method gives a fairly accurate values for micellisation parameters of SDS ($N=51$–64, $\alpha=0.74$–0.75) and DTAB ($N=56$–62, $\alpha=0.77$–0.79), both in good agreement with the literature data. In addition, application of the proposed method does not require the value of the critical micelle concentration (cmc).

Keywords: aggregation number · analytical methods · conductivity · mass action model · micelles

Introduction

The mass action model (MAM) and the phase separation model (PSM) have long been used for the theoretical treatment of the process of micellisation.[1–11] In order to describe the process of micelle formation in solution with ionic surfactants by using these models, three parameters should be determined: critical micelle concentration (cmc), aggregation number (N) and counterion binding parameter (α).

Although a number of cmc definitions[8,12–14] have been proposed, the one commonly used is from Phillips,[8] who defined cmc as the total concentration of surfactant (c_t) corresponding to the maximum change in the gradient of the physical property (Φ) versus c_t function given in Equation (1).

$$\left(\frac{d^3\Phi}{dc_t^3}\right)_{c_t=c_{mic}} = 0 \qquad (1)$$

According to this definition, cmc is commonly determined from the intercept of two straight lines fitting either Φ versus c_t or Φ versus $(c_t)^{1/2}$ functions[15] in the concentration ranges below and above the cmc. A more accurate method for cmc determination, based on the first[16] or the second derivative of Φ versus c_t function,[17,18] has been proposed. Although, in most cases the above-mentioned methods give fairly accurate values of cmc, there is still the problem of precise determination of cmc in cases of small micelles, in which the cmc is more difficult to determine experimentally. Additionally, different experimental techniques often give quite different cmc values.

In order to determine N and/or α one should be able to calculate the species inventories for all total concentrations of surfactant (c_t). Since MAM gives only implicit dependence of species concentrations, it is common practice to use the PSM approximation of the constant monomer concentration (c_x) above the cmc; this makes the calculation of species inventories straightforward. At this point it has to be stressed (although long known from theory[10,11] and potenciometric measurements[19–27], yet sometimes overlooked) that the monomer concentration above the cmc is all but constant, increasing even after the cmc until it reaches the maximum, and then starts to decrease. It can be shown[25] that c_x for SDS drops to half of its maximum value at $c_t \approx 10 \times$ cmc, raising an interesting question of reliability of N and/or α literature values determined by using the PSM approximation (regardless of experimental technique used for the determination).

Static light scattering (SLS), fluorescence quenching and small angle neutron scattering (SANS) are widely used for N determination.[28–31].

Conductivity,[14,15,32–46] potentiometric,[19,20,22,27,47–50] electrophoretic mobility[51] and NMR[52–54] measurements are commonly used for determination of α. In most cases, N or α

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are determined separately. An exception is the SANS measurement, which can be used for simultaneous determination of both parameters[30,55]. In addition, attempts for simultaneous determination of α and N from the conductivity data have been made by Shanks and Franses.[37] The method of Shanks and Franses (S–F method) is also interesting, because it is based on the mass action model for micellisation of the ionic surfactant, so it is expected that it can provide more reliable values of micellisation parameters. These authors showed that α (0.72 for SDS) could be determined in accordance with the literature values, whereas the N values demonstrated some discrepancy (39–56 for SDS).

Simultaneous determination of cmc, α and N by fitting the κ versus c_t function by using the S–F method is accompanied by some degree of mathematical complexity arising from calculating the species inventories for a given c_t. In addition, the authors reported that optimised values of N were closely related to the initial guess values set before the optimisation procedure began.[37]

On the other hand, some authors tried to use the first derivative of conductivity with respect to the c_t function ($d\kappa/dc_t$)[33,34,36,40,41,56,57] for determination of N and/or α. With the exception of the Moroi et al.[36] and part of the Nishikido method[41], all the above-mentioned methods are based on the phase separation model, which can be regarded as their drawback, especially when taking into account the fact that the $d\kappa/dc_t$ function can be easily used in accordance with MAM.

Therefore, it seems worth it to develop a simple but accurate method for the determination of α and N, based on fitting the $d\kappa/dc_t$ values with the equation derived from the mass action model. It will be shown here that the exact numerical value of cmc is not required for the application of the method proposed, which can be helpful whenever cmc is difficult to determine.

For validation of the proposed method, sodium dodecylsulphate and dodecyltrimethylammonium bromide was chosen, for which the generally adopted values of micellisation parameters (see legends of Table 1 and Table 3 later) are $\alpha_{SDS}=0.72$–0.77, $N_{SDS}\approx 64$,[2,36,37] $\alpha_{DTAB}=0.75$–0.77 and $N_{DTAB}\approx 57$,[17] although considerable discrepancy can be found when comparing different techniques, especially in the case of aggregation numbers[37].

