Growth of Giant Rodlike Micelles of Ionic Surfactant in the Presence of Al3⁺ Counterions

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To interpret quantitatively experimental data for the growth of rodlike anionic surfactant micelles in the presence of Al3⁺ ions, we undertook experimental and theoretical investigations. We determined the micelle size, shape, and interactions by light scattering and examined the binding of Al3⁺ ions to the micelles by ultrafiltration. Independent static and dynamic light scattering measurements indicated that the effect of the micelle—micelle interactions in these solutions can be neglected. The major factor promoting the micelle growth turns out to be the binding of Al3⁺ ions to the micelle surfaces, which considerably affects the standard chemical potential of the aggregated surfactant molecules and can alter the micellization constant by orders of magnitude. The latter effect was described theoretically. The model of micelle growth, extended in this way, compared well with the experimental data. The model provides a quantitative description of the micelle size and charge as functions of the surfactant and electrolyte concentrations. It turns out that the rodlike micelles have a lower surface charge than the spherical ones, and this makes their growth energetically favorable. A practical application may follow from the markedly greater solubilization efficiency of the studied rodlike micelles compared to the spherical ones.

1. Introduction

As it is known, the spherical surfactant micelles undergo a transition to larger rodlike aggregates with the increase of surfactant concentration. It was established experimentally that the formation of rodlike micelles of ionic surfactants is enhanced by the addition of electrolyte and/or decreasing the temperature,2 as well as by increasing the length of the surfactant hydrocarbon chain.11–13 Note that the aforementioned experimental studies were performed using monovalent (1:1) electrolyte.

It was recently established14 that the presence of multivalent counterions (Ca2⁺, Al3⁺) in solutions of anionic surfactant (sodium dodecyl dioxyethylene sulfate, SDP2S) strongly enhances the formation of rodlike micelles. A qualitative explanation of this fact is that a multivalent counterion, for example, Al3⁺, can bind together three surfactant headgroups at the micelle surface, thus causing a decrease of the area per headgroup. In accordance with the theory by Israelachvili et al.,1,15 this will induce a transition from spherical to cylindrical micelles.

The experiment14 showed that the formation of rodlike micelles in the presence of multivalent counterions differs from the micellization in the presence of 1:1 electrolyte in several aspects:

(i) The multivalent counterions are much more effective than the monovalent counterions as promoters of the formation of rodlike micelles. For example, at 8 mM surfactant (SDP2S) concentration, the molar concentration of Na⁺ needed to cause a transition from spherical to rod-like micelles is 230 times larger than the respective molar concentration of Al3⁺.

(ii) In the presence of multivalent counterions, cylindrical micelles (of aggregation number up to 4000) appear at relatively low surfactant concentration14 (from 2 to 8 mM) corresponding to isotropic solutions. In other words, the average distance between the micelles is larger than the micelle average length, and liquid–crystal-like ordering of micelles does not appear.

(iii) When the concentration of multivalent counterions is fixed and the surfactant concentration is varied, one observes cylindrical micelles at the lower surfactant concentrations and spherical micelles at the higher surfactant concentrations. This is exactly opposite the case of monovalent counterions. The explanation is that the transition from sphere to rod occurs at a given ratio of surfactant to electrolyte; in the excess of electrolyte (of...
multivalent counterions), cylindrical micelles are reformed, whereas in the excess of surfactant, the micelles are spherical. It should also be noted that the giant cylindrical micelles in the presence of Al$^{3+}$ studied in ref 14 are rather rigid; the persistent length of the thermally excited undulations is typically larger than the length of a micelle. Hence, in this case, one deals with rodlike (rather than wormlike) micelles. The data for the micelle growth in the presence of 3:1 electrolyte reported in ref 14 do not conform (and should not be expected to conform) to the available theoretical models designed for the case of 1:1 electrolyte$^{15,16}$ (see the discussion in section 2.3 below). The latter fact stimulated us to undertake a theoretical study of the micellar growth in the presence of multivalent electrolyte. Moreover, we carried out some additional experiments in order to compare the data with the theoretical predictions.

As a basis of the theoretical interpretation below, we used the model by Missel et al.$^3$ (the “ladder model”) which was recently extended to mixed micelles$^7$ and modified to account for the temperature effects with nonionics.$^{18}$ This theoretical model has been confirmed by several experimental works.$^{8-10,13}$ Its basic equations are summarized below for the needs of subsequent citation. Missel et al.$^3$ demonstrated that the expressions for the solute chemical potentials in an ideal solution

$$\mu_1 = \mu_1^0 + kT \ln X_1, \quad \mu_n = \mu_n^0 + kT \ln X_n \quad (1.1)$$

can be successfully applied to the micellar solutions of ionic surfactants at relatively high concentrations of 1:1 electrolyte; here $X_1$ and $X_n$ are the mole fractions of the free monomers and the micelles of aggregation number $n$ in the solution; $\mu_1^0$ and $\mu_n^0$ are the respective standard chemical potentials, $k$ is the Boltzmann constant, and $T$ is temperature. Then, the condition of chemical equilibrium, $\mu_n = \mu_{n+1}$, is used to derive the micelle-sized distribution

$$X_n = X_1^0 \exp[-(\mu_n^0 - \mu_{n+1}^0)/kT] \quad (1.2)$$

As known from the experiment, the micelles of aggregation number $1 < n < n_0$ are unstable, and the more stable micelles have aggregation number $n \geq n_0$. Then, the mole fraction of surfactant monomers initially placed in the solution is

$$X = X_1 + \sum_{n=n_0}^{\infty} nX_n \quad (1.3)$$

Missel et al.$^3$ supposed that the micelles of aggregation number $n = n_0$ are spherical and that the bigger micelles have prolate spherocylindrical shape, see Figure 1. In other words, each micelle consists of a cylindrical part containing $n - n_0$ molecules and two hemispherical end caps, each of which contains $n_0/2$ molecules (Figure 1). Correspondingly, the standard chemical potential of a micelle is presented in the form

$$\mu_n^0 = \mu_{n_0}^0 + (n - n_0)\mu^0 \quad (1.4)$$

where $\mu_{n_0}^0$ is the standard chemical potential of a spherical micelle of aggregation number $n_0$, and $\mu^0$ is the standard

![Figure 1](image)

**Figure 1.** A schematic picture of a rodlike micelle.

The chemical potential of each of the monomers in the solution is

$$\mu_n = \mu_n^0 + kT \ln X_n \quad (1.1)$$

which

$$X_n = \frac{1}{K} \left( \frac{X_1}{X_0} \right)^n, \quad n \geq n_0 \quad (1.5)$$

where

$$K = \exp[-(\mu_0^0 - \mu_1^0)/kT], \quad X_0 = \exp[(\mu_0^0 - \mu_1^0)/kT] \quad (1.6)$$

Experimentally, the mass average aggregation number

$$n_m \approx \left( \sum_{n=n_0}^{\infty} n^2 X_n \right) / \left( \sum_{n=n_0}^{\infty} nX_n \right) \quad (1.7)$$

is measured by light scattering. From eqs 1.5–1.7 one can derive

$$n_m \approx n_0 + 2K(X - X_1)^{1/2} \quad (1.8)$$

In the original version of eq 1.8 (see ref 3) $X_0$ is used instead of $X_1$; however, it was established$^{13}$ that $X_0 \approx X_1$ with an accuracy about 5–15%. In our case $X_0 \approx X_1$ is a good approximation, in so far as $X \gg X_0$, and the small differences between $X_0$ and $X_1$ are immaterial for the precision of eq 1.8. It was established$^3$ that eq 1.8 agrees well with the experimental data for SDS micelles in the presence of NaCl. On the other hand, as mentioned above, our experimental data for SDP 2S in the presence of AlCl$_3$ + NaCl did not comply with eq 1.8 (see section 2.3 below). This could be attributed to the effect of the added 3:1 electrolyte on the electrostatic interactions in the system. One can distinguish the following two types of electrostatic effects in micellar solutions of ionic surfactants:

(i) Electrostatic energy of micellization. This is the work to bring a charged surfactant monomer from “infinity” and to incorporate it within a micelle with account for the double layer formed around the micelle.$^{9,15,20}$

(ii) Electrostatic interaction between the micelles in solution. This effect can be important for higher micelle concentrations and/or lower electrolyte concentrations; it is investigated in refs 21–23.

Our analysis (see below) shows that, for the studied system effect, (ii) is negligible, whereas the effect (i) is of primary importance. In fact, when we tried to interpret the data for the growth of micelles in the presence of Al$^{3+}$

ions, our first hypothesis was that the differences between our data and the ladder model can be attributed to the electrostatic micelle--micelle interactions. The latter should be stronger than those in the system studied by Missel et al.\textsuperscript{3} because of the lower ionic strength of our solutions. However, we noticed next that, in spite of the lower value of the ionic strength, it is large enough to make the electrostatic micelle--micelle interactions an effect of higher order. Indeed, in our case, the Debye screening length is $\kappa^{-1} \approx 2$ nm (see eq 3.13 below), whereas the average length of the rodlike micelles is on the order of dozens of nm. Hence, the electrostatic micelle--micelle interactions should be dominated by the steric (excluded volume) interactions, just as it is in the case of the micelles with Na\textsuperscript{+} studied in ref 3.

