Growth of wormlike micelles in nonionic surfactant solutions:
Quantitative theory vs. experiment

Krassimir D. Danov a, Peter A. Kralchevsky a, Simeon D. Stoyanov b, c, d, Joanne L. Cook e, Ian P. Stott e, Eddie G. Pelan b, f

a Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Sofia 1164, Bulgaria
b Unilever Research & Development Vlaardingen, 3133 AT Vlaardingen, The Netherlands
c Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands
d Department of Mechanical Engineering, University College London, WC1E 7JE, UK
e Unilever Research & Development Port Sunlight, Bebington CH63 3JW, UK
f School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

ABSTRACT. Despite the considerable advances of molecular-thermodynamic theory of micelle growth, agreement between theory and experiment has been achieved only in isolated cases. A general theory that can provide self-consistent quantitative description of the growth of wormlike micelles in mixed surfactant solutions, including the experimentally observed high peaks in viscosity and aggregation number, is still missing. As a step toward the creation of such theory, here we consider the simplest system – nonionic wormlike surfactant micelles from polyoxyethylene alkyl ethers, C i E j. Our goal is to construct a molecular-thermodynamic model that is in agreement with the available experimental data. For this goal, we systematized data for the micelle mean mass aggregation number, from which the micelle growth parameter was determined at various temperatures. None of the available models can give a quantitative description of these data. We constructed a new model, which is based on theoretical expressions for the interfacial-tension, headgroup-steric and chain-conformation components of micelle free energy, along with appropriate expressions for the parameters of the model, including their temperature and curvature dependencies. Special attention was paid to the surfactant chain-conformation free energy, for which a new more general formula was derived. As a result, relatively simple theoretical expressions are obtained. All parameters that enter these expressions are known, which facilitates the theoretical modeling of micelle growth for various nonionic surfactants in excellent agreement with the experiment. The constructed model can serve as a basis that can be further upgraded to obtain quantitative description of micelle growth in more complicated systems, including binary and ternary mixtures of nonionic, ionic and zwitterionic micelles, which determine the viscosity and stability of various formulations in personal-care and house-hold detergency.

Keywords: Wormlike micelles; Micelle growth; Nonionic surfactants; Micelle free energy; Polyoxyethylene alkyl ethers.

* Corresponding author. Tel.: +359 2 962 5310
E-mail address: pk@lcpe.uni-sofia.bg (P.A. Kralchevsky)
Contents
1. Introduction
   1.1. Micellization and micelle shape transformations
   1.2. Theoretical modelling of micellization and micelle growth
   1.3. Goal and structure of the article
2. Thermodynamics of micelle growth
   2.1. General equations
   2.2. Growth of rodlike micelles – linear aggregate model
3. Systematization of experimental data for nonionic wormlike micelles
4. Molecular aspects of the model
   4.1. Molecular geometric parameters
   4.2. Components of micelle free energy
   4.3. Model of spherocylindrical micelles
5. Chain-conformational free energy
   5.1. Formulation of the variational problem
   5.2. Expression for the free energy per molecule
6. Quantitative predictions of the theoretical model
   6.1. Determination of the radius of micelle cylindrical part
   6.2. Determination of the spherical cap radius
   6.3. Chemical potential vs. free energy per molecule
   6.4. Numerical data for the free-energy components
7. Comparison of theory and experiment
   7.1. Temperature dependence of the headgroup cross-sectional area
   7.2. Cylinder radius and size of the end-caps
8. Summary and conclusions
Acknowledgements
Appendix A. Analytical solution of the variational problem
References

1. Introduction

1.1. Micellization and micelle shape transformations

In 1913, the existence of self-assembled surfactant aggregates was suggested by McBain [1], who introduced the term “micelles” in relation to the interpretation of experimental data for the electrolytic conductivity and osmotic activity of carboxylate solutions [2,3]. McBain considered two types of aggregates: (i) small oligomeric surfactant clusters with approximately 10 molecules, and (ii) lamellar (disclike) aggregates consisting of two layers of 50 to 100 soap molecules. Harkins et al. [4] recognized that the orientations and
packing of surfactant molecules at an interface depend on the molecular shape, which is closely related to the possible shapes of the micelles in the bulk. The micellar structures proposed by Hess, Philippoff et al. [5–7] represent McBain lamellar aggregates separated by layers of water. Harkins et al. [8–10] used lamellar (disclike) micelles to interpret their X-ray and solubility data. They introduced the idea that the micelles could have also cylindrical and ellipsoidal shapes [11]. The proposed small lamellar micelles are energetically unfavorable because of the contact of surfactant tails with water at their periphery. Adam [12] proposed the idea that “molecules larger at their polar ends will naturally pack into a curved film having the hydrocarbon side concave and the water attracting side convex, and such a film will fit the surface of an emulsion of oil dispersed in water”, which in fact postulates the possibility to have spherical micelles (Fig. 1a). Hartley [13–15] suggested that the surfactant aggregates tend to present the minimum surface to the water, they are “roughly spherical of the largest radius with none of the heads being submerged in the paraffin interior”. Corrin and Harkins [16,17] interpreted their experimental data assuming spherical shape of the micelles. The surfactant concentration, at which spherical micelles appear, was called critical micelle concentration (CMC). The definite answer of the question about the shapes of micelles and self-assembly of surfactant in solutions was not found from experimental and theoretical viewpoints up to 1951, when Philippoff [18] concluded that “all standard methods for determining the shape of dissolved particles, indicate that there is no significant departure of the shape of soap micelles from a sphere…. A practically spherical shape does not mean the micelles are true spheres: cubes, short cylinders, prisms or spheroids are all indistinguishable”. A comprehensive historical review on the early studies on micellization was published by Vincent [19].

![Fig. 1](image)

Fig. 1. Schematic presentation of the structure of surfactant aggregates in aqueous solutions: (a) spherical micelle; (b) spherocylindrical (rodlike, wormlike) micelle.

The development of powerful experimental techniques (static and dynamic light scattering, small angle X-ray and neutron scattering, electron paramagnetic resonance, nuclear magnetic resonance, etc.) gave the possibility to study complex self-assembly, phase behavior and structural behavior of surfactant solutions and microemulsions. It was established that the
micelles can have different shapes, sizes, aggregation numbers, and compositions depending on surfactant and salt concentrations: small spherical and ellipsoidal micelles; discs; cylindrical and wormlike micelles; branched micelles; vesicles, and different types of lamellar structures. The real microstructure of micellar systems in solutions were revealed by using small angle scattering [20] and cryogenic transmission electron microscopy (cryo-TEM) [21].

Very frequently, concentrated surfactant solutions contain rodlike/wormlike micelles [22]. Such micellar systems find applications in personal-care and home-care detergency; drug delivery; oilfield industry; turbulent drag-reduction applications, etc. [23–26]. Disclike micelles (nanodiscs or bicelles) [27,28] are a rare form of surfactant self-assembly as compared to the others types of micelles. Disclike micelles were experimentally observed in both single-component and mixed systems, and ribbon-like micelles were observed as well [29-31].

The concentrated surfactant solutions show complex phase behavior and non-monotonic trends in their viscoelastic properties, with one or two peaks in the zero-shear viscosity as a function of surfactant concentration, temperature, pH, and concentration of added salt [32–59]. The viscosity of micellar solutions is directly related to their microstructure. The viscosity increases with the rise of concentrations of surfactant and added salt – the micelles transform from spheres to small elongated ellipsoids, cylinders (rods); the longer cylindrical (rodlike) aggregates are termed wormlike micelles because of their flexibility. The concentration, at which the micelles transform from spheres to cylinders is known as the second CMC. Upon variation of composition of the micellar system, the wormlike micelles may undergo a subsequent shape transformation, which leads to decrease in viscosity at higher concentrations of surfactant and/or electrolyte. Thus, a peak appears in the concentration dependence of viscosity. Several possible reasons for the decrease of viscosity at higher concentrations have been reported: (i) shortening of the wormlike micelles; (ii) formation of multiconnected (branched) micelles; (iii) shape transition to discs; (iv) phase transition to lamellar or liquid crystal mesostructures; (v) formation of spherical swollen micelles, and (vi) phase separation [60–78]. From practical viewpoint it is important to control the micelle shape, size and aggregation number in order to produce formulations with well-defined physicochemical and rheological properties.

The transition region between spherical and wormlike micelles deserves a special attention. With the nonionic surfactant C_{12}E_{5}, Talmon et al. [79] observed coexistence of
spheroidal and threadlike micelles, but short and medium length cylindrical micelles were absent.

1.2. Theoretical modelling of micellization and micelle growth

The theoretical physicochemical reasons for micellization were first considered by Debye [80,81]. Hobbs [84] extended the Debye theory to electrolyte solutions and obtained semi-empirical expressions for the increase of micelle size and decrease of the CMC with the rise of salt concentration. Halsey [83] studied one-dimensional growth and formation of plate-like micelles. Ooshika and Reich [84,85] showed that the surface energy of the water/micelle-core interface is that, which opposes the headgroup repulsion. These authors proposed the minimization of the free energy of the whole solution (containing surfactant monomers, water molecules, and micellar aggregates) as a general principle for determining the micelle size and the CMC. Debye and Anacker [86] showed that at high salt concentrations the ionic micelles should be rodlike. Statistical mechanical theory was first applied for description of the micelle formation and CMC in Refs. [87,88], where spherical and ellipsoidal shapes of the micelles were considered. Contributions from the molecular degrees of freedom (translation, rotation, and vibration), solvent interactions, and electrostatic forces were taken into account [87–89].

The Tanford free energy model combined concepts formulated in the simpler earlier theories and included the most important physicochemical factors that control the micelle formation and growth [90–92]. Israelachvili, Mitchel, and Ninham [93] developed the first geometry-based approach to predict the self-assembly of surfactant molecules in aggregates of different shapes. They introduced the packing parameter, $p$, which characterizes the geometry of the various possible aggregates: $p = 1/3$ for spheres; $1/3 < p < 1/2$ for ellipsoidal, globular and toroidal shapes; $p = 1/2$ for cylinders; $1/2 < p < 1$ for vesicles and $p = 1$ for bilayers (lamellas). They considered the wormlike micelles as “cylindrical micelles with globular ends”, in which the radius of the cylindrical part is less than, or equal to, the radius of the endcaps (truncated spheres; see Fig. 1b), and introduced the concept of “linear aggregates”. The Tanford energy approach was applied to aggregates of different shapes to explain the formation of micelles and their shape transformations on the basis of general thermodynamic principles [93]. Review on the theoretical models that predict the CMC and electric conductivity of micellar surfactant solutions (phase separation model; mass action model; molecular thermodynamic models, and the quantitative structure-property relationship approach) can be found in Ref. [94].
The current picture of the rodlike micelles was introduced by Debye and Anacker [86] and experimentally confirmed by Scheraga and Backus [95], who pointed out that the micellar size distribution should be highly polydisperse. Using a stepwise association model, Mukerjee derived the popular formula showing that the mean mass aggregation number of the cylindrical micelles, $n_M$, is proportional to the square root of surfactant concentration [96-98]:

$$n_M \approx 2[K(X_S - X_S^0)]^{1/2}$$

Here, $X_S$ is the molar fraction of surfactant in the solution; $X_S^0$ is a constant parameter close to the value of $X_S$ at the CMC; the proportionality coefficient, $K$, was called “the micellar growth parameter” [93,99-101]. For simplicity, Misel et al. [100] considered the rodlike micelles as cylinders with hemispherical caps and equal radii corresponding to the extended length of surfactant tail. They assumed that the chemical potentials of molecules in the micelle cylindrical part, $\mu_c$, and in the spherical end-caps, $\mu_s$, are different and derived a simple formula for the micellar growth parameter,

$$k_B T \ln K = n_s(\mu_s - \mu_c)$$

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $n_s$ is the total number of surfactant molecules in the caps. Analogous result was obtained also for disclike micelles [101]. Detailed review on the different thermodynamic models used in the literature for the description of micellar solutions can be found in Ref. [102]. The thermodynamic theory of growth of nonionic cylindrical micelles is described in Refs. [93,99–101].