Theory: The conductivity of the ionic surfactant solution is given by Equation (2), in which λ is the molar conductivity of the corresponding ionic species and X, Y, and Mic represent the surfactant ion, counterion, and micelle, respectively

$$\kappa = \lambda_X c_X + \lambda c_Y + \lambda_{Mic} c_{Mic} \tag{2}$$

According to MAM, concentrations of the ionic species are defined as Equations (3a)–(3c), in which ξ_c is the extent of the reaction divided by the total volume (V) of the solution ($\xi_c=\xi/V$).

$$c_{Mic} = \frac{1}{N}\xi_c \tag{3a}$$

$$c_X = c_t - \xi_c \tag{3b}$$

$$c_Y = c_t - \alpha\xi_c \tag{3c}$$

Combining Equations (3a–c) and Equation (2) leads to Equation (4):

$$\kappa = \lambda_s c_t - \xi_c\left(\lambda_s - (1-\alpha)\lambda_Y - \frac{\lambda_{Mic}}{N}\right) \qquad \lambda_s = \lambda_X + \lambda_Y \tag{4}$$

Taking into account the Evans equation[45] for molar conductivity of the spherical micelle [Eq. (5)]

$$\lambda_{Mic} = \lambda_X N^{5/3}(1-\alpha)^2 \tag{5}$$

and by combining Equations (4) and (5), we get Equation (6):

$$\kappa = \lambda_s c_t - \xi_c\left(\lambda_s\left(1 - N^{2/3}(1-\alpha)^2\right) - \lambda_Y\left((1-\alpha) - N^{2/3}(1-\alpha)^2\right)\right) \tag{6}$$

The term Q is defined in Equation (7).

$$Q = \lambda_s\left(1 - N^{2/3}(1-\alpha)^2\right) - \lambda_Y\left((1-\alpha) - N^{2/3}(1-\alpha)^2\right) \tag{7}$$

Combining Equations (6) and (7), we now get Equation (8).

$$\kappa = \lambda_s c_t - \xi_c Q \tag{8}$$

Although λ_s and Q are functions of c_t, in the first approximation one can consider them as constants and accordingly we get Equation (9).

$$\left(\frac{d\kappa}{dc_t}\right) = \lambda_s - Q\left(\frac{d\xi_c}{dc_t}\right) \tag{9}$$

According to MAM, the first derivative of ξ_c with respect to c_t is Equation (10), in which the constants A, B, D and E are defined in Equations (11a)–(11d).

$$\left(\frac{d\xi_c}{dc_t}\right) = \frac{Ac_t\xi_c - B\xi_c^2}{c_t^2 - D\xi_c^2 + Ec_t\xi_c} \tag{10}$$

$$A = N(1+\alpha) \tag{11a}$$

$$B = 2N\alpha \tag{11b}$$

$$D = N\alpha(1+\alpha-1/N) \tag{11c}$$

$$E = N(1+\alpha^2-(1+\alpha)/N) \tag{11d}$$

After introducing Equation (10) into Equation (9) we obtain Equation (12).

$$\left(\frac{d\kappa}{dc_t}\right) = \lambda_s - Q\frac{Ac_t\xi_c - B\xi_c^2}{c_t^2 - D\xi_c^2 + Ec_t\xi_c} \tag{12}.$$

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From Equation (8) it is evident we can formulate Equation (13).

$$\xi_c = \frac{\lambda_s c_t - \kappa}{Q} \tag{13}$$

Combining Equations (13) and (12), finally leads to Equation (14).

$$\left(\frac{d\kappa}{dc_t}\right) = \lambda_s - \frac{Ac_t(\lambda_s c_t - \kappa) - B\frac{(\lambda_s c_t - \kappa)^2}{Q}}{c_t^2 - D\left(\frac{\lambda_s c_t - \kappa}{Q}\right)^2 + Ec_t\frac{(\lambda_s c_t - \kappa)}{Q}} \tag{14}$$

In this paper, the values of $d\kappa/dc_t$ were calculated from experimental κ versus c_t values by using the local second-order polynomial regression. The procedure is as follows: through each of the three adjacent experimental points (first, through points 1, 2 and 3; then through points 2, 3 and 4; and so on) the quadratic function was fitted. Each obtained quadratic function ($\kappa = ac_t^2 + bc_t + c$) was derivatived with respect to c_t and the value of $d\kappa/dc_t$ was calculated for each middle point (for point 2 by using first quadratic function, for point 3 by using second quadratic function, and so on). Once the values of $d\kappa/dc_t$ were calculated from the conductometric data, they can be considered as the "measured values of the first derivative".