We should mention in advance the following. After a closer inspection of the problem, we established that the key for understanding the micelle growth is the fact that the Al\textsuperscript{3+} ions do bind strongly to the anionic surfactant headgroups on the micelle surface. This effect can be detected by independent surface tension measurements, the results of which have been reported and interpreted in a separate paper.\textsuperscript{24} Physically, the binding of Al\textsuperscript{3+} ions to the micelle surface considerably affects the standard chemical potential of the surfactant monomers incorporated within the micelles. The respective change in the difference, $\mu_{0}^m_{0}/\mu_0$, enters eq 1.6 multiplied by the aggregation number $n_0 \approx 56$ in the argument of an exponential function. That is the reason why the binding of counterions quantitatively has a very strong effect on the value of the micellization constant, $K$ (see eq 1.6), which can vary by orders of magnitude when the bulk concentration of Al\textsuperscript{3+} is varied (see also Figure 14 below).

In other words, for the investigated micellar solutions the effect of micelle--micelle electrostatic and steric interactions on the micelle growth turns out to be quite immaterial when compared with the powerful effect of the counterion binding on the standard chemical potential of the aggregated monomers and, consequently, on the micellization constant, $K$.

In the next section, we present and discuss experimental data obtained by ultrafiltration and laser light scattering. Further, we propose a quantitative interpretation of the experimental findings. We pay special attention to the dependence of the equilibrium constant (the growth parameter), $K$, on the electrolyte concentration and to the binding of Al\textsuperscript{3+} ions to the micelles. The results reveal the cause for the micelle growth and give information about the surface charge of the micelles and its variation with the length of the rodlike aggregates.

2. Experiments and Discussion

2.1. Solutes and Solutions. The surfactant used in the present work was sodium dodecyl dioxyethylene sulfate (SDP2S), Empicol ES870, Wilson Co. (UK), with the structure CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}(OC\textsubscript{2}H\textsubscript{4})\textsubscript{2}OSO\textsubscript{3}Na. All micellar solutions were prepared by using deionized water (Milli-Q, Organex grade). All experiments with AlCl\textsubscript{3} were carried out between 18 and 24 h after the preparation of the solutions.

It might seem questionable whether the Al\textsuperscript{3+} ions exist in the solutions in trivalent form or in the form of complexes with the OH\textsuperscript{-} ions. It is known that, below pH = 4.0, the dissolved Al is present mostly in the form of trivalent ions.\textsuperscript{25–27} In our case, the dissolved AlCl\textsubscript{3} decreases the pH of the solutions to about 3.0–3.5, and our estimates based on the data\textsuperscript{26–27} about the stability of the various compounds, Al(OH)\textsuperscript{3+}, Al(OH)\textsuperscript{2+}, and Al(OH)\textsubscript{4}–, showed that the fraction of Al\textsuperscript{3+} is above 98% at pH = 3.0 and above 95% at pH = 3.5.

The effect of pH on micellar size was checked using samples containing 8 mM SDP2S and 0.024 M NaCl at pH = 5.5. Then the pH was lowered by adding small portions of 0.1M H\textsubscript{2}SO\textsubscript{4} at continuous stirring. The micelle hydrodynamic radius, $R_n$, was measured by light scattering (see section 2.2) for samples with pH = 2.5, 3.5, and 5.5; for each solution the values of $R_n$ have been measured after 18, 24, and 48 h from the preparation of the solution. The measured values of $R_n$ were found to be the same, $R_n = 2.2 \pm 0.3$ nm, for the studied ranges of pH and solution age. Therefore, one can conclude that micellar growth is not affected by the variation of pH in the range 2.5–5.5 when Al\textsuperscript{3+} ions are absent. In other words, the relatively low pH of the solutions containing AlCl\textsubscript{3} (pH = 3–3.5) is not the factor which causes the growth of the long rodlike micelles; it seems rather that the presence of Al\textsuperscript{3+} ions promotes the micelle growth in these solutions.

We determined the critical micellization concentration (cmc) of SDP2S in the presence of Al\textsuperscript{3+} by measuring the average intensity of the scattered light (static light scattering, SLS) as a function of the surfactant concentration. The appearance of micelles led to a break point in the concentration dependence after which the intensity of the scattered light increased linearly with the micellar concentration. Results for the cmc of SDP2S in the presence of different amounts of monovalent (Na\textsuperscript{+}) and trivalent (Al\textsuperscript{3+}) counterions are presented and discussed in ref 24. It is necessary to mention only that the cmc depends mostly on the ionic strength, $I_0$, and rather weakly on the specific type of the dissolved ions, a fact which is consistent with the results of other studies.\textsuperscript{28,29} For SDP2S we experimentally established\textsuperscript{24} that in cmc decreases linearly with $I_0$ in the concentration range 0.024 < $I_0$ < 0.128 M

$$\text{In cmc} = -11.444 - 0.7573 \ln I_0$$

Similar dependence has been experimentally established for other surfactants.\textsuperscript{30}

The determination of cmc by static light scattering was not very accurate in our case. The reason for this is that cmc is very low, and the presence of Al\textsuperscript{3+} ions causes precipitation of the surfactant in some solutions (typically for concentrations below cmc). To verify the SLS results, we obtained\textsuperscript{24} independent data for cmc by measuring surface tension isotherms of SDP2S at $I_0 = 0.024$ M in the presence of NaCl or AlCl\textsubscript{3} only. In both cases we determined cmc = 1 x 10\textsuperscript{-4} M which is close to the result from the static light scattering.

In ref 14 we established experimentally that the transition from spherical to rodlike micelles is influenced by the surfactant-to-multivalent-counterion ratio defined as follows:

$$\xi = c_{SM}/(Zc_{AT})$$

where $c_{SM}$ is the molar concentration of surfactant molecules in micellar form, $c_{AT}$ is the total molar concentration of the multivalent counterion (of valence $Z$ > 1) in solution. In other words, $\xi$ equals the ratio of the net charge of the micellar ionizable groups to the net charge of the dissolved multivalent counterions (Al\textsuperscript{3+}, Ca\textsuperscript{2+}, etc.). One could expect that one Al\textsuperscript{3+} ion can bind three anionic surfactant headgroups at the micelle surface. This would lead to a decrease of the optimal area per headgroup and will favor the growth of the micelles, as predicted by the theoretical model of Israelachvili et al.\textsuperscript{15} For $\xi > 1$ there is an excess of Al\textsuperscript{3+} ions in the solution and one can experimentally establish that long rodlike micelles grow in the solution.\textsuperscript{14} On the other hand, for $\xi > 1$ the amount of the Al\textsuperscript{3+} ions in the

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solution is not sufficient to interconnect all of the anionic headgroups on the micelle surfaces. Experimentally, one finds that for \( z > 1 \), the surfactant is organized into small spherical micelles.\(^{14}\)

The dependence of micelles size on the surfactant concentration was experimentally studied at constant ratio, \( z \), and constant ionic strength, \( I_0 = 0.024 \) M, of the input electrolyte (NaCl and AlCl\(_3\)). To achieve an increase of \( z \) at fixed \( I_0 \), we added to the solution of the lowest \( z \) a portion of NaCl solution with the same ionic strength, \( I_0 = 0.024 \) M. Thus, the experimentally controlled variables are the surfactant concentration, \( c_s \), the surfactant-to-aluminum ratio, \( \xi \), and the ionic strength of the added electrolyte, \( I_0 \). It should be noted that \( I_0 \) is not the true ionic strength of the solution in so far as it does not include the contribution of the dissolved ionic surfactant, SDP2S. A more rigorous calculation of the true ionic strength, \( I \), has been proven to be useful in determining the mass distribution of samples with polycrystalline structure in the micelle size; moreover, this method minimizes the influence of “dust” particles.

### 2.2. Light Scattering Experiments

The light scattering measurements were performed using the Autosizer 4700C (Malvern, Ins., U.K.) supplied with a K7032 CE 8-multitiplet correlator. The light source was an argon laser (Innova 70, coherent), operating at a 488 nm wavelength of vertical plane polarized light. The apparatus has the capability of working at the different scattering angles in the range 10 to 150°. The temperature in all experiments was automatically maintained at \( 27 \pm 0.1 \) °C. The samples were filtered with Millex (Millipore, Bedford, MA) filters 100, 220, and 450 nm before the measurements were taken to avoid the influence of dust particles. The surfactant concentration was varied from 0.075 to 0.3 wt % (2–8 mM) of SDP2S. This concentration range was low enough to avoid multiple light scattering. On the other hand, the concentration of the SDP2S micelles was high enough to allow measurements at low laser power (between 50 and 100 mW). Thus, the results were not influenced by a local heating of the samples caused by the beam. Measurements at various powers of the initial laser beam were carried out; the obtained results of the initial laser beam were also checked. For large micelles the intensity measurements were performed using the Autosizer 4700C produced by Malvern Instruments Ltd. (U.K.). It is equipped with built-in software based on the exponential sampling method-multimodal analyses, especially designed for polycrystalline samples. At the first step of the data processing, the diffusion coefficient distribution by intensity was determined from the measured autocorrelation function, \( g^{(2)}(t) \). Next, from the obtained intensity vs diffusivity distribution, the mass distribution of the particles (micelles) was calculated by means of the Rayleigh–Gans–Debye theory.\(^{22}\) This method has been proved to be useful in determining the mass distribution of samples with polycrystalline structure in the micelle size; moreover, this method minimizes the influence of “dust” particles.