The value of CMC is determined by the difference between the chemical potentials of a surfactant molecule in the state of free monomer in the bulk and when incorporated in a micelle. This difference is typically of the order of $10^{-16}$ $k_B T$, so that small inaccuracies in the calculated chemical potentials do not essentially affect the predicted value of the CMC. In contrast, according to Eq. (1.2) errors in the calculated $\mu_c$ and $\mu_s$, of the order of $0.1 k_B T$, multiplied by (e.g.) $n_s = 70$, lead to enormous relative errors in the micellar growth parameter, $K$. This circumstance makes the quantitative prediction of $K$ extremely difficult and sensitive to the precise calculations of the different contributions to the micelle excess free energy. Hence, the use of exact thermodynamic relations and correct values of the input molecular parameters is needed. To identify the best quantitative theory among the various possible models, one has to compare their predictions with reliable sets of experimental data for $K$. The experimental determination of $K$ is based on measuring the dependence of micelle mean mass
aggregation number, $n_M$, on the surfactant molar fraction $X_S$, followed by fits of the data with Eq. (1.1). The available sets of experimental data for determination of $K$ are not so many; they include data for ionic surfactants in the presence of various salts [103–118] and data for nonionic surfactants and their mixtures [119–132].

After 1990, Nagarajan and Ruckenstein [133–142] and Blankschtein et al. [143–152] developed molecular-thermodynamic approaches to the theory of micellization, transitions in micelle shape, and solubilization, which will be abbreviated NR and BS approaches, respectively. There are two main differences between these two approaches (models), as follows.

First, the theoretical expressions used to quantify contributions of different origin to the micelle free energy are different in the BS and NR models. For example, the BS model takes into account the Tolman effect on the micelle hydrocarbon/water interfacial tension, $\sigma$, which makes $\sigma$ curvature dependent, whereas $\sigma$ is assumed curvature independent in the NR model. Moreover, in the NR model the conformational free energy of surfactant tails in the micellar core is calculated by using the mean-field theory due to Semenov [153], while the BS model uses a different theory of chain packing in amphiphilic aggregates [154–161], which leads to different curvature dependence. In the electrostatic component of free energy of ionic surfactant micelles, the effect of counterion binding is taken into account in the BS approach [150,151], whereas this effect is missing in the NR approach.

Second, both the NR and BS approaches use minimization of the total free energy of the wormlike micelles with respect to the radius of their cylindrical parts. Furthermore, in the NR approach the free energy of the spherical end-caps is also minimized with respect to their radius and the most probable (optimal) micelle shape is calculated. In the BS approach, $\mu_s$ is estimated in a different way, viz. as the value of the free energy per molecule in a separate spherical micelle of aggregation number $n_s$. The equilibrium value of $n_s$ refers to the minimal micellar free energy. The latter could correspond either to a local minimum at a certain micellar radius, $R$, in the physical interval $0 < R \leq l$ (with $l$ being the length of the extended surfactant molecule), or to the free energy value at $R = l$, if the free energy decreases with the rise of $R$. In the cases considered in Refs. [162,163], computations based on the chain-packing theory used by these authors show that the optimal spherical micelle corresponds to the case $R = l$. 

7
The NR and BS approaches have been applied in different studies for molecular-thermodynamic modeling of specific ion effects on the micellization and growth of ionic surfactant micelles [164–166].

A theoretical approach, which is alternative to the molecular-thermodynamic modeling, is the computer simulation using, e.g., molecular dynamics. Cross-grained molecular dynamic simulations have been used to investigate the mechanisms of self-assembly of surfactant molecules; transitions from spherical to rodlike micellar shapes; branching of micelles, and the formation of more complex micellar structures [167–184]. These calculations give impressive qualitative pictures, which help to visualize and clarify the structural assumptions made in the molecular thermodynamic approach. At present, quantitative information about the values of the micellar growth parameter, $K$, of large wormlike micelles cannot be obtained using cross-grained molecular dynamics because of computer limitations. Another promising method for computer simulation of self-assembled structures in concentrated surfactant solutions is the dissipative particle dynamics (DPD), which is a mesoscale simulation technique developed in the works by Warren et al. [185-187].

1.3. Goal and structure of the article

As already mentioned, a general molecular-thermodynamic theory that provides a self-consistent quantitative description of the growth of wormlike micelles in solutions of nonionic, ionic, zwitterionic, and mixed surfactant solutions, including the experimentally observed peaks in viscosity and aggregation number, is still missing. As a step toward the creation of such theory, here we focus our attention on the simplest system – nonionic wormlike surfactant micelles. Our goal is to construct a molecular-thermodynamic model, which is in agreement with the available experimental data for nonionic wormlike micelles. For this goal, in Section 2 we present the thermodynamic basis of theory in a form that is appropriate for further generalization. In Section 3, we have collected and systematized the available experimental data for the mean aggregation number, $n_M$, of wormlike nonionic micelles, which are fitted with Eq. (1.1) to determine the micelle growth parameter, $K$ at various temperatures. We found that neither the NR, nor the BS model can give quantitative description of the obtained set of data for $K$. To solve the problem, we constructed various versions of models that contain “fragments” from the NR and BS models, as well as other formulas, which are necessary to close the system of equations. Thus, by trials and errors we arrived at a new model, which is in excellent agreement with the full set of experimental data for nonionic wormlike micelles. This model is described in Section 4. The expression for the
chain-conformation component of micelle free energy is considered separately in Section 5, where the Semenov formulas [153] are generalized for arbitrary values of the packing parameter, \( p \). (Note that this parameter can vary in the range \( 1/3 \leq p \leq 3/8 \) for the micelle end-caps, and this variation should be taken into account when minimizing the micelle free energy.) Section 6 presents the principles of the computational procedure and reports theoretical predictions about the micelle free-energy curves. The contributions from different free-energy components are compared and the issue about the chemical equilibrium between the micelle cylindrical part and the spherical end-caps is discussed. Finally, in Section 7 the model is compared with the data for wormlike micelles in aqueous solutions of polyoxyethylene alkyl ethers, \( C_iE_j \) (as usual, \( C \) stands for carbon atom; \( E \) stands for ethylene-oxide group; \( i \) and \( j \) denote the numbers of the respective groups). The micelles from these surfactants grow with the rise of \( T \) because of shrinkage of the ethylene-oxide headgroups due to enhanced segment-segment attraction.

2. Thermodynamics of micelle growth

2.1. General equations

Here, the thermodynamic relations are presented in general form based on preceding studies [93,99-101,134,143,188]. Let us consider a micellar aqueous solution of a single nonionic surfactant. The mole fractions of the various components in the solution are defined by the expressions:

\[
X_w = \frac{N_w}{N_w + N_S}, \quad X_1 = \frac{N_1}{N_w + N_S}, \quad X_k(s) = \frac{N_k(s)}{N_w + N_S} \quad \text{for} \quad k > 1
\]

Here, \( N_w \) is the number of water molecules; \( N_S \) is the total number of surfactant molecules in the solution; \( N_1 \) is the number of surfactant molecules in monomeric form; \( N_k(s) \) is the number of aggregates that are composed of \( k \) surfactant molecules; \( s \) denotes the shape of the aggregate – for example, we may have cylindrical and disclike micelles that have the same aggregation number, \( k \), but different shapes. The total free energy of the micellar solution, \( G \), can be expressed in the form:

\[
G = N_w(\mu_w^o - k_BT + k_BT \ln X_w) + N_1(\mu_1^o - k_BT + k_BT \ln X_1) \\
+ \sum_{k > 1; s} N_k(s) [g_k^o(s) - k_BT + k_BT \ln X_k(s)] + G_{int}
\]
Here, $\mu_W^o$ is the standard chemical potential of the water molecules; $\mu_1^o$ is the standard chemical potential of free monomers in the aqueous solution, and $g_{k}^o(s)$ is the standard free energy of an aggregate of given shape $s$ and aggregation number $k$. The free energy of interactions between the micelles, $G_{\text{int}}$, is proportional to the micelle volume fraction [143,144]; its contribution to $G$ is important for sufficiently high micelle volume fractions. Here, we consider the cases, in which the contribution of $G_{\text{int}}$ to the total free energy $G$ is negligible.

At equilibrium, the free energy $G$ has a minimum with respect to the variations of the numbers of all components, $N_1$ and $N_k(s)$, $k > 1$. At that, the total number of surfactant molecules in the solution must be constant:

$$N_S = N_1 + \sum_{k>1,s} kN_k(s)$$

(2.3)

The minimization of $G$ under the constraint given by Eq. (2.3) leads to:

$$\frac{\partial G}{\partial N_k} - \lambda \frac{\partial N_S}{\partial N_k} = 0, \quad k \geq 1$$

(2.4)

where $\lambda$ is a Lagrange multiplier. The substitution of Eqs. (2.2) and (2.3) into Eq. (2.4) yields:

$$\mu_1^o + k_BT \ln X_1 = \lambda , \quad g_{k}^o(s) + k_BT \ln X_k(s) = k\lambda \quad \text{for} \quad k > 1$$

(2.5)

Apparently, $\lambda$ is the chemical potential of the free surfactant monomers. Eliminating $\lambda$ between the two expressions in Eq. (2.5), we obtain:

$$X_k(s) = \{X_1 \exp[-f_k^o(s)/k_BT] \}^k \quad \text{for} \quad k > 1$$

(2.6)

$$f_k^o(s) = \frac{g_k^o(s)}{k} \quad \text{for} \quad k > 1$$

(2.7)

where $f_k^o(s)$ is the free energy per surfactant molecule in a micelle of aggregation number $k$. Unlike the case of uniform bulk phases, for micelles $g_k^o(s)$ is not simply proportional to $k$ and, consequently, $f_k^o(s)$ is different from the chemical potential of a surfactant molecule in the respective micelle.
In principle, at given $f_k^o(s)$ and $\mu_k^o$, Eq. (2.6) determines the size distribution of the micelles of given shape with respect to their aggregation number, $k$. At that, $X_1$ is determined from the mass conservation law, Eq. (2.3). However, practical applications of this general system of equations are impossible because of computational restrictions and slow convergence of the series in Eq. (2.3); for details, see Section 2.2. For this reason, some simplifying assumptions are used.

One possible simplification is to specify the shape of the micellar aggregate, which for wormlike micelles can be spherocylindrical, and in the limiting case of small micelles – spherical. Then, in Eq. (2.3) the sum with respect to $s$ has to be replaced with its maximal addend, which corresponds to the optimal (most probable) micellar shape:

$$X_S = \frac{N_S}{N_W + N_S} = X_1 + \sum_{k > 1} kX_k(s_{opt,k})$$  \hspace{1cm} (2.8)

Here, the subscript ‘opt’ denotes that the respective quantity refers to the optimal shape of a micelle with aggregation number $k$. In view of Eq. (2.8), the mean mass (weight) micelle aggregation number, $n_M$, can be calculated from the expression [100]:

$$n_M = \frac{1}{X_S - X_1} \sum_{k > 1} k^2 X_k(s_{opt,k})$$  \hspace{1cm} (2.9)

Likewise, the number-average micelle aggregation number, $n_N$, is [100]:

$$n_N = (X_S - X_1)\left[\sum_{k > 1} X_k(s_{opt,k})\right]^{-1}$$  \hspace{1cm} (2.10)

The above general equations can be used for theoretical predictions of the CMC, the micelle size distribution, and the growth of single component surfactant micelles. Their application to rodlike micelles is described in the next section.

2.2. Growth of rodlike micelles – linear aggregate model

Here, we consider surfactant solutions, in which the optimal aggregate shape is spherical or spherocylindrical (rodlike, wormlike); see Fig. 1. Let $n_t$ be the aggregation number, at which the transition from spherical to spherocylindrical aggregates takes place. In other words, for $k \geq n_t$ the micelles possess a well pronounced cylindrical part (Fig. 1b). The free energy of such aggregates can be expressed in the form [188]:

$$g_k^o(s_{opt,k}) = k\mu_c(R_{opt}) + k_BT E_{sc} \quad (k \geq n_t)$$  \hspace{1cm} (2.11)
where $\mu_c(R_{opt})$ is the chemical potential of a surfactant molecule in the micelle cylindrical part of radius $R_{opt}$, which corresponds to the optimal shape $s_{opt,k}$; $E_{sc}$ is the dimensionless excess energy due to the spherical caps. In Eq. (2.11), $g_k^0(s_{opt,k})$ grows linearly with $k$. For this reason, the respective aggregates have been called “linear aggregates” [188]. The substitution of Eq. (2.11) into Eq. (2.6) yields:

$$X_k(s_{opt,k}) = \frac{1}{K} \{ X_1 \exp\left[ -\frac{\mu_c(R_{opt}) - \mu_{i0}}{k_B T}\right]\}^k \quad (k \geq n_t)$$

(2.12)

where the micelle growth parameter, $K$, is defined as follows:

$$K = \exp E_{sc}$$

(2.13)

Because of its direct relation to $K$, the parameter $E_{sc}$ can be also termed “micelle growth parameter”. Furthermore, using the definitions

$$q = \frac{X_1}{X_B}, \quad \ln X_B = \frac{\mu_c(R_{opt}) - \mu_{i0}}{k_B T}$$

(2.14)

as well as Eq. (2.12) and the mathematical formula

$$\sum_{k=m}^{\infty} \frac{k^n q^k}{k!} = -q \frac{d}{dq} \left( \frac{q^m}{1-q} \right), \quad |q|<1$$

(2.15)

we can represent Eq. (2.8) in the form:

$$X_S = X_1 + \sum_{k=1}^{n_t} k X_k(s_{opt,k}) + \frac{q_{ni}^n}{K} \left[ \frac{q}{(1-q)^2} + \frac{n_t}{1-q} \right]$$

(2.16)

On the one hand, the necessary condition for convergence of the series is $q < 1$, i.e. the mole fraction of free monomers, $X_1$, should be smaller than $X_B$. On the other hand, $n_t$ is a large number (e.g. $n_t = 200$); then, $q$ should be close to 1 – otherwise $q^{n_t}$ would be a small number and then the mass fraction of the rodlike micelles would be negligible. Hence, we should have $X_1 \approx X_B$. Some authors call $X_B$ the second CMC [162,163].