If α, N, λ_s and λ_Y are taken to be the fitting parameters, they can be optimised by using the least-squares method based on the difference between the "measured values of the first derivative" and $d\kappa/dc_t$ values calculated by using Equation (14). Nonlinear regression analysis was performed by using the OriginPro 7.0 program.

Conductivity models description: Three conductivity models were tested for α and N determinations:

Model A: The fitting parameters for this model were α and N. For λ_s and λ_Y, fixed values of S_1 (slope of the straight line fitting κ versus c_t function in the concentration range below cmc) and $\lambda_Y = \lambda_Y^\infty$ were used, respectively. Accordingly, at 25 °C, the values of $\lambda_Y = \lambda_{Na^+} = 50.1\ S\,cm^2\,mol^{-1}$ and $\lambda_Y = \lambda_{Br^-} = 78.1\ S\,cm^2\,mol^{-1}$ were used for SDS and DTAB, respectively.

Model B: The fitting parameters for this model were α, N and λ_s. The values of λ_Y were the same as in model A. In addition, λ_s was allowed to vary (in order to restrict the optimised λ values to a physically most reasonable range of values) in the range from 63 to 68 $S\,cm^2\,mol^{-1}$ for SDS and from 83 to 91.5 $S\,cm^2\,mol^{-1}$ for DTAB. These λ_s values corresponded to the first and last points of the concentration range III (see below), and were calculated by using the Kohlrausch equation. The Kohlrausch equation parameters were calculated from the experimental conductivity data in the concentration range below cmc

Model C: The fitting parameters for this model were α, N, λ_s and λ_Y. The values of λ_s were allowed to vary in the same range as in model B. Furthermore, λ_Y values were varied from 43 to 46.3 S $cm^2\,mol^{-1}$ for Na^+ (SDS) and from 68 to 72.2 $S\,cm^2\,mol^{-1}$ for Br^- (DTAB). These λ_Y values were calculated according to the theoretical Debye-Hückel-Onsager equation for the concentration range III.

Conductivity models were tested in three concentration ranges: from about cmc to 1.5 × cmc (I), cmc to 2 × cmc (II) and cmc to 2.5 × cmc (III). The exact concentration ranges are listed in the legends of Tables 2 and 4 below.

Results and discussion

SDS solution: Two SDS titrations were performed. Figure 1 shows a curve of the conductivity versus total SDS concentration for the second titration.

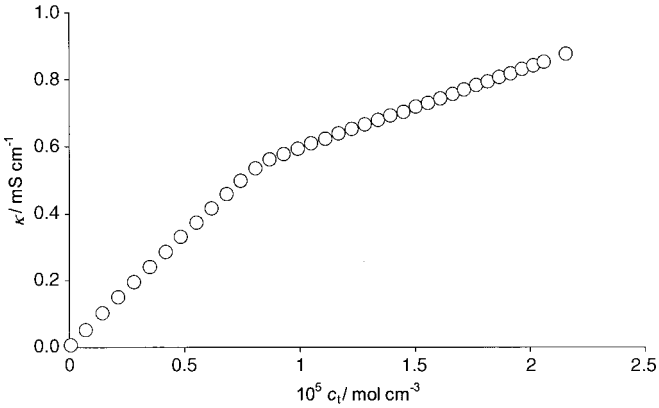

Figure 1. Conductivity of the SDS solution at 25 °C (titration 2).

Two slopes, S_1 (for $c_t < cmc$) and S_2 (for $c_t > cmc$), were calculated for each titration and used for the determination of α using the Evans method[45] with $N = 64$.[2,36] For both titrations, α was calculated to be 0.77. In addition, parameters of the Kohlrausch equation were calculated. The calculated parameters as well as their comparison with literature data are given in Table 1.

Since all calculated parameters from Table 1 are in accord with literature values, one can conclude that both titrations

Table 1. Parameters calculated from the conductivity versus concentration data for the SDS solutions at 25 °C. Comparison with the literature data.

	c_{mic} [$mmol\,dm^{-3}$]	α	S_1 [$S\,cm^2\,mol^{-1}$]	S_2 [$S\,cm^2\,mol^{-1}$]	λ_X^∞ [$S\,cm^2\,mol^{-1}$]	K_H [$S\,cm^2\,mol^{-1}/mol\,dm^{-3})^{1/2}$]
titration 1	8.11	0.77	65.917	24.78	23.12	65.24
titration 2	8.33	0.77	65.368	24.23	21.68	57.87
literature	(8.1–8.4)[a]	(0.72–0.77)[b]	(65.5–66.5)[c]	(24.1–26)[c]	(21.6–23.1)[d]	–

[a] References [14,17,32–38,40–44,58,59]. [b] References [27,37,59,60]. [c] References [36,44]. [d] References [37,42,44].