The polydispersity index of the SDP2S micelles formed in the presence of Al\(^{3+}\) was found to be the same (the variance is between 0.3 and 0.5) as that of those formed in water solutions containing SDS and high NaCl concentrations, see ref 32. As mentioned above, the ladder model accounts for the fact that the rodlike micelles are strongly polycrystalline and provides an expression, eq 1.5, for their size distribution.

The static light scattering technique gives the radius of gyration of the micelles, \( R_G \), which is determined from the angular dependence of the scattered light.\(^{13,22}\) The scattered intensity, \( I_s \), is measured as a function of the scattering angle, \( \theta \). Next, we plotted the data as \( I_s^{-1} \) vs \( q^2 \) in accordance with the equation:\(^{14,22}\)

\[
I_s^{-1}(q) = I_{s0}^{-1}(1 + 1/3(R_Gq)^2 + \ldots)
\]

and from the slope of the straight line, we determined \( R_G \). This method for determining \( R_G \) is applicable for any micellar shape except for q belonging to the interval \( q_{min} \leq q \leq q_{max} \), where \( q_{min}R_G > 0.1 \) and \( q_{max}R_G < 0.1 \) (out of this interval, experimental problems appear).\(^{22}\) The lowest scattering angle in our intensity measurements experiments was 30°, while the largest one depended on the size of the measured scattering objects. \( q_{max} \) was determined from the plot of the experimental data for \( I_s^{-1} \) vs \( q^2 \); for \( q > q_{max} \), the data deviated from the straight line dependence. In all experiments, we worked with \( q_{max}R_G < 0.1 \). For large micelles \( R_G > 45 \) nm, the intensity measurements were carried out using 10–15 different scattering angles in the range 30°–60°. The experimental procedure usually began with measuring the intensity at various angles in the interval 30°–90°. For that purpose, we used a large round glass cell (Burchard cell, Malvern Ins., U.K.), especially designed for intensity measurements at various angles. The preliminary information for the radius of gyration of micelles helped us to choose the appropriate working range. After that, we performed at least three runs for each sample, and the final result was calculated by averaging. The influence of the intensity of the initial laser beam was also checked. For large micelles \( R_G > 45 \) nm the temperature dependence of the scattered intensity was measured, in the limits of 3–5%. For smaller micelles, the angular dependence of the scattered intensity was not well pronounced, and it was not possible to obtain a reliable result.

The value of the ratio \( R_{min} \equiv R_G/R_H \) depends on the micelle shape and size, see, e.g., Table 1 in ref 33. It is established that, for impermeable spheres, \( R_{min} \approx 0.775 \); for monodisperse random

\[ K_1 = Dq^2, \quad K_2 = K_3 = \ldots = 0 \] (2.6)
length, determined in ref 14, which corresponds to a rigid rod. Solutions. Another indication is the value of the micelle persistent length, determined in this way, which corresponds to a rigid rod.

To determine the length of the rodlike micelles, \( L_r \), from the light scattering data (\( L \) is the sum of the length of the cylinder plus the radii of the two hemispherical caps, see Figure 1), we used the same model as in ref 14. We assumed that the radius of the rod is constant and equal to the radius of the smallest spherical micelles (those with \( n = n_0 \)). On the other hand, the length of the rod, \( L_r \), can vary with the surfactant and electrolyte concentration. \( L \) is calculated from the time dependence of the intensity autocorrelation function of the scattered light by using eqs 2.3–2.14 in ref 14. The value of \( L \) determined in this way (from the apparent hydrodynamic radius of the micelles) we denoted by \( L_{H} \).

On the other hand, \( L \) can be independently determined from the measured radius of gyration \( R_G \) (static light scattering technique) by means of eqs 2.15, 2.16, and 3.2 in ref 14. The value of \( L \) determined in this way, we denoted by \( L_C \). In particular, to calculate \( L_C \) we used the values of the persistent length, \( l_p \), determined in ref 14, as follows: \( l_p = 190 \text{ nm} \) for \( I_0 = 0.024 \text{ M} \) and \( l_p = 165 \text{ nm} \) for \( I_0 = 0.064 \text{ M} \).

In Figure 2, we plotted \( L_{H} \) vs \( L_C \) for solutions of SDP2S in the presence of NaCl and AlCl_3. The full points were measured at ionic strength \( I_0 = 24 \text{ mM} \), whereas the empty points were measured at \( I_0 = 64 \text{ mM} \); the various points correspond to different values of \( \xi \), varying between 0.25 and 0.9. The data complies well with the line \( L_{H} = L_C \) (Figure 2). The fact that the data for \( L_{H} \) vs \( L_C \) are in general agreement with the line \( L_{H} = L_C \) for various values of \( \xi \) and \( I_0 \) shows that the determined micelle length is not sensitive to the micelle–micelle interactions in the framework of the experimental error, which can be up to 10–15%. Indeed, theoretically, \( L_{H} \) and \( L_C \) depend on the micelle–micelle interactions in a quite different way. \( L_{H} \) and \( R_G \) depend on the interactions through the thermodynamic second virial coefficient in the expansion of the osmotic pressure, whereas \( L_{H} \) and \( R_H \) depend on the interactions through the kinetic second virial coefficient in the expansion of the diffusion coefficient, see, e.g., ref 32.) If there were a pronounced effect of the interactions, this in general would result in differences between the values of \( L_{H} \) and \( L_C \) varying with \( \xi \) and \( I_0 \), which is not the case (Figure 2).

In Figure 3, we present the determined micellar aggregation number \( n_m \) vs \((X - X_m)^{1/2}\) at ionic strength \( I_0 = 0.024 \text{ M} \) in the presence of \( \text{Al}^{3+} \) and \( \text{Na}^+ \). For each curve, \( \xi \) is kept constant, cf. eq 2.2; the lines are guides to the eye, rather than theoretical fits.

The above result is not surprising in view of the criterion proposed by Missel et al.\(^9\) Comparing theory and experiment, these authors established that the micelle–micelle interactions become important only when

\[
X \frac{A_j}{X} = R_G (\frac{4 \pi}{3} N_m^{1/3}) \geq 0.45
\]

Here \( R_G \) is the average micelle radius of gyration, \( N_m = 18 \text{mol} / ([X - X_m]N_{A}) \), with \( N_A \) being the Avogadro number, is the average volume per micelle in the solution, \( X \) is the surfactant molar fraction at which the mean distance between the micelles is equal to the mean micellar radius of gyration. For the solutions investigated by us, \( X \frac{A_j}{X} \leq 0.30 \), and according to eq 2.8, the micelle–micelle interactions were negligible (in first approximation). To make this estimate, we used the experimentally measured values of \( R_G \). For example, with the largest surfactant concentration, \( c_s = 8 \text{ mM} \) and \( \xi = 0.67 \), we measured \( R_G = 32 \text{ nm} \); for comparison, the Debye screening length (cf. eq 3.13 below) is 1 order of magnitude smaller, \( x^{-1} \approx 2 \text{ nm} \). Thus, one may conclude that the electrostatic micelle–micelle interaction is small compared with the excluded volume interaction; the latter, in view of the criterion \( X \frac{A_j}{X} \leq 0.30 \), is sufficiently small and does not affect the light scattering data. Note that additional suppression of the electrostatic micelle–micelle interaction stems from the decrease of the micelle surface charge due to the binding of \( \text{Al}^{3+} \) ions, see section 2.4 below.

We should also note that our light scattering data were not affected by multiple light scattering. Indeed, it is easy to estimate the existence of multiple light scattering because in such a case, a typical halo picture is observed in the light scattering experiment. It is due to the secondary scattered light. In all experiments carried out by us, the laser beam passing through the micellar solutions was clear without any halo. In addition, the theoretical estimates\(^{11}\) also show that the multiple light scattering is negligible in the concentration range 0.05–0.3 wt % corresponding to our experiments.

### 3. Mean Mass Aggregation Number

From the radius and length of the rodlike micelles, determined as explained above, we calculated the micelle aggregation number, \( n_m \), see eq 1.7, following the procedure of ref 14, which is described in Appendix 1 below.

In Figure 3 we present the determined micellar aggregation number \( n_m \) vs \((X - X_m)^{1/2}\) at ionic strength \( I_0 = 24 \text{ mM} \), the latter being the same for all curves. As mentioned above, experimentally we achieved a constant \( \xi \) at fixed ionic strength by diluting step by step the initial concentrated solution with a solution of NaCl of the same ionic

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strength containing the surfactant of concentration equal to the cmc. The curves with \( \xi = 0.90, 1.00, \) and 1.15 represent new experimental data, whereas the curves with \( \xi = 0.67, 0.73, 1.07, \) and 1.23 were taken from Figure 5 in ref 14.