One of the aforementioned difficulties, related to numerical computations using the distribution Eq. (2.12), is due to the fact that it contains exponentiation with base, which is very close to 1, and an exponent $k$ that is a large number. Fortunately, for linear aggregates the series can be summed up analytically using Eq. (2.15). Thus, the series in Eqs. (2.9) and (2.10) acquire the form:
\[ \sum_{k>1} k^2 X_k(s_{opt,k}) = \sum_{1<k<n_1} k^2 X_k(s_{opt,k}) \]

\[ + \frac{q^{n_1}}{K} \left[ \frac{q^2 + q}{(1-q)^3} + \frac{2n_1q}{(1-q)^2} + \frac{n_1^2}{1-q} \right] \]

\[ \sum_{k>1} X_k(s_{opt,k}) = \sum_{1<k<n_1} X_k(s_{opt,k}) + \frac{q^{n_1}}{K(1-q)} \]

(2.17)

(2.18)

If the predominant part of the surfactant exists in the form of large rodlike micelles, then \( q \to 1 \) and one can use power expansions for \( 1-q \ll 1 \). Then, the mean micelle aggregation numbers in Eqs. (2.9) and (2.10) can be expressed in the form [93,100,101]:

\[ n_M = 2[K(X_S - X_S^0)]^{1/2} + \frac{6n_t(n_t-1)+1}{4[K(X_S - X_S^0)]^{1/2}} + \ldots + 2[K(X_S - X_S^0)]^{1/2} \approx 2[K(X_S - X_S^0)]^{1/2} \]

(2.19)

\[ n_N = [K(X_S - X_S^0)]^{1/2} + n_t - \frac{1}{2} + \frac{2n_t(n_t-1)+1}{8[K(X_S - X_S^0)]^{1/2}} + \ldots + [K(X_S - X_S^0)]^{1/2} \]

(2.20)

where \( X_S^0 \) is the intercept of the plot of \( m_M^2 \) or \( m_N^2 \) vs. \( X_S \). The series expansions in Eqs. (2.19) and (2.20) are valid if the predominant part of surfactant exists in the form of rodlike micelles. In general, \( X_S^0 \) is close to \( X_1 \), but it is not completely identical with \( X_1 \), because it contains contributions from the sums over \( 1 < k < n_t \) in Eqs. (2.16) – (2.18). In Section 3, Eq. (2.19) is used for interpretation of light-scattering data, which are in excellent agreement with this equation. Deviations of experimental data from Eq. (2.19) at the lower concentrations could be due to insufficiently large mass fraction of the rodlike micelles in the solution; for example, see Ref. [144] – Fig. 7 therein. Deviations from Eqs. (2.19) and (2.20) at high surfactant concentrations could be due to micelle–micelle interactions.

3. Systematization of experimental data for nonionic wormlike micelles

Systematic light-scattering study on the growth of rodlike nonionic surfactant micelles has been published in Refs. [123-131]. The mean mass aggregation number was determined by data interpretation based on the Sato light-scattering theory of micellar solutions [189]. The micelle growth was investigated for polyoxyethylene alkyl ethers, \( C_iE_j \), at various \( i \) and \( j \), and at various temperatures. Experimental data for the growth of \( C_{12}E_6 \) and \( C_{12}E_8 \) micelles are published also in Ref. [119], where the data for \( C_{12}E_6 \) are in good agreement with those reported in Ref. [123].
Fig. 2. Plots of the experimental micelle mean mass aggregation number, $n_M$, vs. $(X_S - X_S^0)^{1/2}$ in accordance with Eq. (2.19) for (a) $C_{10}E_5$ and (b) $C_{10}E_6$ at various temperatures. $X_S$ is the total surfactant molar fraction in the aqueous solution; $X_S^0$ is a constant parameter – see the text.

In Fig. 2a and b, experimental data from Ref. [127] for the mean mass aggregation numbers, $n_M$, of the micelles in $C_{10}E_5$ and $C_{10}E_6$ aqueous solutions are plotted vs. $(X_S - X_S^0)^{1/2}$ in accordance with Eq. (2.19). For all experimental points, the surfactant concentration is well above the critical micelle concentration (CMC). The data excellently comply with linear dependences. From their slope the experimental values of $\ln K = E_{sc}$ are determined and listed in Table 1. The general trend is that the dimensionless excess energy of the spherical caps, $E_{sc}$, increases with the rise of temperature $T$, but decreases with the increase of the number of ethylene-oxide groups, $j$.

Figs. 3a,b and c, show plots of $n_M$ vs. $(X_S - X_S^0)^{1/2}$ for micellar solutions of $C_{12}E_5$, $C_{12}E_6$, and $C_{12}E_7$ at various temperatures – data from Refs. [123,125]. Figs 3d,e and f show analogous plots of data from Refs. [123-125] for $C_{14}E_6$, $C_{14}E_7$, and $C_{14}E_8$. Again, the data are in excellent agreement with Eq. (2.19) and the values or $E_{sc}$ determined from the slopes of the straight lines are given in Table 1. The data for $C_iE_j$ in Figs 2 and 3 illustrate the tendency that at fixed $i$, the aggregation number $n_M$ decreases with the rise of $j$ (with the rise of headgroup size). In contrast, at fixed $j$, $n_M$ increases with the rise of $i$ (with the length of the alkyl chain). For example, at $T = 40$ °C and $j = 6$, the values of $E_{sc}$ are 16.1, 20.9 and 26.5, respectively, for $C_{10}E_6$, $C_{12}E_6$, and $C_{14}E_6$. We recall that the micelle aggregation number $n_M$ grows proportionally to $\exp(E_{sc}/2)$; see Eqs. (2.13) and (2.19).
Fig. 3. Plots of the experimental micelle mean mass aggregation number, \( n_M \), vs. \( (X_S - X_S^0)^{1/2} \) in accordance with Eq. (2.19) for (a) \( C_{12}E_5 \); (b) \( C_{12}E_6 \); (c) \( C_{12}E_7 \); (d) \( C_{14}E_6 \); (e) \( C_{14}E_7 \), and (f) \( C_{14}E_8 \) at various temperatures. \( X_S \) is the total surfactant molar fraction in the aqueous solution; \( X_S^0 \) is a constant parameter – see the text.

The effect of temperature, \( T \), is also significant. For example, for \( C_{14}E_7 \), the values of \( E_{sc} \) are 17.0, 20.5 and 23.5, respectively, for \( T = 25 \), 35 and 45 °C (Table 1). This effect could be explained with the intersegment attraction in the polyoxyethylene headgroup [188,190],

15
which leads to decrease of its volume and area per molecule at the micelle surface. This effect is quantified in Section 7.1.

Fig. 4. Plots of the experimental micelle mean mass aggregation number, $n_M$, vs. $(X_S - X_S^0)^{1/2}$ in accordance with Eq. (2.19) for (a) $C_{16}E_8$ and (b) $C_{18}E_8$ at various temperatures. $X_S$ is the total surfactant molar fraction in the aqueous solution; $X_S^0$ is a constant parameter – see the text.

Fig. 4 compares data for $n_M$ vs. $(X_S - X_S^0)^{1/2}$ from Ref. [124] for micellar solutions of surfactants of longer chainlength, viz. $C_{16}E_8$ and $C_{18}E_8$. All experimental points correspond to surfactant concentrations well above the CMC ($X_S >> X_S^0$). The effect of alkyl chainlength is clearly visible in Fig. 4: the range of variation of $n_M$ for $C_{18}E_8$ is one order of magnitude greater than for $C_{16}E_8$.

Table 1 summarizes the values of the dimensionless excess energy of the spherical caps, $E_{sc}$, determined from the slopes of the lines in Figs. 2, 3 and 4 in accordance with Eqs. (2.13) and (2.19). We used the data in this table for quantitative verification of the molecular-thermodynamic model of micelle growth; see below.

It should be noted that in Refs. [123-127] values of the free energy parameter $g_2$ are reported. The parameter $g_2$ is approximately related to the dimensionless excess free energy $E_{sc}$ by the equation:

$$\frac{g_2}{k_B T} = E_{sc} - \ln M$$

(3.1)

where $M$ is the molecular mass of the respective surfactant expressed in g/mol. The values of $g_2$ are with about 5–6 $k_B T$ smaller than those of $E_{sc}$. 

16
Table 1. Excess energy of the micelle spherical caps $E_{sc}$ (in $k_B T$ units) for various C$_i$E$_j$ surfactants at different temperatures determined from the slopes of the lines in Figs. 2, 3 and 4.

| $T$ [°C] | $E_{sc}$ | $T$ [°C] | $E_{sc}$ | $T$ [°C] | $E_{sc}$ |
|----------|----------|----------|----------|----------|----------|
| C$_{10}$E$_5$ | 45 | 21.9 | 45 | 23.5 |
| 25 | 17.6 | 50 | 22.6 | 50 | 24.5 |
| 30 | 18.6 | C$_{12}$E$_7$ | 55 | 25.1 |
| 35 | 19.3 | 45 | 18.1 | C$_{14}$E$_8$ |
| 40 | 20.3 | 48 | 18.9 | 40 | 15.0 |
| 42 | 20.7 | 50 | 19.3 | 45 | 17.2 |

| C$_{10}$E$_6$ | 52 | 19.5 | 50 | 18.9 |
| 30 | 14.1 | 55 | 20.2 | 55 | 20.8 |
| 35 | 14.9 | 58 | 20.5 | 60 | 21.7 |
| 40 | 16.1 |
| 45 | 16.9 | C$_{14}$E$_6$ | 60 | 21.0 | 65 | 22.6 |
| 50 | 17.8 | 15 | 20.3 | 25 | 16.9 |
| 55 | 18.7 | 17 | 21.1 | 30 | 17.0 |
| 60 | 20.4 | 20 | 22.3 | 35 | 17.3 |

| C$_{12}$E$_5$ | 22 | 23.0 | 40 | 20.7 |
| 15 | 21.4 | 25 | 24.0 | 45 | 22.3 |
| 20 | 22.5 | 30 | 25.0 | 50 | 23.3 |
| 25 | 23.7 | 35 | 26.0 | C$_{18}$E$_8$ |
| 30 | 24.6 | 40 | 26.5 |

| C$_{12}$E$_6$ | C$_{14}$E$_7$ | C$_{14}$E$_8$ | 33 | 22.7 |
| 25 | 17.8 | 25 | 17.0 | 35 | 24.3 |
| 30 | 18.9 | 30 | 18.5 | 40 | 26.4 |
| 35 | 20.0 | 35 | 20.5 | 45 | 27.9 |
| 40 | 20.9 | 40 | 22.2 | 50 | 29.1 |

In addition to the data for aggregation number $n_M$, experimental data for the *viscosity* of C$_{12}$E$_5$, C$_{12}$E$_6$, C$_{12}$E$_7$, and C$_{14}$E$_7$ micellar solutions have been obtained in Ref. [128], where it is demonstrated how the viscosity of these solutions increases with the rise of the length of the respective wormlike micelles.
4. Molecular aspects of the model

4.1. Molecular geometric parameters

First, let us consider some geometrical relations needed for the modeling of spherical and spherocylindrical micelles. All volumes, surface areas and radii refer to the micelle hydrocarbon core.