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are suitable for the application of the new method for a simultaneous determination of N and α.

Comparison of the $d\kappa/dc_t$ values for both titrations is shown in Figure 2 and optimised parameters from the fitting procedure are given in Table 2. An example of experimental data fit is shown in Figure 3.

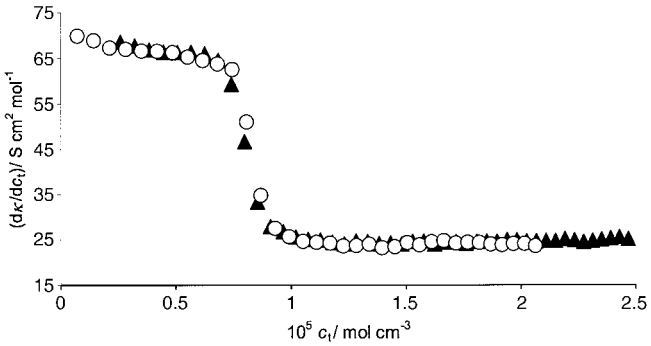

Figure 2. Comparison of the first derivative of the conductivity with respect to the total SDS concentration function between titration 1 (open circles) and titration 2 (full triangles) at 25 °C.

DTAB solution: Again two titrations were performed for DTAB. Figure 4 shows the conductivity versus total DTAB concentration curve for the first titration. By using the same procedure as described for SDS, the data, displayed in Table 3, were calculated for the DTAB solution at 25 °C.

Comparison of the values of both titrations is shown in Figure 5, and optimised parameters from the fitting procedure are given in Table 4. An example of experimental data fit is shown in Figure 6.

Considering Tables 2 and 4, the following conclusion can be drawn. The determined (optimal) values of α range from 0.730 to 0.762 (SDS) and from 0.759 to 0.802 (DTAB), depending on the conductivity model used and on the titration

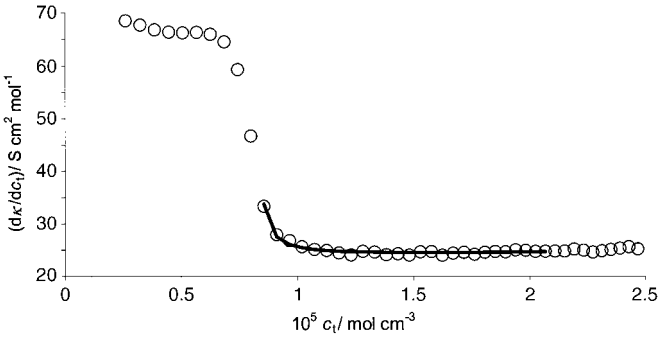

Figure 3. An example of the data fit for SDS solution at 25 °C (titration 2, model C, concentration region III). Open circles represent the values calculated from the experimental data; the line represents the fitted values.

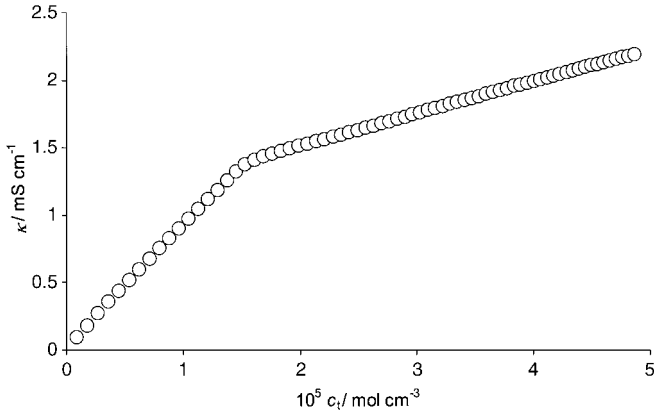

Figure 4. Conductivity of the DTAB solution at 25 °C (titration 1).

itself, but they are constant when compared over different concentration ranges. In general, conductivity model C gives somewhat higher α values than models A and B, but, as will be explained later, such observation should be taken with

Table 2. Optimised parameters for the micellisation of SDS at 25 °C—a comparison between different conductivity models used.[a]