The theoretical models of micellar growth in the presence of 1:1 electrolytes predict that the plots of \( n_{\text{m}} \) vs \( (X - X_j) \) should be straight lines, see eq 1.8. The data for \( \xi < 1 \) really conform to straight lines (Figure 3), but this does not mean that the traditional ladder model fits the data. Indeed, the intercepts of those lines are negative (about \(-1300\)), whereas eq 1.8 predicts that the intercept must be equal to the aggregation number of the smallest spherical micelles, \( n_{\text{m}} \). We experimentally determined that \( n_{\text{m}} \approx +56 \) for SDP2S micelles. In other words, the intercepts of the straight lines for \( \xi < 1 \) differ in both magnitude and sign from the prediction of eq 1.8. Moreover, negative values of \( n_{\text{m}} \) are physically meaningless. Other experimental curves (those with \( \xi = 1.00 \) and \( \xi = 1.07 \)) are not linear at all. Therefore, one can conclude that the traditional ladder model of micelle growth \( \xi \leq 1 \) (designed for 1:1 electrolyte solutions) is not applicable (and should not be expected to be applicable) to the interpretation of data for the micellar growth in the presence of 3:1 electrolyte.

On the other hand, it should be noted that, in the absence of Al(III) ions (in the presence of 1:1 electrolyte only), the micelles of the investigated surfactant SDP2S grow in accordance with the prediction of the traditional ladder model (see Figure 3 in ref 35). In other words, the specific type of surfactant used in our experiment (ethoxylated alkyl sulfate) is not the reason for the difference between theory and experiment.

To interpret the data in Figure 3, we have taken into account the effect of the 3:1 electrolyte on the parameter \( K \) in eq 1.6, see section 2.3. Here, K is the constant that determines the fraction of Al(III) bound to the surface of the micelles. In this respect, useful information can be obtained by means of ultrafiltration experiments.

2.4. Ultrafiltration Experiments. As is known, the multivalent counterions bind strongly to the negatively charged surface of the anionic micelles and can be removed from the solution by performing ultrafiltration experiments using a membrane with appropriate pores sizes. When the micelles are rejected by an efficient ultrafiltration membrane, all the ions, including the electric double layers around the micelles, are retained, and the counterion concentration in the solution permeating through the pores is identical to that of the surrounding aqueous medium.

We applied this method to determine the background concentration of the unbound Al(III) counterions, \( c_{\text{AB}} \), in solutions containing 2 and 8 mM SDP2S at ionic strength \( I_0 = 24 \) mM and at different values of the total input concentration of Al(III), \( c_{\text{AT}} \). The ultrafiltration experiments were carried out at room temperature (22 ± 2 °C) in dead-end mode in a 100-mL stirred cell. The transmembrane pressure was kept constant at 0.5 atm during the experiments. We used a polysulfonic membrane with molecular weight cut-off of 6000 which is small enough to permit the retention of the smallest SDP2S micelles. The cell was initially filled with 50 mL of the solution, and samples of 2 mL were taken throughout the run which were then used for the spectrophotometric determination of the Al(III) concentration in the permeate, \( c_{\text{AB}} \). For that purpose, we used a colorimetric reaction between the ammonium salt of the aurin-tricarboxylic acid (Aluminon, Sigma) and the Al(III) ions taking place at low pH values.

In Figure 4, we plotted the experimental data for \( c_{\text{AB}}/c_{\text{SM}} \) and \( c_{\text{AB}}/c_{\text{AT}} \) vs \( \xi \) for \( c_0 = 8 \) mM, where \( c_{\text{SM}} = c_{\text{AT}} - \) cmc is the average concentration of the surfactant in micellar form and \( c_{\text{AT}} \) is the total surfactant concentration. The ratio \( c_{\text{AB}}/c_{\text{AT}} \) expresses the part of the aluminum ions which are not associated with the micelles; one sees in Figure 4 that this part decreases from 32 to 11% with the increase of \( \xi \). In other words, the predominant part of Al(III) ions in the investigated solutions (from 68 to 89%)

\[ 3\xi^2 + (\xi + 3E\xi - 1)x - E = 0 \]  

where we introduced the notation

\[ x = c_{\text{AB}}/c_{\text{SM}} \quad E = B/c_{\text{SM}} \]

Solving eq 2.11 we obtained

\[ x = \frac{1}{6\xi^2}[(\xi + 3E\xi - 1)]^2 + [(\xi + 3E\xi - 1)^2 + 2E\xi]^2 \]

We selected the physical root of eq 2.11 which gives \( x = 0 \) (no Al(III) in the permeate) for \( \xi = 1 \) (no Al(III) in solution), cf. eq 2.2. It is interesting to note that, for high surfactant concentrations when \( E \to 0 \) (see eq 2.12), eq 2.13 reduces to


that is, for $\xi \geq 1$, the whole amount of $Al^{3+}$ is associated with the micelles.

We fitted the experimental data for $c_0 = 2$ and 8 mM with eq 2.13 using the standard least-squares method; $B$ was varied as an adjustable parameter. Thus, we determined $B = 8.5 \times 10^{-3}$ M from the best fit. The solid curve in Figure 4 is drawn by means of eq 2.13 with the above value of $B$. The agreement between theory and experiment seems quite satisfactory in view of the low accuracy of determination of $C_{Na}$ with the colorimetric reaction and the simplifications made when deriving eq 2.13.

Fortunately, it turns out that the theoretical dependence of $N_{Mic} vs (X - X_t)^{1/2}$ (see below) is not sensitive to the value of $B$.

3. Double Layer Contribution to the Constant of Micellization

3.1. Effect of the Counterion Adsorption on the Constant of Micellization. As already mentioned, our experimental data plotted in Figure 3 do not agree with the prediction of the available theory of micelle growth, eq 1.8, at fixed constant of micellization, $K$. Note, however, that $K$ can indirectly depend on the surfactant mole fraction $X$ in the following way. As explained above, to obtain a curve at fixed $\xi$ (Figure 3), we started the measurements from the most concentrated solution (8 mM SDP2S), which is further step-by-step diluted with NaCl solution of the same ionic strength, containing also SDP2S, thus originating from the dissolved SDP2S, $AlCl_3$, and NaCl. Greater than the number of the solute molecules, one may consider the number of the water molecules in the solution is much the same as that of the mixed micelles.

The investigated SDP2S micellar solutions contain various micro-ions, $DP2S^-, Al^{3+}, Na^+$, and $Cl^-$, originating from the dissolved SDP2S, $AlCl_3$, and NaCl.

In particular, SDP2S exists in the solution in both micellar and monomeric form, the concentration of the monomers being equal to cmc. Moreover, the binding of $Al^{3+}$ to the surfactant micelles is accompanied by release of $Na^+$ counterions from the micelles. The background concentration of the $Na^+$ ions, $C_{Na}$, can be calculated by means of the following expression

$$C_{Na} = C_{NT} + 3(C_{AT} - C_{AB}) + \left[ C_s - cmc - 3(C_{AT} - C_{AB}) \right] \alpha_{Na} + cmc \quad (3.1)$$

Where $C_{NT}$ expresses the total input concentration of $Na^+$ to the dissolved NaCl; the term $3(C_{AT} - C_{AB})$ stands for the $Na^+$ counterions replaced from the surface of each micelle by adsorbed $Al^{3+}$ ions; the next term, $\left[ C_s - cmc - 3(C_{AT} - C_{AB}) \right] \alpha_{Na}$, accounts for the $Na^+$ ions dissociated from the micelle headgroups, which are not occupied by adsorbed $Al^{3+}$; $\alpha_{Na}$ denotes the average degree of charging of the micelle headgroups free of adsorbed $Al^{3+}$ (0 < $\alpha_{Na} < 1$); the fact that $\alpha_{Na} < 1$ suggests that some $Na^+$ ions are not adsorbed to the micelle surface; finally, the term $cmc$ in eq 3.1 stands for the $Na^+$ ions dissociated from the free surfactant monomers in the solution. As mentioned earlier, in our experiments the apparent ionic strength of the input electrolyte (NaCl and $AlCl_3$), $I_0$, is kept constant, $I_0 = 24$ mM

$$C_{NT} + 6C_{AT} = I_0 = const \quad (3.2)$$

Next, the true background ionic strength of the solution can be calculated

$$I_t = I_0/2(C_{AB} + C_{NB} + 3C_{AT} + C_{NT} + cmc) \quad (3.3)$$

The term $3C_{AT} + C_{NT}$ expresses the concentration of the $Cl^-$ ions dissociated from the dissolved $AlCl_3$ and $NaCl$, and the last term (cmc) in eq 3.3 accounts for the presence of ionized surfactant monomers in the solution. The substitution of $C_{NB}$ and $C_{NT}$ from eqs 3.1 and 3.2 into eq 3.3 yields

$$I_t = I_0 + 3C_{AB} - 3C_{AT} + cmc + 1/2(C_s - cmc - 3C_{AT} + 3C_{AB}) \alpha_{Na} \quad (3.4)$$
In our calculations we took into account also the fact that the critical micellization concentration (cmc) depends on the ionic strength, see eq 2.1

\[
c_{SM} = c_s - \text{cmc}(l_0); \quad c_{SM}^0 = c_s - \text{cmc}(l_0); \quad c_{AT} = \frac{c_{SM}^0}{3} \tag{3.5}
\]

Let us mention in advance that for the solutions studied by us, the true ionic strength, \( I_0 \), calculated from eq (3.4), appears to be close to \( l_0 = 24 \) mM and is not sensitive to the variation of \( \varepsilon \). Moreover, \( \text{cmc}(l_0) \approx 0.1 \) mM is too low compared to \( l_0 \) and, therefore, gives a negligible contribution to \( l_1 \).