**Spherical micelle** (Fig. 1a): The volume, $V_s$, and the surface area, $A_s$, are related to the radius, $R_s$, as follows:

$$V_s = \frac{4}{3} \pi R_s^3 , \quad A_s = 4 \pi R_s^2 , \quad p = \frac{V_s}{A_s R_s} = \frac{1}{3} \frac{V_s}{R_s^3} \quad (4.1)$$

where $p$ is the packing parameter [93,188].

**Cylindrical part of a spherocylindrical micelle** (Fig. 1b): The cylinder volume, $V_c$, the lateral surface area, $A_c$, and the packing parameter, $p$, are related to the cylinder radius, $R_c$, and length, $L_c$, as follows:

$$V_c = \pi R_c^2 L_c , \quad A_c = 2 \pi R_c L_c , \quad p = \frac{V_c}{A_c R_c} = \frac{1}{2} \quad (4.2)$$

For prolate ellipsoids or caps of spherocylindrical micelles, the values of $p$ are between 1/3 and 1/2 see below.

**Spherical caps of a spherocylindrical micelle** (Fig. 1b): The end-caps have the shape of truncated sphere. The total volume of the two truncated spheres, $V_{sc}$, and the total area of their spherical surfaces, $A_{sc}$, are related to the sphere radius, $R_s$ and the radius of the cylindrical part (of the truncated circle), $R_c$, as follows:

$$V_{sc} = \frac{4}{3} \pi R_s^2 [R_s + (R_s^2 - R_c^2)^{1/2}] + \frac{2}{3} \pi R_c^2 (R_s^2 - R_c^2)^{1/2} \quad (4.3)$$

$$A_{sc} = 4 \pi R_s [R_s + (R_s^2 - R_c^2)^{1/2}] , \quad R_c \leq R_s \quad (4.4)$$

The packing parameter of the caps is defined as follows [136,142]:

$$p = \frac{V_{sc}}{A_{sc} R_s} , \quad \frac{1}{3} \leq p \leq \frac{3}{8} \quad (4.5)$$
The minimal value, \( p = 1/3 \), corresponds to hemispherical caps \((R_c/R_s = 1)\), whereas the maximal value, \( p = 3/8 \), is realized at \( R_c/R_s = \sqrt{3}/2 \approx 0.866 \).

The numbers of surfactant molecules contained in the cylindrical part and in the spherical end-caps of a spherocylindrical micelle, \( n_c \) and \( n_s \), are:

\[
\begin{align*}
\frac{n_c}{V_c} &= \frac{V_c}{n_c}, & \frac{n_s}{V_{sc}} &= \frac{V_{sc}}{n_c} \\
\text{where } n_c \text{ is the number of carbon atoms in the alkyl chain and } v(n_c) \text{ is its volume.}
\end{align*}
\]

(4.6)

The extended chainlength, \( l \), and the chain volume, \( v \), can be calculated from the Tanford expressions [191]:

\[
\begin{align*}
l(n_c) &= l(CH_3) + (n_c - 1)l(CH_2) \\
v(n_c) &= v(CH_3) + (n_c - 1)v(CH_2)
\end{align*}
\]

(4.7) (4.8)

The volumes of the CH$_3$ and CH$_2$ groups, estimated from the temperature dependence of the volume of aliphatic hydrocarbons, are [101,136]:

\[
\begin{align*}
v(CH_3) &= [54.3 + 0.124(T - 298)] \times 10^{-3} \text{ nm}^3 \\
v(CH_2) &= [26.9 + 0.0146(T - 298)] \times 10^{-3} \text{ nm}^3
\end{align*}
\]

(4.9) (4.10)

where \( T \) is the absolute temperature. For the lengths per CH$_3$ and CH$_2$ group, the following values have been used [191]:

\[
\begin{align*}
l(CH_3) &= 0.280 \text{ nm}; & l(CH_2) &= 0.1265 \text{ nm}
\end{align*}
\]

(4.11)

Geometrical parameters for other types of surfactant tails can be found in Ref. [136].

4.2. Components of micelle free energy

As mentioned in the Introduction, we tried different versions of the theoretical model with different expressions for the free energy components and various values of the parameters that enter these expressions. Here, we present only the best model, which is in quantitative agreement with the data for single-component nonionic wormlike micelles in Section 3, as well as with data for mixed nonionic wormlike micelles that will be considered in a subsequent paper.
For nonionic surfactant micelles, the standard free energy per molecule incorporated in an aggregate, $f_k^o$, can be expressed as a sum of the following components:

$$f_k^o = \mu_m^o + f_\sigma + f_{hs} + f_{conf}$$  \hfill (4.12)

Here, $\mu_m^o$ is a standard chemical potential of the surfactant molecule in the micelle, which accounts for molecular internal degrees of freedom; $f_\sigma$ is the contribution of the interfacial tension, $\sigma$, of the boundary between the micelle hydrocarbon core and the surrounding water phase at the micelle surface (Fig. 5a); $f_{hs}$ accounts for the steric repulsion between the headgroups of surfactant molecules; $f_{conf}$ accounts for the conformational free energy of the surfactant hydrocarbon chains inside the micelle (Fig. 5b). Except $\mu_m^o$, all other terms in Eq. (4.12) depend on the micelle shape.

**Interfacial tension component.** The interfacial free energy per molecule, $f_\sigma$, is due to the contact area of the micelle hydrocarbon interior with the water phase at the micelle surface – see the “oil”-water interface in Fig. 5a; $f_\sigma$ can be calculated from the expression [162,188]:

$$f_\sigma = \sigma(a - a_0)$$  \hfill (4.13)
where $a$ is the area per surfactant molecule at the boundary between the micelle hydrocarbon core and the outer water phase (Fig. 5c) and $a_0$ is the surface area excluded by the surfactant headgroup, i.e. the geometric cross-sectional area of the headgroup. The area per molecule has been calculated from the expression:

$$a = \frac{v}{pR} \tag{4.14}$$

where $v$ is to be determined from Eqs. (4.8) – (4.10); $R = R_c$ for the cylindrical part of a spherocylindrical micelle; $R = R_s$ for the spherical end-caps, and $p$ is the value of the packing parameter for the respective geometry; see Eqs. (4.2) and (4.5).

**Fig. 6.** Experimental data for the n-paraffin/water interfacial tension, $\sigma_{ow}$, vs. the number of carbon atoms in the paraffin chain, $n_C$, at various temperatures, $T$. The solid lines are fits with Eq. (4.17).

In comparison with the emulsion and microemulsion drops, the surfactant micelles are the objects of the highest surface curvature. Following Ref. [143], we estimated the micelle interfacial tension taking into account its curvature dependence described by the Tolman equation [192-194]:

$$\sigma = \sigma_{ow} \left[ 1 + \frac{1}{p} \frac{\delta \gamma}{R} \right]^{-1} \tag{4.15}$$
\( \sigma_{ow} = \sigma_{ow}(n_C) \) is the interfacial tension between the bulk oil and water phases, \( p \) is the packing parameter, and \( \delta_T \) is the Tolman length that has been calculated from the expression [143]:

\[
\delta_T(n_C) = 0.225 \frac{l(n_C)}{l(11)} \text{ (nm)}
\]  

(4.16)

Here, \( l(n_C) \) is given by Eqs. (4.7) and (4.11); \( \sigma_{ow} \) can be calculated from the equation:

\[
\sigma_{ow} = 47.12 + 1.479 n_C^{0.5422} - 0.0875(T - 293)
\]  

(4.17)

We obtained Eq. (4.17) by fitting a set of experimental data for \( \sigma_{ow} \) from Refs. [195-197]; see Fig. 6. As usual, \( n_C \) is the number of carbon atoms in the alkyl chain and \( T \) is the absolute temperature.

**Headgroup steric repulsion component.** This is the contribution from the repulsion between the surfactant headgroups at the micelle surface due to their finite size (Fig. 5a). This effect has been taken into account using the repulsion term in the two-dimensional van der Waals equation; see Ref. [102] and the references cited therein:

\[
f_{hs} = -k_B T \ln\left(1 - \frac{a_0}{a}\right)
\]  

(4.18)

Here, \( a \) and \( a_0 \) have the same meaning as in Eq. (4.13); see Fig. 5c. In principle, the excluded area \( a_0 \) could be determined by fitting surface-tension isotherms with the van der Waals model; see e.g. Refs. [198-202].

**Chain-conformation component.** This contribution to the micelle free energy is related to the variety of conformations of surfactant hydrocarbon chains in the restricted space of the micellar interior (Fig. 5b). The first statistical theory of this effect was proposed by Dill and Flory [203-206], who used lattice statistics. Ben-Shaul and coauthors [154,157-160,163] extended the Dill-Flory theory and developed a mean field theory of amphiphile chain organization in micellar aggregates. An alternative approach was developed by Semenov [153] and applied to micellar aggregates by Nagarajan and Ruckenstein [136]. In our computations, we found that the best agreement between theory and experiment can be achieved if an expression for the chain-conformation free energy per molecule, \( f_{conf} \), which generalizes the Semenov [153] equations, is used. This expression reads (Appendix A):

\[
\frac{f_{conf}}{k_B T} = \frac{3\pi^2 R^2}{16 l_{sg}^2} c_{conf}(p)
\]  

(4.19)
where $c_{\text{conf}}(p)$ is a dimensionless coefficient:

$$
c_{\text{conf}}(p) = \frac{4p^2}{1 + 3p + 2p^2} \quad (4.20)
$$

In Eq. (4.19), $R = R_c$ for the cylindrical part of a spherocylindrical micelle; $R = R_s$ for the spherical end-caps; $p$ is the value of the packing parameter for the respective geometry; see Eqs. (4.2) and (4.5); $l$ is the extended chainlength given by Eqs. (4.7) and (4.11); $l_{sg}$ is the length of a segment of a surfactant hydrocarbon tail. Dill, Flory and coauthors [203-205] suggested that a suitable value is $l_{sg} = 0.46$ nm (for paraffin chains), which was used in our calculations. In Section 5 and Appendix A, we have derived Eqs. (4.19) and (4.20) by extending the Semenov theory [153]. The latter gives the values of $c_{\text{conf}}$ only for $p = 1/3, 1/2$ and 1. In particular, for a spherical and cylindrical micelles ($p = 1/3$ and $1/2$) Eq. (4.20) yields $c_{\text{conf}} = 1/5$ and $1/3$, respectively. For the end-caps, $1/3 \leq p \leq 3/8$, $c_{\text{conf}}$ is to be calculated from Eq. (4.20).

### 4.3. Model of spherocylindrical micelles

The standard free energy of a spherocylindrical micelle (Fig. 1b) of aggregation number $k = n_c + n_s$ can be expressed in the form:

$$
g_k^0 = n_c f_c + n_s f_s \quad (k \geq n_t) \quad (4.21)
$$

where, as usual, $n_c$ and $n_s$ are the numbers of molecules in the cylindrical parts and in the spherical end-caps of the micelle; $f_c$ and $f_s$ are the respective free energies per molecule. Because $k = n_c + n_s$, Eq. (2.11) can be presented in the form

$$
g_k^0 = (n_c + n_s) f_c + k_B T E_{sc} \quad (k \geq n_t) \quad (4.22)
$$

We have taken into account the fact that the addition of molecules to the cylindrical part of the micelle leads to a linear increase of its free energy, so that $\mu_c = f_c$, i.e. the chemical potential of a surfactant molecule in the cylindrical part coincides with the respective free energy per molecule. The comparison of Eqs. (4.21) and (4.22) yields an equation for calculating the dimensionless excess free energy of the spherical end-caps:

$$
E_{sc} = n_s \frac{f_s - f_c}{k_B T} \quad (4.23)
$$
The free energies per molecule, \( f_c \) and \( f_s \), can be expressed from Eq. (4.12) for the geometries of cylinder and spherical end-caps. Because the standard chemical potential \( \mu_m^0 \) is independent of micelle shape, Eq. (4.23) can be represented in the form

\[
E_{sc} = n_s \frac{\Delta f_s - \Delta f_c}{k_B T}
\]  
(4.24)

where \( \Delta f_s = f_s - \mu_m^0 \) and \( \Delta f_c = f_c - \mu_m^0 \). In other words, to calculate \( E_{sc} \) we do no need the value of \( \mu_m^0 \). In view of Eqs. (4.12), (4.13), (4.18) and (4.19), the free energies per molecule can be expressed in the form:

\[
\frac{\Delta f_x}{k_B T} = \frac{f_\sigma + f_{hs} + f_{conf}}{k_B T}
\]

\[
= \frac{\sigma}{k_B T} (a - a_0) - \ln(1 - \frac{a_0}{a}) + \frac{3\pi^2R^2}{16l_{seg} l_{conf}(p)}
\]  
(4.25)

where the values of \( \sigma, a, R \) and \( p \) have to be substituted for the respective geometries (cylinder of spherical cap); for details – see Sections 6.1 and 6.2.