Model	Titration	Concentration ranges[b]	$\alpha \pm \sigma$	$N \pm \sigma$	$\lambda_s \pm \sigma$ [S cm² mol⁻¹]	$\lambda_{Na^+} \pm \sigma$ [S cm² mol⁻¹]	ss/ν[c]
A	1	I	0.754 ± 0.004	66 ± 5	**65.9**	**50.1**	0.238
		II	0.753 ± 0.003	65 ± 3	**65.9**	**50.1**	0.160
		III	0.753 ± 0.002	65 ± 3	**65.9**	**50.1**	0.111
	2	I	0.751 ± 0.002	62 ± 2	**65.4**	**50.1**	0.098
		II	0.751 ± 0.003	63 ± 3	**65.4**	**50.1**	0.204
		III	0.751 ± 0.003	63 ± 3	**65.4**	**50.1**	0.158
B	1	I	0.730 ± 0.007	40 ± 6	66.7 ± 0.3	**50.1**	0.073
		II	0.732 ± 0.005	42 ± 5	66.6 ± 0.3	**50.1**	0.082
		III	0.736 ± 0.005	46 ± 5	66.5 ± 0.2	**50.1**	0.077
	2	I	0.736 ± 0.004	46 ± 4	65.7 ± 0.1	**50.1**	0.028
		II	0.745 ± 0.009	55 ± 10	65.5 ± 0.3	**50.1**	0.210
		III	0.746 ± 0.008	57 ± 9	65.5 ± 0.2	**50.1**	0.161
C	1	I	0.750 ± 0.570	41 ± 10	66.6 ± 0.8	45 ± 273	0.094
		II	0.746 ± 0.131	42 ± 8	66.6 ± 0.5	46 ± 37	0.089
		III	0.747 ± 0.059	44 ± 7	66.3 ± 0.4	46 ± 16	0.088
	2	I	0.762 ± 0.278	46 ± 5	65.7 ± 0.3	43 ± 94	0.034
		II	0.761 ± 0.197	56 ± 16	65.5 ± 0.4	46 ± 52	0.237
		III	0.761 ± 0.085	57 ± 12	65.5 ± 0.3	46 ± 22	0.175

[a] Bold numerals refer to the values that were kept constant during the fitting. [b] Concentration region in mmol dm^{-3}: titration 1: I: 8.6–12.3, II: 8.6–16.23, III: 8.6–20.67; titration 2: I: 8.7–12.8, II: 8.7–16.63, III: 8.7–20.6. [c] ss is the sum of squares and $\nu = Nd - Np$, where Nd is number of data points and Np is number of parameters fitted.

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Table 3. Parameters calculated from the conductivity versus concentration data for the DTAB solutions at 25 °C. Comparison with the literature data.

	c_{mic} [mmol dm^{-3}]	α	S_1 [S cm^2 mol^{-1}]	S_2 [S cm^2 mol^{-1}]	λ_X^∞ [S cm^2 mol^{-1}]	K_H [S cm^2 mol^{-1}/mol dm^{-3})$^{1/2}$]
titration 1	15.24	0.79[a]	89.995	24.093	24.75	98.63
titration 2	15.18	0.80[a]	90.335	22.439	27.28	114.37
literature	(15.0–15.6)[b]	(0.75–0.77)[c]	–	–	$\approx$22.3[d]	-

[a] Calculated by using Evans method with $N=57$.[17] [b] References [17,18,61]. [c] References [17,47,50][d] Reference [17].

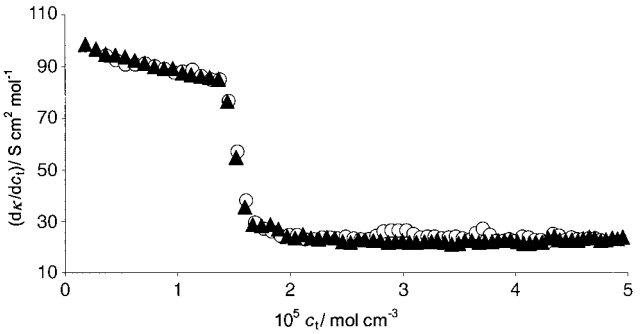

Figure 5. Comparison of the first derivative of the conductivity with respect to total DTAB concentration function between titration 1 (open circles) and titration 2 (full triangles) at 25 °C.

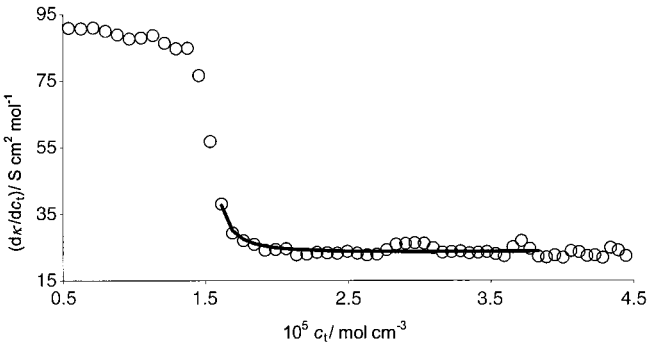

Figure 6. An example of the data fit for DTAB solution at 25 °C (titration 1, model C, concentration region III). Open circles represent the values calculated from the experimental data, and the line represents the fitted values.

some reservations. Additionally, we notice strong dependence of optimal α values on N and λ_s values.