### 3.3. Energy Contribution Due to the Diffuse Electric Double Layer.

The energy of the electric double layer formed around a micelle gives a contribution to the standard chemical potential of a surfactant molecule incorporated into such a micelle and, consequently, to the equilibrium constant \( K \), see eq 1.6. Following refs 3 and 9, we assumed that the double-layer and non-double-layer contributions to the standard chemical potentials are additive, and then from eq 1.6 one obtains \(^{3,9}\)

\[
K = K_{dl}K_{ndl} \tag{3.6}
\]

where by definition

\[
\ln K_{dl} = \frac{n_0(g^d - g^d_0)}{kT} \tag{3.7}
\]

Here \( K_{dl} \) and \( K_{ndl} \) denote the double-layer and non-double-layer contributions into the equilibrium constant \( K \); \( g^d \) represents the electrostatic energy per surfactant molecule incorporated into a micelle. Here and hereafter, the indices “s” and “c” denote “spherical” and “cylindrical” micelle, respectively. Theoretical expressions for \( g^d \) have been derived by Mitchell and Ninham \(^{19}\) and Missel et al. \(^9\), for the case of a symmetrical (1:1) electrolyte. Our aim below is to derive an expression for \( g^d \) for the case when a mixture of 1:1 and 3:1 electrolytes (NaCl and AlCl\(_3\)) is present in the solution. The energy \( g^d \) can be calculated by means of the expression \(^{3,9,38}\)

\[
g^d = \frac{e}{\sigma} \int_0^\infty \psi_0(x)dx \tag{3.8}
\]

where \( e \) is the elementary charge, \( \sigma \) denotes the surface charge density, and \( \psi_0 \) is the surface potential. To determine the dependence \( \psi_0(x) \), we have to solve the Poisson equation

\[
\frac{d^2\psi}{dr^2} + \frac{m}{r} \frac{d\psi}{dr} = -\frac{4\pi}{\varepsilon} \rho(r), \quad m = 0, 1, 2 \tag{3.9}
\]

Here \( \psi \) and \( \rho \) are the electric potential and bulk charge density, respectively, and \( r \) is the coordinate along the normal to the charged surface; \( m = 0 \) for flat surface, \( m = 1 \) for cylindrical, and \( m = 2 \) for spherical surface. \( \rho \) can be expressed by means of the Boltzmann equation

\[
\rho = e c_{\text{NB}} \exp\left(\frac{-e\psi}{kT}\right) + 3e c_{\text{AB}} \exp\left(\frac{-3e\psi}{kT}\right) - e(c_{\text{NB}} + 3c_{\text{AB}}) \exp\left(\frac{e\psi}{kT}\right) \tag{3.10}
\]

where, as usual, \( c_{\text{NB}} \) and \( c_{\text{AB}} \) are the background concentrations of Na\(^+\) and Al\(^3+\). Combining eqs 3.9 and 3.10 one can derive

\[
\frac{d^2\psi}{dx} + \frac{m}{x} \frac{d\psi}{dx} = \sinh \psi = 6I^2 \exp(y) \sinh^2 y \tag{3.11}
\]

where we have introduced the notation

\[
x = \kappa r, \quad y = -\frac{e\psi}{kT} \tag{3.12}
\]

\[
\kappa^2 = \frac{8\pi e^2 I_0}{e kT}, \quad \lambda^2 = \frac{c_{\text{AB}}}{I_0} \tag{3.13}
\]

The boundary condition at the charged surface is \( dy/dx = -4\pi e/\kappa \); in the above notation this equation takes the form

\[
\frac{dy}{dx} = \frac{4\pi e}{kT \kappa} = -s \quad \text{for} \quad x = \kappa R \tag{3.14}
\]

The latter equation defines the parameter \( s \). Following the procedure of Wiersma et al., \(^{39}\) which has been also utilized by other authors, \(^{3,9,40}\) we multiply eq 3.11 by \( m dy/dx \), integrate, and then set \( y = 0 \) and \( y' = 0 \) for \( x \to \infty \); the result is

\[
\int_{x=0}^{x=\infty} \frac{dy'^2}{dx} dx / 2 + \lambda^2 (e^y - 1)^2 (1 + 3e^{-y}) + \int_{y=0}^{y=\infty} \frac{m dy'^2}{dx} dx \tag{3.15}
\]

Let us denote

\[
Y_0 = y'|_{x=\kappa R} \tag{3.16}
\]

Then we use the approximation \(^{3,9,39,40}\)

\[
\int_{x=0}^{x=\infty} \frac{1}{x} \frac{dy'^2}{dx} dx \approx -\frac{1}{\kappa R} \int_{y=0}^{y=\infty} \frac{dy}{dx} \frac{dy}{dx} \tag{3.17}
\]

To estimate the last integral, we substitute \( dy/dx \) for a flat interface (\( m = 0 \)). Using some appropriate approximations from eq 3.15 (with \( m = 0 \)) we derive

\[
-\int_{y=0}^{y=\infty} \frac{dy}{dx} \approx 8 \sinh^2 Y_0 / 4 + \lambda^2 (u) \tag{3.18}
\]

where

\[
u = \sqrt{\exp(y_0) - 1} \tag{3.19}
\]

\[
J(u) = \frac{1}{2} u^3 + u - \frac{1}{2} (\arctan u) + \frac{3}{2} u/(1 + u^2) \tag{3.20}
\]

Next, the combination of eqs 3.14–3.19 yields

---


\[
s = \left\{ 4 \sinh^2 \frac{Y_0}{2} + \lambda^2 u(1 + 3e^{-\gamma_0}) + \frac{2m}{\kappa R} \left[ 8 \sinh^2 \frac{Y_0}{4} + \lambda j(u) \right] \right\}^{1/2} \tag{3.21}
\]

Note that for \( \lambda = 0 \) (no Al\(^{3+}\) ions in the solution), eq 3.21 reduces to the respective expression of Mitchell and Ninham\(^{39}\) for 1:1 electrolyte. The integration means of the expression to consist of two parts: (i) the (bound) to the micelle surface. 41

Stern layer free counterions involved in Brownian motion and (ii) the multiplier 3 accounts for the fact, that one Al\(^{3+}\) neutralizes three surfactant headgroups. In fact, eqs 3.25

The area per surfactant headgroup, \( a \), calculated from the results for the micelle shape and aggregation number (see Appendix 1), is \( a = 1.48 \text{ nm}^2 \) for the spherical micelles and \( a = 0.64 \text{ nm}^2 \) for the cylindrical ones. These values are markedly larger than the area per molecule in a dense flat surfactant adsorption monolayer, which is ca. 0.35 \text{ nm}^2. Therefore, it is possible for some Al\(^{3+}\) ions to be intercalated among the surfactant headgroups at the micelle surface, thus, partially neutralizing the surface charge of the micelles (Figure 6). In such a case

\[
\sigma = -\alpha \frac{e}{a} \tag{3.23}
\]

where \( \alpha \) is an apparent degree of dissociation (charging) of the ionizable headgroups on the surface of a micelle (0 < \( \alpha < 1 \)). The parameter \( \alpha \) expresses the fraction of the “nonneutralized” headgroups

\[
\alpha = 1 - \theta_A - \theta_N \tag{3.24}
\]

where \( \theta_A \) and \( \theta_N \) are the occupancies of the Stern layer by Al\(^{3+}\) and Na\(^{+}\) ions\(^{43}\)

\[
\theta_N = \frac{b_N \alpha_{NB}}{1 + b_N \alpha_{NB} + b_A \alpha_{AB}}, \quad \theta_A = \frac{3 \Gamma_A}{\Gamma_s} = \frac{b_A \alpha_{AB}}{1 + b_N \alpha_{NB} + b_A \alpha_{AB}} \tag{3.25}
\]

\( \Gamma_s \) and \( \Gamma_A \) denote adsorption of surfactant and Al\(^{3+}\); the multiplier 3 accounts for the fact that one Al\(^{3+}\) ion neutralizes three surfactant headgroups. In fact, eqs 3.25 represent Langmuir isotherms for the competitive adsorption of Al\(^{3+}\) and Na\(^{+}\) in the Stern layer. The adsorption parameters in eqs 3.25 are to be determined from the expressions\(^{3,44}\)

\[
\text{Stern Layer}\quad \text{Subsurface}\quad \text{Diffuse Layer}
\]

\[
\begin{align*}
\Phi_A &= \frac{3e^2}{\varepsilon_{st} kT} \left( \frac{1}{r_a} - \frac{1}{\sqrt{r_a^2 + \delta^2}} \right) \\
\Phi_N &= \frac{9e^2}{\varepsilon_{st} kT} \left( \frac{1}{r_a} - \frac{1}{\sqrt{r_a^2 + \delta^2}} \right)
\end{align*}
\tag{3.27}
\]

Here \( \delta \) is the distance between points D and P (the thickness of the Stern layer), and \( r_a \) (see Figure 7) is estimated, assuming hexagonal packing of the surfactant headgroups; \( \varepsilon_{st} \) is the dielectric constant in the Stern layer, which is expected to be different (smaller) from the dielectric constant of the bulk water because of the water molecules belonging to the hydration shells around the ions.\(^{30,45}\) Likewise, one obtains an expression for \( \Phi_N \)

\[
\Phi_N = \frac{3e^2}{\varepsilon_{st} kT} \left( \frac{1}{r_a} - \frac{1}{\sqrt{r_a^2 + \delta^2}} \right) \tag{3.28}
\]

Now we have all of the equations necessary to calculate \( g^2 \) and \( K_{dl} \); cf. eqs 3.6 and 3.7. The procedure of calculations is described in Appendix 2.