According to Eq. (4.24), \( E_{sc} \) is proportional to the difference between two quantities of close magnitude, \( \Delta f_s \) and \( \Delta f_c \). As seen in Table 1, the values of \( E_{sc} \) are in the range between 15 and 30. At aggregation number \( n_s = 60 \), this variation corresponds to \( \Delta f_s - \Delta f_c \) in the range between 0.25 and 0.50 \( k_B T \); see Eq. (4.24). Hence, even contributions of the order of 0.1 \( k_B T \) in \( \Delta f_s \) and \( \Delta f_c \) are considerable! For this reason, not only all free energy components in Eq. (4.25) are important, but also the curvature dependence of \( \sigma \), expressed by the Tolman equation, Eq. (4.15), and the dependence of \( c_{conf} \) on \( p \), given by Eq. (4.20), are essential for achieving agreement between theory and experiment.

As mentioned in Section 2, the experimental mean aggregation number \( n_M \), as well as the growth parameter \( E_{sc} = \ln K \) determined from the slopes of the experimental lines (Section 3), refer to the optimal micelle shape (denoted by the subscript ‘opt’ in the equations). In view of Eq. (2.11), the optimal micelle shape should correspond to the minimal values of \( \mu_c (= f_c) \) and \( E_{sc} \). As described in Section 6.1, the condition for minimum of \( \Delta f_c \), along with Eq. (4.25), can be used to determine the radius of the cylindrical part of the micelle, \( R_c \). Likewise, in Section 6.2 it is demonstrated that the condition for minimum of \( E_{sc} \), along with Eqs. (4.24) and (4.25), can be used to determine the radius of the spherical end-caps, \( R_s \).
5. Chain-conformational free energy

5.1. Formulation of the variational problem

Here, the considerations are general and applicable to micelles of spherical, cylindrical and lamellar shape, as well as for self-assemblies of other values of the packing parameter, \( p \). In his remarkable paper [153], by minimization of the free energy of the system of chains Semenov derived expressions describing the equilibrium chain-conformation in the hydrocarbon core of a micelle. In Ref. [153], only the formulation of the problem and the final results for sphere \((p = 1/3)\), cylinder \((p = 1/2)\) and lamella \((p = 1)\) are given. The derivation of some of the basic equations and the solution of the minimization problem (which is rather non-trivial) was not published. We succeeded to reproduce Semenov’s derivation, and further to generalize his result for any \( p \) values, including the range \( 1/3 \leq p \leq 3/8 \) corresponding to the micelle end-caps, and the range \( 1/2 < p < 1 \) corresponding to vesicles.

![Fig. 7](image)

Fig. 7. (a) The surfactant chain is anchored at the micelle surface \((r = 0)\) and its end is at \( r = r_0 \); \( r(n) \) is the distance from the \( n \)-th segment to the micelle surface; \( l_{sg} \) is the length of a segment. (b) Chain-conformation coefficient \( c_{\text{conf}}(p) \) vs. the packing parameter \( p \) (the solid line); the dashed line corresponds to \( c_{\text{conf}} = 3p/5 \). The inset shows \( c_{\text{conf}}(p) \) in the whole range \( 1/3 \leq p \leq 1 \); the dots correspond to the \( p \) values for sphere, cylinder and lamella.

Following Semenov [153], let us consider the surfactant chain as a continuous string with extended length \( l = N_{sg}l_{sg} \) and volume \( v = N_{sg}l_{sg}^3 \), where \( N_{sg} \) is the number of segments with characteristic length \( l_{sg} \); see Fig. 7a. The radial axis \( r \) is directed from the micelle surface,
where \( r = 0 \), toward the micelle center, where \( r = R \). (For lamellar micelles, \( r = R \) corresponds to the micelle midplane.) The outer end of the chain is anchored to the micelle surface, whereas the inner end of the chain is located in the micelle interior, at \( r = r_0 \).

The distribution of the chain free ends inside the micelle is characterized by the function \( G(r_0) \). By definition, \( G(r_0)dr_0 \) gives the number of chains, whose ends are located in the interval \( (r_0, r_0 + dr_0) \). The integration of \( G(r_0) \), which is equivalent to summation over all surfactant molecules in the micelle, yields:

\[
N_{agg} = \frac{V}{v} = \int_0^R G(r_0) \, dr_0
\]

(5.1)

where \( N_{agg} \) is the aggregation number of the considered micellar aggregate. As before, \( V \) is the volume of the micelle hydrocarbon interior and \( v \) is the volume of the tail of a single surfactant molecule.

The shape of the chain of a surfactant molecule within the micelle can be characterized by the function \( r(n) \), where \( n \) is the number of the segment, and \( r \) is its radial distance from the micelle surface; \( 0 \leq n \leq N_{sg} \). By definition, at the micelle surface we have \( r(0) = 0 \), whereas \( r(N_{sg}) = r_0 \) for the inner end of the chain. Furthermore, the local extension of the chain (in radial direction) can be characterized by the function [153]:

\[
E(r_0, r) = \frac{dr}{dn}, \quad 0 < r_0 \leq R
\]

(5.2)

The maximal value of this function is \( E(r_0, r) = l_{sg} \) for a segment that is oriented in radial direction \((dr = l_{sg}, \, dn = 1)\). The reciprocal quantity, \( 1/E(r_0, r) = dn/dr \), expresses the number of segments (from a given molecule) per unit length in radial direction. The integral of this quantity gives the total number of segments in the chain:

\[
\int_0^{r_0} \frac{dr}{E(r_0, r)} = N_{sg}
\]

(5.3)

Furthermore, let \( S(r) \) be the area of a surface \( r = \text{const.} \) situated in the micelle core (Fig. 7a). The number of segments of chains contained in the elementary volume \( S(r)dr \) can be presented in the form:

\[
\frac{S(r)dr}{l_{sg}^2} = \int_r^R (dn)G(r_0) \, dr_0
\]

(5.4)
Here, $I_{sg}^3$ is the volume per segment; $(dn)$ is the number of segments (from a given molecule) located in the considered layer of thickness $dr$ and, finally, the integration with respect to $r_0$ is equivalent to summation over all surfactant molecules, whose chain-ends are located in the interval $(r, R)$ and which contribute to the total number of segments contained in the elementary volume $S(r)dr$. It has been assumed that the segment density in the micellar core is uniform. In view of Eq. (5.2), we can represent Eq. (5.4) in the form [153]:

$$S(r) = I_{sg}^3 \int_r^R \frac{G(\eta_0)}{E(\rho_0, r)} dr_0$$  \hspace{1cm} (5.5)$$

where $S(r)$ is the area of the surface $r = \text{const.}$, which is placed at distance $r$ from the respective interface. The standard definition of the packing parameter, $p$, is:

$$p = \frac{V}{S(0)R}$$  \hspace{1cm} (5.6)$$

where $S(0)$ is the area of the surface of the micelle hydrocarbon core at $r = 0$; see Fig. 7a. For spherical, cylindrical and lamellar geometries, we have:

$$V = \frac{4\pi}{3} R^3, \quad S(r) = 4\pi (R - r)^2, \quad p = \frac{1}{3} \quad (\text{sphere})$$  \hspace{1cm} (5.7)$$

$$V = \pi R^2 L_c, \quad S(r) = 2\pi (R - r) L_c, \quad p = \frac{1}{2} \quad (\text{cylinder})$$  \hspace{1cm} (5.8)$$

$$V = RS_{lam}, \quad S(r) = S_{lam}, \quad p = 1 \quad (\text{lamella})$$  \hspace{1cm} (5.9)$$

where $0 \leq r \leq R$; $L_c$ is the length of the cylinder, and $S_{lam}$ is the area of the lamella.

The unperturbed end-to-end distance of a chain containing $dn$ segments is $(dn)^{1/2}I_{sg}$ [206]. Inside the micelle, this chain could be extended, so that its ends lie at a distance $dr$ from one another. This corresponds to a local conformation elastic free energy of the considered chain given by the Flory expression [136,153,206]:

$$\frac{d\varphi_{conf}}{k_B T} = \frac{3}{2} \frac{(dr)^2}{[(dn)^{1/2}I_{sg}]^2} = \frac{3}{2} I_{sg}^2 E(\rho_0, r) dr$$  \hspace{1cm} (5.10)$$

The factor $3/2$ accounts for the three-dimensional character of deformation. Next, by integration of Eq. (5.10) one obtains the total conformational free energy for all chains in the micelle [136,153]:

27
\[
\frac{F_{\text{conf}}}{k_B T} = \frac{3}{2l_{sg}^2} \int_0^R G(r_0) \left[ \int_0^{y_0} E(r_0, r) \, dr \right] \, dr_0
\] (5.11)

In the last equation, the integration over \( r \) is equivalent to summation of contributions from all segments of a given molecule, whereas the integration over \( r_0 \) – to summation over all surfactant molecules. The variational problem reduces to minimization of the free energy functional in Eq. (5.11) with respect to variations of \( G \) and \( E \) under constrains given by Eqs. (5.1), (5.3), and (5.5).

5.2. Expression for the free energy per molecule

It is convenient to introduce dimensionless variables as follows:

\[
x = \frac{r_0}{R}, \quad y = \frac{r}{R}, \quad \tilde{G}(x) = \frac{yR}{V} G(r_0), \quad \tilde{E}(x, y) = \frac{N_{sg}}{R} E(r_0, r)
\] (5.12)

Then, the constraints expressed by Eqs. (5.3) and (5.5) acquire the form:

\[
\int_0^x \frac{d y}{\tilde{E}(x, y)} = 1 \quad \text{for } 0 \leq x \leq 1
\] (5.13)

\[
\frac{1}{p} (1 - y)^{1-p} = \int_y^{1} \frac{\tilde{G}(x)}{\tilde{E}(x, y)} \, dx \quad \text{for } 0 \leq y \leq 1
\] (5.14)

We have used Eqs. (5.6) and (5.12), and the relations \( v = N_{sg} l_{sg}^3 \) and \( S(r) = S(0)(1 - y)^{-p} \); the latter relation represents a generalization of the expressions for \( S(r) \) in Eqs. (5.7)–(5.9). As an additional boundary condition, which is necessary to solve the problem, one can use [153]:

\[
\tilde{E}(x, x) = 0 \quad \text{for } 0 \leq x \leq 1
\] (5.15)

which means that the free ends of the molecules are not extended.

The dimensionless form of the expression for the conformational energy, Eq. (5.11), reads:

\[
\frac{F_{\text{conf}}}{k_B T} = \frac{3R^2}{2l_{sg}^2 N_{sg}} \frac{\int_0^1 \tilde{G}(x) \left[ \int_0^x \tilde{E}(x, y) \, dy \right] \, dx}{V}
\] (5.16)

The conformational free energy per molecule is \( f_{\text{conf}} = F_{\text{conf}}/N_{\text{agg}} = F_{\text{conf}}v/V \) and the extended length of the surfactant tail is \( l = N_{sg} l_{sg} \). Then, Eq. (5.16) acquires the form:
The variational problem is related to the minimization of the functional in Eq. (5.17). This problem is solved in Appendix A. The functions $G(x)$ and $E(x, y)$ are determined and their substitution in Eq. (5.17) leads to Eqs. (4.19) and (4.20).

Fig. 7b shows the dependence of the coefficient $c_{\text{conf}}(p)$ on the packing parameter, $p$, calculated from Eq. (4.20). The dots in the inset in Fig. 7b corresponds to the special cases of sphere $c_{\text{conf}}(1/3) = 1/5$; of cylinder $c_{\text{conf}}(1/2) = 1/3$ and of lamella $c_{\text{conf}}(1) = 2/3$. The same results have been obtained also in Ref. [153]. We assume that Eq. (4.20) is applicable also for the spherical caps, for which $1/3 \leq p \leq 3/8$.

Fig. 7b shows that $c_{\text{conf}}$ is greater for the cylindrical part than for the spherical caps. Contrariwise, $R$ is greater for the spherical caps than for the cylindrical part. Insofar as $f_{\text{conf}} \propto R^2 c_{\text{conf}}$, the chain-conformation component of micelle-growth energy, $(E_{\text{sc}})_{\text{conf}} \propto (f_s - f_c)_{\text{conf}}$, can be both positive and negative; see Fig. 8.

In Ref. [136], it was assumed (postulated) that $c_{\text{conf}}(p) = 3p/5$ for the spherical caps. As seen in Fig. 7b (the dashed line), the latter empirical expression leads to smaller values of the chain-conformation free energy, which would essentially affect the theoretical predictions in view of the fine balance of the different components in $E_{\text{sc}}$.