By using the herein proposed new method, aggregation numbers were determined in ranges from 40 to 66 (SDS) and from 48 to 66 (DTAB). Similarly to α, aggregation numbers are dependent on the conductivity model used and titration itself but are constant over different surfactant concentration. When discussing different conductivity models used, we note that model A gives the most consistent values of α and N (comparing same titration through different concentration ranges) with the smallest standard deviation of optimised values. Nevertheless, the conductivity model A is based on a few quite poor approximations referring to λ values and their determinations. First of all, it is well known that λ_s and λ_Y should decrease with the ionic strength of the solution in accordance with the Kohlrausch law, and therefore λ_s and λ_Y have to be smaller than λ_s^∞ and λ_Y^∞. Secondly, the assumption often used in literature that S_1 equals λ_s^∞ in fact represents quite a poor approximation, since λ_s^∞ should be determined from the Kohlrausch equation. Additionally, S_1 is strongly dependent on the concentration range from which it is determined and this fact makes S_1 highly unreliable. To avoid problems relating to the values of S_1 and λ_Y^∞

Table 4. Optimised parameters for the micellisation of DTAB at 25 °C; a comparison between different conductivity models used.[a]

Model	Titration	Concentration ranges[b]	$\alpha \pm \sigma$	$N \pm \sigma$	$\lambda_s \pm \sigma$ [S cm^2 mol^{-1}]	$\lambda_{Na^+} \pm \sigma$ [S cm^2 mol^{-1}]	ss/ν[c]
A	1	I	0.760 ± 0.001	48 ± 2	**90.0**	**78.1**	0.297
		II	0.759 ± 0.002	51 ± 2	**90.0**	**78.1**	0.319
		III	0.759 ± 0.002	51 ± 2	**90.0**	**78.1**	0.340
	2	I	0.776 ± 0.002	66 ± 4	**90.3**	**78.1**	0.327
		II	0.776 ± 0.002	64 ± 3	**90.3**	**78.1**	0.274
		III	0.776 ± 0.002	64 ± 3	**90.3**	**78.1**	0.351
B	1	I	0.761 ± 0.003	55 ± 9	89.7 ± 0.4	**78.1**	0.313
		II	0.763 ± 0.003	62 ± 8	89.5 ± 0.3	**78.1**	0.280
		III	0.761 ± 0.003	55 ± 9	89.7 ± 0.4	**78.1**	0.313
	2	I	0.776 ± 0.006	66 ± 19	90.3 ± 0.8	**78.1**	0.392
		II	0.773 ± 0.004	55 ± 10	90.8 ± 0.6	**78.1**	0.277
		III	0.774 ± 0.004	57 ± 10	90.6 ± 0.6	**78.1**	0.357
C	1	I	0.793 ± 0.649	55 ± 11	89.7 ± 0.9	68 ± 274	0.362
		II	0.785 ± 0.143	63 ± 11	89.4 ± 0.5	72 ± 45	0.308
		III	0.790 ± 0.072	63 ± 11	89.4 ± 0.4	71 ± 24	0.329
	2	I	0.796 ± 0.765	66 ± 24	90.3 ± 1.4	72 ± 268	0.498
		II	0.802 ± 0.166	56 ± 14	90.7 ± 0.9	68 ± 75	0.295
		III	0.797 ± 0.073	60 ± 15	90.5 ± 0.8	71 ± 27	0.369

[a] Bold numerals refer to the values that were kept constant during the fitting. [b] Concentration region in mmol dm^{-3}: titration 1: I: 16.1–22.8; II: 16.1–31.6; III: 16.1–38.3; titration 2: I: 15.9–23.2; II: 15.9–29.3; III: 15.9–37.9. [c] ss is sum of squares and $\nu = Nd - Np$, where Nd is number of data points and Np is number of parameters fitted.