4. Numerical Results and Discussion

4.1. Processing of the Experimental Data. The aim of the numerical procedure is to fit the experimental data from Figure 3 plotted as \( n_0 \) vs [\( K_{dl}(X - X_1) \)]\(^{32}\)

(44) Shchukin, E. D.; Pertsov, A. V.; Amelina, E. A. Colloid Chemistry; Moscow University Press: Moscow, 1982. (In Russian.)
of n

Equation 4.1 is a corollary of eqs 1.8 and 3.6. \( n_M \) is given by the experiment. In addition, \( X - X_1 = 0.018(c_0 - \text{cmc}) = 0.018c_{\text{CMC}} \), where the values of \( c_0 \) and \( \text{cmc} \) (in mol/L) are also known from the experiment; see also eqs 2.1 and 3.5. The aggregation number of the smallest spherical micelles is also known from the experiment; see also eqs 2.1 and 3.5. The equations from the previous section allow the calculation of \( K_{ndl} \) for a given value of \( X \) (see Appendix 2). As \( K_{ndl} \) is not expected to depend on \( X \), eq 4.1 shows that the plot of \( n_M \) vs \( t \) should be a straight line. To fit the data, we apply the least-squares method by minimization of the function

\[
\Psi(\delta, K_{ndl}) = \sum_j \left[ (n_{Mj} - n_M(t_j))^2 \right] \tag{4.2}
\]

where \( (n_{Mj})_j \) and \( t_j \) are values of \( n_M \) and \( t \) calculated from the experimental data; \( n_{Mj}(t_j) \) is calculated by means of eq 4.1 and the summation is carried out over all experimental points. From the best fit of the data for \( \xi = 0.67 \) (see the respective curve in Figure 3) with eq 4.1, we determine \( \delta = 4.6 \, \text{Å} \) and \( K_{ndl} = 1.08 \times 10^7 \). The data (the full circles in Figure 8) comply well with a straight line of intercept \( n_0 = 56 \).

We applied the same numerical procedure (based on eq 4.2) to process the data for the other values of \( \xi \) (0.73 \( \leq \xi \leq 1.23 \)). It turns out that, for these data, the minimum of \( \Psi \) vs \( K_{ndl} \) is rather shallow (flat), and therefore, the value of \( K_{ndl} \) determined by the minimization procedure is rather uncertain. (On the other hand, the minimum of \( \Psi \) vs \( \delta \) is very well pronounced.) We solved the problem in the following way.

Since \( K_{ndl} \) is not expected to depend on \( \xi \), we fixed the value \( K_{ndl} = 1.08 \times 10^7 \), determined for \( \xi = 0.67 \), and processed the data for the other values of \( \xi \) (0.73 \( \leq \xi \leq 1.23 \), see Figure 3) with a single adjustable parameter, \( \delta \). The values of \( \delta \) determined from the best fits are listed in Table 1; all of them are between 4.1 and 4.6 Å, which is a physically reasonable result. The slight decrease of \( \delta \) with the rise of \( \xi \) could be attributed to the increasing "weight" of the spherical micelles when the average micelle size decreases (as mentioned earlier, the area per headgroup is larger for the spherical micelles, for which a smaller \( \delta \) can be expected).

Once we see in Figure 8 that the data from all of the curves in Figure 3, corresponding to \( 0.67 \leq \xi \leq 1.23 \), are in general agreement with the same straight line with intercept and slope corresponding to \( n_0 = 56 \) and \( K_{ndl} = 1.08 \times 10^7 \), see eq 4.1. This result means that the model of micelle growth by Misael et al.

Table 1. Parameter Values Determined from the Fit in Figure 8 for Various Surfactant-to-Al\(^{3+}\) Ratio \( \xi \)

<table>
<thead>
<tr>
<th>( \xi )</th>
<th>( \delta ) (Å)</th>
<th>( \Phi_{A^+} ) (kT)</th>
<th>( \Phi_{S^+} ) (kT)</th>
<th>( \Phi_{M^-} ) (kT)</th>
<th>( \Phi_{I^-} ) (kT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>4.60</td>
<td>4.78</td>
<td>1.72</td>
<td>1.60</td>
<td>0.57</td>
</tr>
<tr>
<td>0.73</td>
<td>4.58</td>
<td>4.76</td>
<td>1.71</td>
<td>1.59</td>
<td>0.57</td>
</tr>
<tr>
<td>0.90</td>
<td>4.50</td>
<td>4.65</td>
<td>1.66</td>
<td>1.55</td>
<td>0.55</td>
</tr>
<tr>
<td>1.00</td>
<td>4.37</td>
<td>4.48</td>
<td>1.59</td>
<td>1.49</td>
<td>0.53</td>
</tr>
<tr>
<td>1.07</td>
<td>4.34</td>
<td>4.44</td>
<td>1.57</td>
<td>1.48</td>
<td>0.52</td>
</tr>
<tr>
<td>1.15</td>
<td>4.18</td>
<td>4.22</td>
<td>1.48</td>
<td>1.41</td>
<td>0.49</td>
</tr>
<tr>
<td>1.23</td>
<td>4.14</td>
<td>4.17</td>
<td>1.45</td>
<td>1.39</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The superscripts c and s denote cylindrical and spherical micelles, respectively.

4.2. Physical Cause for the Micelle Growth.

Processing the experimental data for \( n_0 \) vs \( t = (K_{dl}(X - X_1))^{1/2} \) (see Figure 8), we calculated the values of many physical parameters (such as adsorption energy, micelle surface charge and potential, electrostatic energy per monomer, etc.) which reveal the physical picture and cause of the micelle growth in the investigated system.

Let us start with the adsorption energies, \( \Phi_A \) and \( \Phi_N \), calculated by means of eqs 3.27 and 3.28. Since the areas per headgroup for the cylindrical and spherical micelles are different (\( a_c = 0.64 \, \text{nm}^2; a_s = 1.48 \, \text{nm}^2 \), see Appendix 1), the respective values of \( \Phi_A \) and \( \Phi_N \) are different, see Table 1 and eqs 3.27–3.28; it turns out that the energy of adsorption at a cylindrical micelle is about 2.8 times larger than that at a spherical micelle. In addition, for micelles of the same shape, \( \Phi_A \) is 3 times larger than \( \Phi_N \) due to the 3-fold larger charge of \( A^{3+} \) as compared to \( \text{Na}^+ \).
and concentration, is proportional to $I$. The increase of the bulk $A$ solution is due to the $Na^+$ ions. With the increase of surfactant concentration at fixed $\xi$ and ionic strength (see eqs 2.2 and 3.2), the $Na^+$ ions are replaced by $A^{3+}$ ions, and $c_{NB}$ decreases. In spite of the lower adsorption energy of the $Na^+$ ions ($\Phi_N < \Phi_A$, see Table 1), they can compete with $A^{3+}$ for the adsorption in the Stern layer, especially at the lower values of $X - X_1$, at which $c_{NB}$ is larger than $c_{AB}$, cf. Figures 5 and 9. The true ionic strength of the solutions, $I_1$, calculated from eq 3.4, is very close to $I_0 = 24$ mM for the lowest surfactant concentration ($c = 2$ mM), and it monotonically decreases down to 17–19 mM (depending on $\xi$) for the highest investigated surfactant concentration, $c = 8$ mM. Concerning the screening of the micelle electric potential, this variation of $I_1$ is not significant in so far as the Debye screening parameter $\kappa$ is proportional to $I^{1/2}$, see eq 3.13. It turns out that the variation of the surface charge of the micelles is more important, see below.

Figure 10 presents the occupancy, $\theta_N$, of the Stern layer by $A^{3+}$ as a function of $t = \left(\frac{K_{el}(X - X_1)}{I}\right)^{1/2}$ for the cases of cylindrical and spherical micelles and for various $\xi$. It is not surprising that $\theta_N$ is greater for the cylindrical micelles because the distances between their surfactant headgroups are smaller, and consequently $\Phi_N > \Phi_A$, see Table 1. The increase of $\theta_N$ with the surfactant concentration can be attributed to the increase of the bulk $A^{3+}$ concentration with the rise of $X - X_1$, see Figure 5. At the larger surfactant concentrations, $\theta_N$ approaches 87% for the cylindrical micelles, which means that the micelle surface charges are neutralized to a great extent and that there is not much space left in the Stern layer for the adsorption of $Na^+$ ions.