Further generalization of the Semenov’s approach can give expressions for the chain-conformation free energy in the case of mixed micelles from two and more surfactants with different chainlengths. Such generalization will be reported in a subsequent study.

6. Quantitative predictions of the theoretical model

6.1. Determination of the radius of micelle cylindrical part

The input parameters are the temperature, $T$, the number of carbon atoms in the surfactant alkyl chainlength, $n_C$, and the length of a segment, $l_{\text{sg}} = 0.46$ nm. The headgroup excluded area, $a_0$, can be determined either by molecular size considerations, or it can be determined from the experimental value of $E_{\text{sc}}$ (see below). Next, the length of the extended surfactant chain, $l$, and its volume, $v$, are calculated by using Eqs. (4.7)–(4.11).

For cylindrical geometry, we have $p = 1/2$. At a given radius $R = R_c$, the interfacial tension, $\sigma$, is calculated from Eq. (4.15), along with Eqs. (4.16) and (4.17). The area per
molecule, \(a\), is calculated from Eq. (4.14) and the chain-conformation coefficient, \(c_{\text{conf}}\) – from Eq. (4.20). Finally, \(\Delta f_c\) is computed from Eq. (4.25) as a function of \(R_c\). The optimal cylinder radius is identified with the value of \(R_c\) that corresponds to the minimum of \(\Delta f_c\) in the interval \(1 < R_c \leq l\).

It turned out that for all surfactants, for which data are given in Table 1, the function \(\Delta f_c(R_c)\) has a local minimum in the interval \(1 < R_c < l\), from which the optimal (equilibrium) value of \(R_c\) is determined (see Fig. 8a). In principle, there could be no local minimum, but instead, the minimal value of \(\Delta f_c\) could be at the boundary point \(R_c = l\) (global minimum). However, the latter case was not observed in our computations.

![Plots](image)

**Fig. 8.** Plots of (a) \(\Delta f_c\) vs. \(R_c\) for the micelle cylindrical part and (b) \(E_{sc}\) vs. \(R_s\) for the micelle spherical end-caps for three nonionic surfactants: \(C_{12}E_6\), \(C_{14}E_6\), and \(C_{16}E_8\). Components of different physical origin (c) of \(\Delta f_c = f_\sigma + f_{hs} + f_{\text{conf}}\) and (d) of \(E_{sc} = (E_{sc})_\sigma + (E_{sc})_{hs} + (E_{sc})_{\text{conf}}\) for \(C_{12}E_6\); details in the text. The vertical dashed lines show the positions of the minima, which determine the equilibrium values of \(R_c\) and \(R_s\).
6.2. Determination of the spherical cap radius

The input parameters are the same as in the first paragraph of Section 6.1 and the value of the optimal cylinder radius, $R_c$, has been determined as explained above.

At a given value of the cap radius, $R_s$, we calculate the volume $V_{sc}$; the area $A_{sc}$, and the packing parameter $p$ from Eqs. (4.3)–(4.5). Next, $n_s$ is calculated from Eq. (4.6); $a_0$ – from Eq. (4.14); $\sigma$ – from Eqs. (4.15)–(4.17), and $c_{\text{conf}}(p)$ – from Eq. (4.20). Finally, $E_{sc}$ is computed from Eqs. (4.24) and (4.25) as a function of $R_s$. The optimal radius of the spherical end-caps, $R_s$, corresponds to the minimal value of $E_{sc}$ in the interval $1 < R_s \leq l$.

For all surfactants, for which data are given in Table 1, it turned out that the function $E_{sc}(R_s)$ has a local minimum in the interval $1 < R_s < l$ (see Fig. 8b), from which the optimal value of $R_s$ was determined. In principle, it could happen that the minimal value of $E_{sc}$ is at the boundary point, $R_s = l$, however, this case was not observed in our computations.

The cross-sectional area of the ethylene-oxide headgroups, $a_0$, is temperature dependent: $a_0$ decreases with the rise of temperature, $T$, because of enhanced segment-segment attraction in the polyoxyethylene chains [188,190], which leads to headgroup compaction. There are no theoretical expressions for the $a_0(T)$ dependence. Because of that, using the system of equations described above, we determined $a_0$ from the experimental values of $E_{sc}$ in Table 1 for each temperature, $T$. For this goal, $a_0$ was varied until the value of $E_{sc}$ at the minimum of the $E_{sc}(R_s)$ dependence (Fig. 8b) coincides with the respective $E_{sc}$ value in Table 1. The value of $R_s$ at that minimum is identified with the optimal radius of the spherical end-caps.

6.3. Chemical potential vs. free energy per molecule

The system of equations described in Section 6.2 defines the number of molecules in the end-caps and their excess free energy as functions of $R_s$, viz. $n_s(R_s)$ and $E_{sc}(R_s)$. The requirement for local minimum of $E_{sc}$ (Fig. 8b) leads to:

$$0 = \frac{dE_{sc}}{dR_s} = \frac{dE_{sc}}{dn_s} \frac{dn_s}{dR_s}$$

Combining Eqs. (4.23) and (6.1), we obtain:
\[ 0 = \frac{d}{dn_s} \left[ n_s (f_s - f_c) \right] = \frac{d(n_s f_s)}{dn_s} - f_c = \mu_s - \mu_c \] (6.2)

We have taken into account that \( d(n_f)/dn_s = dg_s/dn_s = \mu_s \), where \( \mu_s \) is the chemical potential of a molecule in the spherical end-caps. In addition, for the cylindrical part of the considered long spherocylindrical micelles we have \( g_c = n_f f_c \), where the free energy per molecule, \( f_c \), is independent of \( n_c \); hence, \( \mu_c = dg_c/dn_c = f_c \). The fact that Eq. (6.2) yields \( \mu_s = \mu_c \) has an important physical meaning, viz. for the optimal micelle, which corresponds to the minimum of the \( E_{sc}(R_s) \) dependence (Fig. 8b), the surfactant molecules in the spherical caps and in the micelle cylindrical part coexist in chemical equilibrium.

For the end-caps, \( g_s \) is not simply proportional to \( n_s \), so that we have:

\[ f_s = \frac{g_s}{n_s} \neq \frac{dg_s}{dn_s} = \mu_s \] (6.3)

For this reason, despite the fact that \( \mu_s = \mu_c = f_c \), we could have \( E_{sc} \propto (f_s - f_c) > 0 \), which makes the cylindrical aggregates energetically favorable, and which represents the necessary condition for the growth of large wormlike micelles; see Eqs. (2.13), (2.19) and (4.23).

If there is no local minimum of \( E_{sc} \), but instead, \( \Delta f_c \) takes its minimal value in the boundary point, \( R_c = l \), Eq. (6.1) does not hold. In such case, \( \mu_s \neq \mu_c \) and the micelle spherical caps are not in chemical equilibrium with the cylindrical part of the micelle. As already mentioned, this case was not observed when applying the model from Section 4 to the systems studied in the present article.

6.4. Numerical data for the free-energy components

The computational procedures described in Sections 6.1 and 6.2 have been applied to calculate the dependencies of the free energy per surfactant molecule in the cylindrical part, \( \Delta f_c \) vs. \( R_c \), and of the excess free energy of the spherical caps, \( E_{sc} \) vs. \( R_s \). As an illustration, in Figures 8a and b we present results for three of nonionic surfactants, \( C_{12}E_6 \), \( C_{14}E_6 \), and \( C_{16}E_8 \). For these surfactants (as well as for all other studied surfactants in Table 1), the optimal values of \( R_c \) and \( R_s \), corresponding to the minima of the respective free energy curves, satisfy the inequality \( R_c < R_s < l \). In Table 2, this is illustrated with data from Figures 8a and 8b.
Table 2. Comparison of the optimal radii $R_c$ and $R_s$ with the chainlength of the extended surfactant molecule, $l$, for three surfactants at $T = 25 \, ^\circ C$.

| Radius/length | $C_{12}E_6$ | $C_{14}E_6$ | $C_{16}E_8$ |
|--------------|-------------|-------------|-------------|
| $R_c$ (nm)   | 1.22        | 1.38        | 1.33        |
| $R_s$ (nm)   | 1.48        | 1.65        | 1.67        |
| $l$ (nm)     | 1.67        | 1.92        | 2.18        |

In view of Eq. (4.25), the free energy per molecule in the cylindrical part represents a sum of three components, $\Delta f_c = f_\sigma + f_{hs} + f_{conf}$, which express the interfacial-tension, headgroup-steric and chain-conformation components of free energy, respectively. In Fig. 8c, these three components are compared for the surfactant $C_{12}E_6$. One sees that they are comparable by magnitude; $f_\sigma$ decreases with the rise of $R_c$, whereas $f_{hs}$ and $f_{conf}$ increase with the rise of $R_c$. For the considered surfactant at $T = 25 \, ^\circ C$, $f_{hs}$ turns out to be somewhat greater than $f_{conf}$. The sum of these three components leads to a minimum in the $\Delta f_c$ vs. $R_c$ curve, which determines the optimal radius of the cylindrical part of the micelle.

In view of Eqs. (4.24) and (4.25), the excess free energy of the micelle spherical end-caps also represents a sum of three components, $E_{sc} = (E_{sc})_\sigma + (E_{sc})_{hs} + (E_{sc})_{conf}$, where the subscripts refer to the respective components of the micelle free energy:

$$ (E_{sc})_z = n_s \frac{(f_z)_s - (f_z)_c}{k_B T}, \quad z = \sigma, hs, conf $$ (6.4)

As before, the subscripts ‘c’ and ‘s’ refer to the cylindrical part and spherical caps of the spherocylindrical micelle, whereas the subscripts ‘$\sigma$', ‘hs’ and ‘conf’ denote the physical nature of the free-energy component. Eq. (6.4) contains the aggregation number of the spherical caps, $n_s$, which increases with the cube of the spherical-cap radius, $R_s$; see Eqs. (4.3) and (4.6). Despite that, $(E_{sc})_{\sigma}$ decreases with the rise of $R_s$ (Fig. 8d) because the non-shielded area of hydrocarbon/water contact decreases with the decrease of surface curvature. In contrast, the steric-headgroup and chain-conformation contributions, $(E_{sc})_{hs}$ and $(E_{sc})_{conf}$, are increasing functions of $R_s$, and are negative for the smaller $R_s$, for which $(f_{hs})_s$ and $(f_{conf})_s$ turn out to be smaller than $(f_{hs})_c$ and $(f_{conf})_c$, respectively; see Eq. (6.4). The total excess free energy, $E_{sc}$, turns out to be a result of a fine balance of components, whose range of variation is considerably greater than that of $E_{sc}$ (Fig. 8d). For the considered surfactant and temperature, the value of $E_{sc}$ at its minimum is determined from the balance of the positive
and the negative \((E_{sc})_{hs}\). The value of \((E_{sc})_{conf}\) at the minimum of \(E_{sc}\) turns out to be close to zero, but the increase of \((E_{sc})_{conf}\) at greater \(R_s\) blocks the growth of larger end-caps.

### 7. Comparison of theory and experiment

#### 7.1. Temperature dependence of the headgroup cross-sectional area

As explained in the last paragraph of Section 6.2, for each nonionic surfactant at each temperature, \(T\), the headgroup cross-sectional area, \(a_0\), was determined in such a way that the minimal value of \(E_{sc}\) (Fig. 8b) coincides with the respective experimental value in Table 1. In Fig. 9, the values of \(a_0\) determined in this way are plotted vs. \(T\). It is remarkable that the values of \(a_0\) for surfactants with identical headgroups collapse on the same master curve, irrespective of their different chainlengths. This result confirms the correctness of our theoretical model, including its part related to the chain-confirmation free energy.

![Fig. 9](image)

**Fig. 9.** Plot of the geometric cross-sectional area per surfactant headgroup, \(a_0\), vs. temperature, \(T\), for \(C_jE_i\) micelles; \(a_0(T)\) is scaled with its value at 303 K (30°C). The points
are determined from the experimental data for \( E_{sc} \) (see the text). The lines are fits with Eq. (6.5).

The data for \( a_0(T) \) in Fig. 9 can be fitted with a quadratic function:

\[
a_0(T) = a_0(303)[1 - b_1(T - 303) - b_2(T - 303)^2]
\]

where \( a_0(303) \) is the value of \( a_0 \) at 303 K (30 °C); \( b_1 \) and \( b_2 \) are adjustable parameters. The obtained values of \( b_1 \) and \( b_2 \) are given in Table 3. In the case of \( C_{10}E_6 \), the last two experimental points (those at 55 and 60 °C, which deviate from quadratic dependence) have not been taken into account when fitting the data. For the surfactants of longer polyoxyethylene chain, \( C_iE_7 \) and \( C_iE_8 \), the data are fitted with straight line (\( b_2 \equiv 0 \)).