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and to make the conductivity model more realistic, models B and C were introduced in which contained λ_s and λ_s and λ_Y, respectively, as additional fitting parameters. It is interesting to note that N values optimised from models B and C are much more similar (when comparing same titration and same concentration range) than is case when comparing model A with B or C. In fact, with exception of the first DTAB1 titration, concentration range III (Table 4), the difference of fitted N values between models B and C never exceeds 2; this can be taken as a proof of the reliability of the said N values. Similarly, we note that models B and C give almost identical λ_s values, which usually, through the limits imposed by the values of their standard error, embraced the constant λ_s values used in model A. Again, it is important to note the strong dependence of N on the λ_s values; this can be clearly seen in Table 2 (compare lines A1I with B1I) in which small changes (about 3%) between fixed (model A) and fitted (model B) λ_s value can produce significant changes (from 66 to 40) in the N value. Therefore, the correlation between fitted parameters is worth of discussing in detail.

Table 5 indictes a strong correlation between all fitted parameters, with positive correlation between the N,α and λ_s,λ_y pairs of parameters and with negative correlation between N,λ_s; N,λ_y; α,λ_s and α,λ_y pairs of parameters. By using the data from Table 5, we can more clearly explain the change in optimal values of fitting parameters. Taking, for example, SDS titration 1 and comparing model A with B, we can see that increase of optimised λ_s value (model B) relative to fixed (model A) λ_s value decrease N and α values (negative correlation coefficient) and taking into consideration the fact that difference between two λ values (0.8–0.6 $S\,cm^2\,mol^{-1}$) is the greatest in this case (compared to all other titration, Table 5), we can easily explain the fact that greatest difference between optimised N and α values occurred in this particular titration. In all other titrations the fixed $\lambda_s = S_1$ values fall into the region imposed by the standard error of the fitted λ_s values and consequently difference of N and α between models A and B decrease. In the case when optimised λ_s equals the fixed S_1 value (Table 4 compare lines A2I with B2I) the N and α values optimised with both models are also equal. Taking into account the uncertainty of S_1 values, it is clear that model B should be preferred over model A, which in turn can provide reliable N only if (by chance) S_1 equals or is close to the optimal λ_s; in all other cases model A should be used only for a quick, rough estimation of micellar parameters. On the other hand, when model C was applied to the same data, optimised α values increase relative to those from model B (as expected, since pair α,λ_y shows strongly negative correlation and λ_y fitted is smaller than λ_y fixed). Interestingly, λ_s and N stay the same as in model B, which might suggested that λ_s is the most critical parameter for minimising the sum of squares, which one might consider as expected in the view of Equation (14). An evident problem accompanied with model C is the high values of standard deviation of optimised λ_y values (and partially of α values) for which the standard deviation is of same (or higher) order as the value of a parameter itself. Explanation for such behaviour can be found in number of data points usually 8 for concentration range I and about 16 for concentration range II, which seem to be too small for optimising the λ_y. Only when model C was applied to concentration range III (usual number of data points was about 26) did the standard deviation of λ_y drop to more acceptable values. It seems that at least 40 or even more data points should be present for obtaining the λ_y with acceptable value of standard deviation. In contrast to λ_y (and in part α), the standard deviations of λ_s and N values optimised with model C do not show such discrepancy, although they are still somewhat greater than is case with models A and B. Models A and B give satisfactory values of standard deviations, which for α and λ_s usually amounts to less than 1% of optimised parameter value and to about 10% in case of aggregation numbers. Usually, the smallest standard deviations were observed in concentration range III. Taking into consideration the above discussion, we can presume that the most reliable values of α and N optimised by herein proposed method are those shown in Table 6.

Table 5. Correlation matrix for SDS, titration 2, conductivity model C and concentration range III.

	N	α	λ_s	λ_{Na+}
N	1	0.735	−0.976	−0.664
α		1	−0.752	−0.995
λ_s			1	0.686
λ_{Na+}				1

Table 6. Mean values (from two titrations) of the optimised micellisation parameters for the aqueous solution of SDS and DTAB at 25 °C. Comparison of values obtained using different conductivity models in concentration range III.

Model	SDS		DTAB	
	$\bar{\alpha}\pm\sigma$	$\bar{N}\pm\sigma$	$\bar{\alpha}\pm\sigma$	$\bar{N}\pm\sigma$
A	0.752 ± 0.002	64 ± 2	0.768 ± 0.001	58 ± 2
B	0.741 ± 0.002	52 ± 5	0.768 ± 0.003	56 ± 7
C	0.75 ± 0.05	51 ± 7	0.79 ± 0.05	62 ± 9