Figure 11 shows the occupancy, $\theta_S$, of the Stern layer by $Na^+$ ions. The latter may occupy adsorption sites free of $A^{3+}$, and that is the reason why $\theta_S$ is larger for the spherical micelles, which bind less $A^{3+}$ than the cylindrical ones, cf. Figure 10. Anyway, in these experiments, $\theta_S$ may increase up to 15% (Figure 11), and it should not be neglected when calculating the micelle surface charge. It is interesting to note that, unlike the surface charge, the calculated surface potential is almost the same for the spherical and cylindrical micelles at the same surfactant concentrations. The dimensionless micelle surface potential, $\psi_0$, cf. eqs 3.12 and 3.16, decreases from 2.5 to 1.6 with the rise of surfactant concentration. The fact that the spherical micelles are markedly more charged as compared to the cylindrical ones, see Figure 12, is very important for the understanding of the physical cause of the micelle growth. The fact is that $\alpha_S > \alpha_C$ leads to a greater electrostatic energy per monomer in the spherical micelles, $g_{el}^S > g_{el}^C$. The difference $g_{el}^S - g_{el}^C$...
Figure 12. Calculated degree of charging, see eq 3.24, for cylindrical and spherical micelles: $\alpha_c$ and $\alpha_s$, respectively, plotted vs $(K_{dl}(X - X_1))^{1/2}$; the symbols correspond to the same values of $(X - X_1)^{1/2}$ as those of the data points in Figure 3.

Figure 13. Calculated difference between the electrostatic energies of a surfactant monomer incorporated in a spherical and cylindrical micelle, $g_s^e$ and $g_c^e$, respectively, plotted vs $(K_{dl}(X - X_1))^{1/2}$ for various $\xi$; the symbols correspond to the same values of $(X - X_1)^{1/2}$ as those of the data points in Figure 3.

is plotted vs $t = (K_{dl}(X - X_1))^{1/2}$ in Figure 13. One sees that $g_s^e - g_c^e$ increases with the increase of the surfactant concentration, $X - X_1$, and with the decrease of $\xi$. The mean aggregation number of the micelles, $n_m$, behaves in the same way, cf. Figure 3. In other words, the formation of larger cylindrical micelles is energetically more favorable because they bear a lower surface charge, and consequently, they have lower electric energy (per monomer) than the spherical micelles. In our case $g_s^e - g_c^e$ is less than 0.14 kT (Figure 13), whereas $g_s^e$ and $g_c^e$, separately, are about 10 times larger (from 1 to 1.5 kT).

In spite of the fact that the difference $g_s^e - g_c^e$ is relatively small (as compared to $g_s^e$ or $g_c^e$), it affects strongly the micellization parameter $K_{dl}$ because it enters eq 3.7 multiplied by the aggregation number $n_m \approx 56$. Figure 14 shows the calculated micellization parameter $K = K_{dl}K_{ndl}$ vs $(X - X_1)^{1/2}$. It turns out that for the investigated solutions, the plots are straight lines, which are different for the different values of $\xi$. Note that the variation of $K$ is, in fact, due to the variation of $K_{dl}$ because, as mentioned earlier, the nondouble-layer contribution into $K$ is expected to be independent of the surfactant and electrolyte concentrations and is determined to be $K_{ndl} = 1.08 \times 10^7$.

4.3. Discussion about the Importance of the Electrostatic Effects. Finally, let us come back to the discussion about the importance of the two types of electrostatic effects in micellar solutions of ionic surfactants as formulated in the Introduction: (i) electrostatic energy of micellization and (ii) electrostatic interaction between the micelles. The whole of our analysis in this study shows that effect (i), rather than effect (ii), is the decisive factor influencing the micelle growth in the presence of $A^{3+}$ ions in the investigated range of solute concentrations. Quantitatively, the most important factor influencing the micelle growth turns out to be the binding of $A^{3+}$ counterions to the micelle surface, which has a very strong effect on the value of the micellization constant, $K$. The latter can vary by orders of magnitude with the increase of $A^{3+}$ ions studied by Missel et al. $^3$ is similar, i.e., the steric nonidealities are predominant. Their importance for the micellar growth can be estimated by means of the criterion, eq 2.8 above, which was derived by Missel et al. $^9$ The latter authors worked with expressions for an ideal solution because in their case, $X/X^* \leq 0.4$, see p 8359 in ref 9. In our case, the nonidealities should be even smaller in so far as for our solutions $X/X^* \leq 0.3$. In other words, following ref 9, we can also claim that the nonidealities in our micellar solutions do not essentially affect the micelle growth.

In addition to the $X/X^*$ criterion, and independently from it, we compared experimental data for $L_G$ and $L_H$, which again show that the micelle–micelle interactions do not essentially affect the micelle size distribution, see Figure 2 and the related discussion.

A fourth argument in favor of the negligibility of the micelle–micelle interactions is the general agreement of
the experimental data with the theoretical line (based on eq 1.1), see Figure 8 above. Note that Figure 8 contains 49 experimental points obtained at various concentrations of surfactant and Al$^{3+}$ and Na$^+$ ions, all of them complying with the same theoretical line, drawn by varying only two adjustable parameters, $\delta$ and $K_{a,Al}$. Moreover, we have determined the values $\delta = 4.64 A$ and $K_{a,Al} = 1.08 \times 10^7$ only from the data with $\xi = 0.67$, and it turns out that the data for all other $\xi$ (0.73 $\leq \xi \leq 1.23$) conform to the same fit without adjusting any parameter. Of all, the intercept of the theoretical line (Figure 8) gives the correct value of the aggregate number of the spherical micelles, $n_0 \approx 56$. We believe this agreement between the theoretical model and the experimental data is not fortuitous.

The above arguments lead us to believe that the theoretical model proposed by us (an extension of the ladder model) is, in general, adequate to the experimental situation.

5. Conclusions

This work was provoked by the finding$^{14}$ that there is no adequate theory for interpreting experimental data for the growth of rodlike micelles in the presence of 3:1 electrolyte. The available ladder model by Missel et al.$^3$ is originally designed for 1:1 electrolyte. To solve the problem, we undertook additional experimental and theoretical investigations. In particular, we demonstrated that the ladder model can be extended to 3:1 electrolytes.

First of all, we gathered additional dynamic light scattering data, see the lines with $\xi = 0.90, 1.00, \text{ and } 1.15$ in Figure 3. The new data confirm the finding in ref 14 that the micellar growth in the presence of Al$^{3+}$ does not obey eq 1.8 at fixed $K$. In addition, the results of independent dynamic and static light scattering measurements imply that the effect of the micelle–micelle interactions on the measured diffusion coefficient and mean mass aggregation number, $n_M$, can be neglected (in first approximation) for the surfactant and electrolyte concentrations used, see Figure 2 and eq 2.8.

We carried out ultrafiltration experiments which revealed that the predominant part (from 68 to 89%) of Al$^{3+}$ is associated with the micelles (Figure 4). We derived an expression, eq 2.13, which allows estimating the concentration, $c_{Al}$, of Al$^{3+}$ remaining in the background solution at a given surfactant concentration, $c_s$, see Figure 5.

The latter dependence of $c_{Al}$ on $c_s$ turns out to be crucial for the interpretation of the experimental data. Indeed, the equilibrium constant, $K$, depends on $c_{Al}$, and in addition, $c_{Al}$ increases with the rise of $c_s$ at fixed $\xi$, see Figure 5. This leads to an indirect dependence of $K$ on $c_s$. It turns out that to check whether our experimental data complies with the ladder model, eq 1.8, one should derive the theoretical dependence of $K$ vs $c_s$. This is done in section 3; see also Figure 14. The comparison of the theory with the experiment shows a good agreement. In particular, the data from all curves in Figure 3 are in agreement with a straight single line in Figure 8 as predicted by the ladder model, complemented with the theory from section 3, see eq. 4.1.

Experimentally we achieved constant $\xi$ at fixed ionic strength by diluting step by step the initial concentrated surfactant solution with solution of NaCl of the same ionic strength containing surfactant of concentration equal to the cmc. The theoretical results from section 3 allowed us to understand what happens with the micelles in the solution when the latter is diluted. The resulting physical picture is the following:

(i) The decrease of the surfactant concentration in these experiments is accompanied by a decrease of the background Al$^{3+}$ concentration (Figure 5).

(ii) This leads to a decrease of the Al$^{3+}$ adsorption in the micelle Stern layer (Figure 10) and to the increase of the surface charge of the micelles (Figure 12).

(iii) The cylindrical micelles have a lower degree of charging and lower electric energy per monomer, $g^4$, compared to the spherical micelles. That is the reason why the formation of cylindrical micelles is energetically favorable. When the solution was diluted the difference between the values of $g^4$ for spherical and cylindrical micelles decreases (Figure 13), and consequently, the micelle size diminishes.

From a practical viewpoint, it should be noted that the long cylindrical micelles formed in the presence of Ca$^{2+}$ and Al$^{3+}$ exhibit a solubilization efficiency markedly larger than that of the common spherical micelles, see Figure 10 in ref 14. In other words, the same amount of surfactant solubilizes more oil when it is organized as large cylindrical (rather than small spherical) micelles. This finding could be employed in detergency. An extension of this study to solutions containing Ca$^{2+}$ was recently carried out.$^{52}$

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Appendix 1: Procedure of Calculation of $n_M$, $a_s$, and $a_c$

We utilized the procedure from ref 14 to calculate the micelle aggregation number, $n_M$, using the radius and the length of the spherocylinders (Figure 1) determined from the dynamic light scattering data (see section 2.2). The procedure itself is the following:

(i) From the measured autocorrelation function of the scattered intensity one calculates the mass average diffusion coefficient, $D$, using exponential sampling method.