**Table 3.** Coefficients determined by fitting the data for \( a_0(T) \) in Fig. 9 with Eq. (6.5).

| Surfactant | \( a_0(303) \), Å² | \( b_1 \), K⁻¹ | \( b_2 \), K⁻² | Regr. coeff. |
|------------|-------------------|----------------|----------------|--------------|
| \( C_iE_5 \) | 35.9±0.5          | (12.3±0.3)×10⁻³ | (1.4±0.2)×10⁻⁴ | 0.9994       |
| \( C_iE_6 \) | 42.3±0.5          | (9.2±0.2)×10⁻³  | (0.5±0.1)×10⁻⁴ | 0.9996       |
| \( C_iE_7 \) | 49.4±0.2          | (9.7±0.2)×10⁻³  | 0              | 0.9995       |
| \( C_iE_8 \) | 57.4±0.5          | (9.4±0.5)×10⁻³  | 0              | 0.9989       |

Using the temperature dependence of the headgroup cross-sectional area \( a_0 \) given by Eq. (6.5) with the parameter values in Table 3 and following the procedure described in Section 6.2, we calculated the theoretical dependence of \( E_{sc} \) on \( T \) for each given surfactant – see the solid lines in Fig. 10. The points in Fig. 10 are the data from Table 1. As it could be expected, the experimental points and the calculated curves are in good agreement because of the fact that the curves are based on the fits in Fig. 9. Fig. 10 visualizes the behavior of the micelle growth parameter, \( E_{sc} \). Figs. 10c and d show that at the same headgroup, \( E_{sc} \) and micelle size increase with the rise of surfactant chainlength, as it should be expected. In addition, Figs. 10a and b show that at the same chainlength, \( E_{sc} \) increases with the diminishing of the surfactant headgroup size characterized by the number of ethoxy groups (i.e. the larger the headgroup, the smaller the micelle). For a similar reason, for each separate
surfactant, $E_{sc}$ increases with $T$ because of the diminishing of headgroup cross-sectional area $a_0(T)$ with the rise of temperature; see Fig. 9.

**Fig. 10.** Plots of the micellar growth parameter, $E_{sc}$, vs. the temperature $T$ for various ethoxylated nonionic surfactants: (a) C$_{10}$E$_5$, C$_{12}$E$_5$, C$_{12}$E$_6$, and C$_{12}$E$_7$; (b) C$_{14}$E$_6$, C$_{14}$E$_7$, and C$_{14}$E$_8$; (c) C$_{10}$E$_6$, C$_{12}$E$_6$, and C$_{14}$E$_6$; (d) C$_{14}$E$_8$, C$_{16}$E$_8$, and C$_{18}$E$_8$. The points are the experimental values of $E_{sc}$ determined from the slopes of the straight lines in Figs. 2 – 4; see Eqs. (2.13) and (2.19). The solid lines are theoretical curves calculated using the model from Section 4 along with Eq. (6.5).

### 7.2. Cylinder radius and size of the end-caps

The model (the minimization illustrated in Figs. 8a and b) predicts the equilibrium values of the radii of the micelle cylindrical part, $R_c$, and of the spherical end-caps, $R_s$, as well as the aggregation number, $n_s$, of the two caps together. The values of $R_c$ and $R_s$ are compared in Fig. 11 for different surfactants at various temperatures. For each separate surfactant, $R_s$ is always greater than $R_c$, which corresponds to the dumbbell-like shape shown in Fig. 1.
most surfactants (Figs. 11a, b and d) the increase of $R_c$ and $R_s$ with the rise of $T$ is linear in the considered temperature range.

**Fig. 11.** Plots of the radii of micelle cylindrical part, $R_c$, and spherical caps, $R_s$, vs. temperature, $T$, for various ethoxylated nonionic surfactants. The points are calculated from the experimental values of $E_{sc}$ in Fig. 10 by means of the theoretical model from Section 4. The dashed lines are guides to the eye.
Fig. 12. Plots of the total aggregation number of the two spherical caps, $n_s$, vs. temperature, $T$, for various ethoxylated nonionic surfactants. The points are calculated from the experimental values of $E_{sc}$ in Fig. 10 by means of the theoretical model from Section 4. The dashed lines are guides to the eye.

As seen in Fig. 12, the calculated total aggregation number of the two spherical caps varies between $n_s = 54$ (for C$_{10}$E$_6$ at 60 ºC) and $n_s = 93$ (for C$_{18}$E$_8$ at 40 ºC). For the smaller chainlengths, C10 and C12, $n_s$ slightly decreases with the rise of temperature (Fig. 12a). For the larger chainlengths, C14, C16 and C18, the dependence $n_s(T)$ has a maximum at a certain temperature (Fig. 12b). In general, for nonionic surfactant micelles the equilibrium values of $R_c$, $R_s$ and $n_s$ are result of a fine balance of the three free-energy components related (i) to the interfacial tension; (ii) to the steric headgroup repulsion, and (iii) to the chain conformations, as illustrated in Fig. 8c and d.

The temperature dependence of the geometric cross-sectional area per surfactant headgroup $a_0(T)$, see Eq. (6.5), has been determined from fits of experimental data by Einaga et al. [123-131]. In Fig. 13, our theoretical model is tested against an independent set of experimental data obtained by Talmon et al. [79]. In Fig. 13, the symbols are data for the mean mass aggregation number, $n_M$, of C$_{12}$E$_5$ micelles obtained from graphical data for the average micelle length $\bar{L}$ in Ref. [79] using Eq. (9) in the same paper along with parameter values given therein. In Fig. 13, the continuous lines are calculated by means of our theory for the respective C$_{12}$E$_5$ concentrations with $a_0(T)$ from Eq. (6.5) and without using any adjustable parameters. The obtained excellent agreement between theory and experiment indicates that our theoretical model successfully passes this test.
Fig. 13. Plots of the experimental micelle mean mass aggregation number, $n_M$, vs. temperature, $T$, for four different concentrations of the nonionic surfactant C$_{12}$E$_5$ denoted in the figure. The symbols are experimental data from Ref. [79], whereas the solid lines are predicted by our theoretical model for the respective C$_{12}$E$_5$ concentrations without using any adjustable parameters.

8. Summary and conclusions

This article presents the first analytical molecular-thermodynamic model, which is in full quantitative agreement with the whole set of available experimental data for the growth of wormlike micelles in single-component nonionic surfactant (polyoxyethylene alkyl ether) solutions. For this goal, we systematized data for the micelle mean mass aggregation number, $n_M$, from which the micelle growth parameter, $E_{sc}$, was determined at various temperatures, $T$; see Figs. 2, 3, 4 and Table 1. None of the available models could give a quantitative description of these data. We constructed a new model, which is based on theoretical expressions for the interfacial-tension, headgroup-steric and chain-conformation components of micelle free energy, along with appropriate expressions for the parameters of the model, including the temperature dependence of the headgroup cross-sectional area, Eq. (6.5), and the curvature and temperature dependence of the interfacial tension, Eqs. (4.15) – (4.17). Special attention was paid to the chain-conformation free energy per molecule, $f_{\text{conf}}$, described by Eqs. (4.19) – (4.20), which generalize the expressions obtained by Semenov [153].

As a result, relatively simple expressions are obtained for the free energies per molecule in the cylindrical part, $\Delta f_c$, spherical caps, $\Delta f_s$, and for the micelle-growth free energy, $E_{sc}$; see Eqs. (4.24) and (4.25). The equilibrium radius of the micelle cylindrical part, $R_c$, is determined from the minimum of the $\Delta f_c(R_c)$ dependence; see Fig. 8a. Likewise, the equilibrium radius of the micelle spherical end-caps, $R_s$, is determined from the minimum of the $E_{sc}(R_s)$ dependence; see Fig. 8b. It is demonstrated, that the condition for minimum of the function $E_{sc}(R_s)$ is equivalent to condition for chemical equilibrium between the micelle cylindrical part and the end-caps with respect to exchange of surfactant molecules (Section 6.3). The radii of the micelle cylindrical parts and spherical end-caps, as well as the aggregation numbers of the end-caps have been determined for various surfactants – see Figs. 11 and 12.

All parameters that enter the free-energy expressions are known (Sections 6.1 and 6.2), which facilitates the theoretical modeling of micelle growth for various nonionic surfactants (Figs. 10–12). An exception was the temperature dependence of the headgroup cross-sectional area, $a_0(T)$, which is due to shrinkage (compaction) of the surfactant ethoxy-headgroups with
the rise of $T$ because of enhanced segment-segment attraction. From available data for single-component micelles we determined $a_0(T)$; see Fig. 9. In a subsequent study, it will be demonstrated that using the obtained $a_0(T)$ values one can predict the aggregation numbers of wormlike micelles in mixed solutions of two nonionic surfactants in excellent agreement with the experiment, without using any adjustable parameters. The constructed model can serve as a basis that can be further upgraded to obtain quantitative description of micelle growth in more complicated systems, including binary and ternary mixtures of nonionic, ionic and zwitterionic micelles, which determine the viscosity and stability of various formulations in personal-care and house-hold detergency.

Acknowledgements

The authors gratefully acknowledge the support from Unilever R&D and from the Horizon 2020 project ID: 692146-H2020-eu.4.b “Materials Networking”. The authors are grateful to Mrs. Mariana Paraskova for her assistance in figure preparation.

Appendix A. Analytical solution of the variational problem

Mathematical formulation of the problem. Our goal is to minimize the free energy functional in Eq. (5.17) with respect to variations of the functions $\tilde{G}(x)$ and $\tilde{E}(x,y)$ under constrains given by Eqs. (5.13) – (5.15). The function $\tilde{G}(x)$ is defined for $0 \leq x \leq 1$, whereas the function $\tilde{E}(x,y)$ is defined in the triangular domain $0 \leq x \leq 1$ and $0 \leq y \leq x$. Integrating Eq. (5.14) with respect to $y$ from 0 to 1 and changing the order of integration we obtain:

$$
1 = \int_0^1 \int_y^1 \frac{\tilde{G}(x)}{\tilde{E}(x,y)} \, dx \, dy = \int_0^1 \int_0^x \frac{\tilde{G}(x)}{\tilde{E}(x,y)} \, dy \, dx = \int_0^1 \tilde{G}(x) \frac{x}{\tilde{E}(x,y)} \, dx \, dy \quad (A.1)
$$

From equations (5.13) and (A.1), we obtain:

$$
1 = \int_0^1 \tilde{G}(x) \, dx \quad (A.2)
$$

In view of Eq. (5.12), Eq. (A.2) is identical with Eq. (5.1). Hence, Eq. (5.1) is automatically satisfied and it does not represent independent constraint.

Solution of the problem. In view of Eq. (5.17), our goal is to minimize the following functional:
\[
\Phi[\tilde{G}, \tilde{E}, \mu_G, \mu_E] = \int_0^x dx \int_0^y dy \tilde{G}(x, y) \tilde{E}(x, y) - \int_0^x dx \mu_E(x) \left[ \int_0^y dy \frac{\tilde{G}(x)}{\tilde{E}(x, y)} - 1 \right] \\
- \int_0^y dy \mu_G(y) \left[ \int_0^x dx \frac{\tilde{G}(x)}{\tilde{E}(x, y)} d_x - \frac{1}{p} (1-y)^{\frac{1-p}{p}} \right]
\]

(A.3)

where \( \mu_E(x) \) and \( \mu_G(y) \) are weight functions, which represent Lagrange multipliers related to the constraints in Eqs. (5.13) and (5.14), respectively. The first variation of the extended functional, Eq. (A.3), reads:

\[
\delta \Phi = \int_0^x dx \int_0^y dy [\tilde{E}(x, y) \delta \tilde{G}(x) + \tilde{G}(x) \delta \tilde{E}(x, y)] \\
- \int_0^x dx \int_0^y dy \frac{\tilde{G}(x)}{\tilde{E}(x, y)} d_x - \frac{1}{p} (1-y)^{\frac{1-p}{p}} \delta \mu_E(x) \\
- \int_0^y dy \int_0^x dx \tilde{G}(x) \frac{1}{\tilde{E}(x, y)} - \frac{1}{p} (1-y)^{\frac{1-p}{p}} \delta \mu_G(y) \\
- \int_0^y dy \mu_G(y) \left[ \int_0^x dx \frac{\delta \tilde{G}(x)}{\tilde{E}(x, y)} + \int_0^x dx \tilde{G}(x) \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] \right]
\]

(A.4)

The necessary condition for stationary point in the functional space, \( \delta \Phi = 0 \) with respect to the variations \( \delta \tilde{G}(x), \delta \tilde{E}(x, y), \delta \mu_E(y) \) and \( \delta \mu_G(x) \), leads to equations for determining the four unknown functions, as follows.