At this point, it is of interest to compare the herein proposed method with another MAM-based conductivity method for simultaneous determination of micellar parameters introduced by Shanks and Franses (S–F method)[37]. These authors concluded that the most reliable α and N values optimised by their method for SDS was $\alpha = 0.72 \pm 0.01$ and $N = 42 \pm 9$. Comparing with literature and herein determined values for SDS one can conclude that herein proposed method gives (regardless of conductivity model used) aggregation numbers that are in better agreement with those determined by other experimental techniques than is case with S–F method. At the same time, both methods give similar α values both in good agreement with the literature data. Additionally, standard deviations of parameters optimised with the herein proposed method are lower than is case with S–F method. When discussing both methods one should note that in contrast to the S–F method

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(and, in fact, all PSM-based methods), the exact value of the cmc is not needed for the application of the herein proposed method. Taking into account the uncertainty of cmc determination, which contributes to the final values of determined parameters, one can consider the herein proposed method as more reliable. On the other hand, Shanks and Franses tried to use more realistic conductivity models (compared to the herein used models) based on the Debye–Hückel–Onsager (D–H–O) equation for dependence of molar conductivity on the ionic strength (I_c) of the solution. However, when using the D–H–O equation for the micellar solution, the problem of the contribution of micelles to I_c emerges. It is well known that the contribution of micelles to I_c differs from that of small ions and at present there is no clear, theoretically sound method for calculating it. An empirical method, based on the "shielding factor", was introduced by Burchfield and Wooley.[2] Although, as shown by Shanks and Franses, the value of the "shielding factor" is somewhat dependent on the values of N and α used for its calculation, it is interesting to note that the S–F method gives substantially lower "shielding factor" values than the Burchfield and Wooley method. According to the S–F method, the best fit of experimental data was achieved (depending on measurement) by using two conductivity models. The first model was one for which I_c equals the concentration of free surfactant ions (the model was denoted 3A by the authors) and in the second model (denoted 3B) it was supposed that "only monomeric ions and a fraction of micellar ions" (see ref. [37]) contribute to the ionic strength. One should note that the S–F conductivity model 3A is highly unrealistic, since it presumes that I_c increases until the maximum monomer concentration occurs, and then starts to decrease with an increase of the total surfactant concentration. As a consequence, after the maximum monomer concentration is reached, molar conductivities would start to increase (rather than decrease) with c_t. Such behaviour is contrary to the Kohlrausch law and difficult to accept. The S–F conductivity model 3B is somewhat more realistic, but gives substantially smaller values of the "shielding factor" (about 0.1 for SDS, when calculated using data given by Shanks and Franses) compared to the value given by Burchfield and Wooley for the same surfactant (0.52).

In fact, both of the above-mentioned S–F conductivity models are base on the presumption that micelles contribute substantially to the conductivity of the surfactant solution but not to its ionic strength. At present, as stated even by Shanks and Franses, "no clear theoretical explanation is known" (see ref. [37]) to support such a hypothesis. Taking into account the above discussion, it seems better, at least in the present author's opinion, to take λ values as constants (in the concentration range considered for fitting) than to use the questionable dependence of λ on surfactant concentration. As long as the concentration range considered for fitting is not too wide, and the optimised molar conductivities fall into the range of realistic values, one can consider the herein proposed method preferable to the S–F method.

When comparing the herein determined values of α and N with literature values, we note excellent agreements for both surfactants, although aggregation numbers optimised with models B and C in the case of SDS seem to be somewhat lower than expected. Nevertheless, it is known that conductometry yields the value of N in terms of the number average, while light scattering provides mass average aggregation numbers, and these values need not be the same, especially in the case of high polydispersity. Additionally, and probably more important, SDS undergoes hydrolysis, and although the SDS solutions were used within two days from preparation, some influence of hydrolyses on the micellisation of SDS cannot be ruled out.

Finally, it has to be stressed that although the results obtained using new method clearly demonstrated that fitting parameters should be taken as constant if concentration ranges used for fitting are enough narrow, this doesn't necessarily mean that concentration dependence of a fitting parameters cannot be monitored. For such purpose one should optimise the parameters in completely different concentration ranges. For example, one can compare the parameters optimised in the range from cmc to $2.5\times$c.m.c with those optimised in the range from $2.5\times$cmc to $5\times$cmc, and so on. The work along these lines is in progress.

Experimental

Sodium dodecyl sulphate (SDS) and dodecyltrimethylammonium bromide (DTAB) of $\geq 99\%$ purity were used as received (Fluka Chemie AG). Doubly distilled water was used. Two stock solutions (for both surfactants) were prepared by weight, and thermostated at 25 °C for two days before measurement. Conductivity was measured with a Metrohm conductometer. Conductivity of water was determined before measurement. Stock solution was progressively added (1 cm^3) using an automatic pipette. The measuring cell was thermostated at (25 ± 0.1) °C. The measured conductivities were corrected for the conductivity of water.

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