(ii) For the smallest spherical micelles from the value of $D$, one calculates the outer (hydrodynamic) radius of the micelle, $R_{out} = R_D$; the value of $R_{out}$ thus obtained coincides (in the framework of the experimental accuracy) with the value $R_{out} = 2.77 \text{ nm}$ determined from the literature data$^{1,20}$ for the lengths of the constitutive fragments of a SDP2S molecule. The radius of the cross section of a rodlike micelle is assumed to be equal to $R_{out}$.

(iii) From the value of $D$ for the rodlike micelles, one calculates their average length, $L_V$, by using eqs 2.8–2.14 in ref 14; $L_V$ includes the length of the cylinder and the two hemispherical caps, see Figure 1.

(iv) The average volume of the hydrophobic core of a micelle, $V_{core}$, is then calculated from the values of $L_V$ and $R_{out}$ by using the following geometrical relationship

$$V_{core} = \pi (R_{out}^2 - L_{head})^2 (L_H - 2R_{out}) + \frac{4}{3}\pi (R_{out}^3 - L_{head}^3) \text{ (A.1)}$$

Here, $L_{head} = 1.1 \text{ nm}$ is the length of the hydrophilic headgroup of a SDP2S molecule (2 oxyethylene groups + 1 SO$_4^-$ group) determined from literature data.$^{1,28}$

(v) Finally, we calculate the average aggregation number

$$n_M = V_{core}/V_{tail} \text{ (A.2)}$$

where $V_{tail}$ is the volume occupied by the hydrocarbon tail
of a single surfactant molecule; for a dodecyl chain, the literature data\(^{1,26}\) yield \(V_{\text{mol}} = 0.3502 \text{ nm}^3\).

The values of areas per headgroup at the surfaces of the spherical and cylindrical micelles, \(a_s\) and \(a_c\), used in the calculation procedure described in Appendix 2, are determined as follows:

(a) From the light scattering data we know that \(n_0 \approx 56\); in addition, the calculations based on the light scattering data and the molecular structure yield \(R = 2.57 \text{ nm}\) for the radius of the sphere at which the centers of the \(\text{SO}_4^-\) groups are located. Then, one obtains the area per \(\text{SO}_4^-\) group at the surface of a spherical micelle to be

\[
a_s = \frac{4\pi R^2}{n_0} = 1.48 \text{ nm}^2 \quad (\text{A.3})
\]

(b) Next, we calculate the area per SDP2S molecule at the sphere, which divides the hydrophobic core of a spherical micelle from its hydrophilic headgroup region

\[
a_s^{(\text{core})} = \frac{4\pi R_{\text{core}}^2}{n_0} = 0.63 \text{ nm}^2 \quad (\text{A.4})
\]

where \(R_{\text{core}} = 1.67 \text{ nm}\) is the radius of the micelle hydrophobic core; \(R_{\text{core}} = 1.67 \text{ nm}\) is also the length of a dodecyl chain.

(c) Then we use the "packing constraint" of Israelachvili et al.\(^{15}\) to calculate the area per surfactant molecule at the dividing surface between the hydrophobic core and the hydrophilic headgroup region of a cylindrical micelle

\[
a_c^{(\text{core})} \approx a_s^{(\text{core})}/1.5 = 0.42 \text{ nm}^2 \quad (\text{A.5})
\]

(d) Finally, we estimate the area per \(\text{SO}_4^-\) group at the surface of a cylindrical micelle using the following geometrical relationship

\[
a_c = a_c^{(\text{core})} \frac{R}{R_{\text{core}}} = 0.64 \text{ nm}^2 \quad (\text{A.6})
\]

Note that \(a_s/a_c = 2.3\), but nevertheless, the packing constraint, eq A.5, is satisfied.

**Appendix 2: Numerical Procedure for Fitting the Experimental Data**

The aim of the numerical procedure is to fit the experimental data from Figure 3 plotted as \(n_M \text{ vs } t = [K_{\text{dl}}(X - X_i)]^{1/2}\), see eq 4.1. \(n_M\) is given by the experiment. In addition, we have \(X - X_i = 0.018(c_c - \text{cmc}) = 0.018c_{\text{CM}}\) where the values of \(c_c\) and \(\text{cmc}\) (in \(\text{mol/L}\)) are also known from the experiment. Therefore, the main efforts are directed to the calculation of \(K_{\text{dl}}\) for given values of \(c_{\text{CM}}\) and \(\xi\).

1. The input parameters are \(R = 2.57 \times 10^{-7} \text{ cm}, e = 4.8 \times 10^{-10} \text{ CGSE units}, K_T = 4.1 \times 10^{-14} \text{ erg}, \epsilon = 77.5, \epsilon_{\text{sd}} = 55.5\); the diameters of \(\text{Na}^+\) and \(\text{Al}^{3+}\) ions are \(\delta_N = 0.72 \text{ nm}\) and \(\delta_A = 0.96 \text{ nm}\), respectively; the aggregation number of the smallest spherical micelles is \(n_0 = 56\). The values of \(\xi\) for these separate experimental curves are shown in Figure 3; \(c_{\text{SM}}\) is an input variable characterizing the experimental points, see also eq 3.5. The constant in the Langmuir isotherm, eq 2.13, is also known: \(B = 8.5 \times 10^{-5} \text{ M}\).

In the case of cylindrical micelle we set

\[
m = 1, \quad a = 0.64 \text{ nm}^2 \quad (\text{B.1})
\]

In the case of spherical micelle we set

\[
m = 2, \quad a = 1.48 \text{ nm}^2 \quad (\text{B.2})
\]

(see Appendix 1 for the values of \(a\)). The adjustable parameters are \(K_{\text{dl}}\) and the thickness of the Stern layer, \(\delta\), see eqs 3.6 and 3.27. From the input value of \(\delta\), we calculate \(\Phi_A\) and \(\Phi_N\) from eqs 3.27 and 3.28.

2. For given \(c_{\text{SM}}\) and \(\xi\), we calculate \(c_{\text{AB}}\) from eqs 2.12 and 2.13. Then, \(I_i\) is calculated from eq 3.4, and \(c_{\text{AB}}\) is calculated from the equation

\[
c_{\text{AB}} = 2I_i - I_0 - 9c_{\text{AB}} + 3c_{\text{AT}} - \text{cmc} \quad (\text{B.3})
\]

which follows from eqs 3.3 and 3.4; \(I_0 = 0.024 \text{ M}\) and \(a_{\text{Na}} \approx 0.20\); the results are not sensitive to the value of \(\alpha_{\text{Na}}\). Then we calculate \(\alpha\) and \(\lambda\) from eq 3.13.

3. Further, assuming a tentative value of \(y_0\), we calculate \(u, J, (u), s, b_n,\) and \(b_0\) from eqs 3.19–3.21 and 3.26. Then, \(\alpha(y_0)\) is calculated from eqs 3.24 and 3.25. The results are substituted in the equation

\[
\alpha^2 \left( \frac{4\pi e^2}{\epsilon k T \alpha^2} \right)^2 = 4 \sinh^2 \frac{y_0}{2} + \lambda^2 u^6 (1 + 3e^{-y_0}) + \frac{2m}{\epsilon k R} \left[ 8 \sinh^2 \frac{y_0}{4} + \lambda J \left( \frac{u}{4} \right) \right] \quad (\text{B.4})
\]

(stemming from eqs 3.14, 3.21, and 3.23), which is solved numerically to determine \(y_0\). In this way, one obtains also the values of \(\theta_s, \theta_n,\) and \(\alpha\).

4. Next, we calculate \(g\) by means of eq 3.22, where \(e, u, \) and \(s\) are given by eqs 3.21 and 3.23. The integral in 3.22 is to be solved by numerical integration.

5. The values of \(g\) calculated for cylinder, eq B.1, and for sphere, eq B.2, are substituted in eq 3.7, and thus, \(K_{\text{dl}}\) is determined.

6. For each experimental value of \(X - X_i\), we calculate the quantity \(t = [K_{\text{dl}}(X - X_i)]^{1/2}\). The theoretical value of \(n_M\) is calculated by means of eq 4.1.

7. The adjustable parameters \(\alpha\) and \(K_{\text{dl}}\) are determined from the fit of the experimental data for \(n_M \text{ vs } t\) by means of the least-squares method by minimization of the function \(\psi(\alpha, K_{\text{dl}})\) in eq 4.2. For \(\xi = 0.67\) we obtain \(K_{\text{dl}} = 1.08 \times 10^7\). Since \(K_{\text{dl}}\) is not expected to depend on \(\xi\), we fixed \(K_{\text{dl}} = 1.08 \times 10^7\) and processed the data for the other values of \(\xi (0.73 \leq \xi \leq 1.23, \text{see Figure 3})\) with a single adjustable parameter, \(\delta\).