(i) Setting zero the coefficients before \( \delta \mu_E(y) \) and \( \delta \mu_G(x) \), we obtain Eqs. (5.13) and (5.14), respectively.

(ii) Setting zero the terms containing the independent variation \( \delta \tilde{G}(x) \), we obtain:

\[
\int_0^x dx \delta \tilde{G}(x) \int_0^y dy \tilde{E}(x, y) - \int_0^y dy \mu_G(y) \left[ \int_0^x dx \frac{\delta \tilde{G}(x)}{\tilde{E}(x, y)} \right] = 0
\]

(A.5)

Exchanging the order of integration in the last term, we derive

\[
\int_0^y dy \delta \tilde{G}(x) \left[ \int_0^x dx \tilde{E}(x, y) - \frac{\mu_G(y)}{\tilde{E}(x, y)} \right] = 0
\]

(A.6)

Hence, the weight function \( \mu_G(y) \) must satisfy the integral equation:

\[
\int_0^y dy \frac{\mu_G(y) - \tilde{E}(x, y)^2}{\tilde{E}(x, y)} = 0 \quad \text{for } 0 \leq x \leq 1
\]

(A.7)

(iii) Setting zero the terms containing the independent variation \( \delta \tilde{E}(x, y) \), we obtain:
\[
\int_0^x \int_0^y \tilde{G}(x) \delta \tilde{E}(x, y) - \int_0^x \int_0^y \mu_E(x) \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] \\
- \int_0^y \int_0^x \mu_G(y) \frac{1}{\tilde{E}(x, y)} \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] = 0
\]  
(A.8)

which can be represented in the form:

\[
\int_0^x \int_0^y \tilde{G}(x) \tilde{E}^2(x, y) + \mu_E(x) \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] + \int_0^y \int_0^x \mu_G(y) \frac{1}{\tilde{E}(x, y)} \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] = 0
\]  
(A.9)

Changing the order of integration in the last term, we obtain:

\[
\int_0^x \int_0^y \tilde{G}(x) \tilde{E}^2(x, y) + \mu_E(x) + \mu_G(y) \tilde{G}(x) \delta \left[ \frac{1}{\tilde{E}(x, y)} \right] = 0
\]  
(A.10)

Hence, the respective necessary condition for extremum reads:

\[
\tilde{G}(x) \tilde{E}^2(x, y) + \mu_E(x) + \mu_G(y) \tilde{G}(x) = 0
\]  
(A.11)

Thus, we obtain an expression for \( \tilde{E}(x, y) \):

\[
\tilde{E}^2(x, y) = -\frac{\mu_E(x)}{\tilde{G}(x)} - \mu_G(y)
\]  
(A.12)

Setting \( y = x \) in Eq. (A.12) and using Eq. (5.15), we obtain:

\[
\mu_G(x) = -\frac{\mu_E(x)}{\tilde{G}(x)}
\]  
(A.13)

The combination of Eqs. (A.12) and (A.13) yields:

\[
\tilde{E}(x, y) = [\mu_G(x) - \mu_G(y)]^{1/2}
\]  
(A.14)

This result for \( \tilde{E}(x, y) \) was published by Semenov [153] without proof.

Furthermore, we substitute \( \tilde{E}(x, y) \) from Eq. (A.14) into Eq. (5.13) and obtain the following integral equation:

\[
1 = \int_0^x \frac{dy}{[\mu_G(x) - \mu_G(y)]^{1/2}} \quad \text{for } 0 \leq x \leq 1
\]  
(A.15)

Using the substitution \( d[\mu_G(y)]/dy = 1/f(\mu_G) \), we transform Eq. (A.15) into an Abel type integral equation:

\[
1 = \int_{\mu_G(0)}^{\mu_G(x)} \frac{f(\mu_G) d[\mu_G(y)]}{[\mu_G(x) - \mu_G(y)]^{1/2}}
\]  
(A.16)

which has the following solution:
\[
f(\mu_G) = \frac{1}{\pi[\mu_G(y) - \mu_G(0)]^{1/2}} \tag{A.17}
\]

To verify that, one can substitute Eq. (A.17) in Eq. (A.16), which leads to an integral that can be solved analytically:

\[
\frac{1}{\pi} \int_a^b \frac{dz}{[(b-z)(z-a)]^{1/2}} = 1 \tag{A.18}
\]

The following notations have been used: \( z = \mu_G(y); \ b = \mu_G(x), \) and \( a = \mu_G(0). \) The substitution of Eq. (A.17) in the definition \( d y = f(\mu_G) d[\mu_G(y)] \) yields:

\[
d y = \frac{1}{\pi[\mu_G(y) - \mu_G(0)]^{1/2}} d[\mu_G(y)] = \frac{2}{\pi} d[\mu_G(y) - \mu_G(0)]^{1/2} \tag{A.19}
\]

Integrating the last equation, we derive:

\[
\frac{\pi}{2} y = [\mu_G(y) - \mu_G(0)]^{1/2} \tag{A.20}
\]

Thus, the solution for the weight function \( \mu_G(y) \) is:

\[
\mu_G(y) = \mu_G(0) + \left( \frac{\pi}{2} \right)^2 y^2 \tag{A.21}
\]

Substituting the last expression in Eq. (A.14), we find \( \tilde{E}(x,y) \) in explicit form:

\[
\tilde{E}(x,y) = \frac{\pi}{2} (x^2 - y^2)^{1/2} \tag{A.22}
\]

To determine \( \mu_G(0) \), we substitute Eqs. (A.21) and (A.22) into Eq. (A.7):

\[
\int_0^x \mu_G(0) + \left( \frac{\pi}{2} \right)^2 (2y^2 - x^2) \frac{dy}{\pi(x^2 - y^2)^{1/2}} = 0 \quad \text{for } 0 \leq x \leq 1 \tag{A.23}
\]

The integral in Eq. (A.23) can be solved analytically, and its solution gives \( \mu_G(0) = 0. \) Further, from Eqs. (A.21) and (A.13) we determine the two Lagrange multipliers:

\[
\mu_G(y) = \left( \frac{\pi}{2} \right)^2 y^2, \quad \mu_k(x) = -\left( \frac{\pi}{2} \right)^2 x^2 \tilde{G}(x) \tag{A.24}
\]

To find \( \tilde{G}(x) \), we substitute Eq. (A.22) in Eq. (5.14):

\[
\frac{\pi}{2p} (1 - y)^{\frac{1+p}{p}} = \int_y^{1-y} \frac{\tilde{G}(x)}{(x^2 - y^2)^{1/2}} dx \quad \text{for } 0 \leq y \leq 1 \tag{A.25}
\]

Eq. (A.25) is an Abel type integral equation. Its general solution reads [207]:
\[ \tilde{G}(x) = -\frac{d}{dx} \left[ \int_{x}^{1} \frac{1}{p(z^2 - x^2)^{1/2}} \frac{1-p}{z} \ d z \right] \text{ for } 0 \leq x \leq 1 \quad (A.26) \]

In the special case of \textit{lamellar} geometry, \( p = 1 \), the integral in Eq. (A.26) acquires the form:

\[ \int_{x}^{1} \frac{z}{(z^2 - x^2)^{1/2}} \ d z = (1 - x^2)^{1/2} \quad (A.27) \]

so that Eq. (A.26) yields:

\[ \tilde{G}(x) = \frac{x}{(1 - x^2)^{1/2}} \quad (A.28) \]

Likewise, for \textit{cylindrical} geometry, \( p = 1/2 \), one obtains:

\[ \int_{x}^{1} \frac{2z(1-z)}{(z^2 - x^2)^{1/2}} \ d z = (1 - x^2)^{1/2} - x^2 \ \text{artanh}[(1 - x^2)^{1/2}] \quad (A.29) \]

\[ \tilde{G}(x) = 2x \ \text{artanh}[(1 - x^2)^{1/2}] \quad (A.30) \]

Analogously, for \textit{spherical} geometry, \( p = 1/3 \), one derives:

\[ \int_{x}^{1} \frac{3z(1-z)^2}{(z^2 - x^2)^{1/2}} \ d z = (1 - x^2)^{1/2} (1 + 2x^2) - 3x^2 \ \text{artanh}[(1 - x^2)^{1/2}] \quad (A.31) \]

\[ \tilde{G}(x) = 6x \left\{ \text{artanh}[(1 - x^2)^{1/2}] - (1 - x^2)^{1/2} \right\} \quad (A.32) \]

One could use also the expression \( \text{artanh}[(1 - x^2)^{1/2}] = \ln\left[ \frac{1}{x} + (\frac{1}{x^2} - 1)^{1/2} \right] \). The results for \( \tilde{G}(x) \) in the special cases \( p = 1/3, 1/2, \) and \( 1 \), expressed by Eqs. (A.28), (A.30) and (A.32), coincide with the expressions obtained by Semenov [153].

The substitution of \( \tilde{E}(x,y) \) from Eq. (A.22) into Eq. (5.15) yields:

\[ \frac{f_{\text{conf}}}{k_B T} = \frac{3\pi^2 R^2}{16l_{\text{seg}}^2} c_{\text{conf}}(p), \text{ where} \quad (A.33) \]

\[ c_{\text{conf}}(p) = \int_{0}^{1} x^2 \tilde{G}(x) \ d x \quad (A.34) \]

Furthermore, substituting the general form of \( \tilde{G}(x) \) from Eq. (A.26) into Eq. (A.34), we get:

\[ c_{\text{conf}}(p) = -\int_{0}^{1} x^2 \frac{d}{dx} \left[ \int_{x}^{1} \frac{1}{p(z^2 - x^2)^{1/2}} \frac{1-p}{z} \ d z \right] \ d x \quad (A.35) \]

Integrating by part in Eq. (A.35), we obtain:
\[ c_{\text{conf}}(p) = 2 \frac{1}{p} \left[ x \left( 1 - z \right)^{\frac{1-p}{p}} \right] \left( \frac{z^2 - x^2}{(z^2 - x^2)^{1/2}} \right) dx \]  

(A.36)

The change of the order of integration leads to:

\[ c_{\text{conf}}(p) = 2 \frac{1}{p} \left( z^2 (1 - z)^{\frac{1-p}{p}} \right) dx \left( z^2 - x^2 \right)^{1/2} dx \]  

(A.37)

which finally yields:

\[ c_{\text{conf}}(p) = 2 \frac{1}{p} \left( z^2 (1 - z)^{\frac{1-p}{p}} \right) dz = \frac{4p^2}{1 + 3p + 2p^2} \]  

(A.38)

Equations (A.33) and (A.38) are identical with Eqs. (4.19) and (4.20) in the main text. It should be noted that the more general equations (A.25) and (A.26), as well as Eqs. (A.33)–(A.38), represent new results.

References

[1] McBain JW. Colloids and their viscosity. Discussion. Trans Faraday Soc 1913; 9: 99–101.
[2] McBain JW, Cornish ECV, Bowden RC. Studies of the constitution of soap in solution: Sodium myristate and sodium laurate. J Chem Soc Trans 1912; 101: 2042–56.
[3] McBain JW, Salmon CS. Colloidal electrolytes: Soap solutions and their constitution. Proc R Soc Lond A 1920; 97: 44–65.
[4] Harkins WD, Davies ECH, Clark GL. The orientation of molecules in the surfaces of liquids, the energy relations at surfaces, solubility, adsorption, emulsification, molecular association, and the effect of acids and bases on interfacial tension (Surface energy VI). J Am Chem Soc 1917; 39; 541–96.
[5] Hess K, Gundermann J. Röntgenographische Untersuchungen an ruhenden und strömenden kolloiden Lösungen. Ber Dtsch Chem Ges 1937; 70:1800–8.
[6] Hess K, Philippoff W, Kiessig H. Viskositätsbestimmungen, Dichtemessungen und Röntgenuntersuchungen an Seifenlösungen. Kolloid Z 1939; 88: 40–51.
[7] Philippoff W. Micelles and X-rays. J Colloid Sci 1950; 5: 169–91.
[8] Harkins WD, Mattoon RW, Corrin ML. Structure of soap micelles indicated by X-rays and the theory of molecular orientation. I. Aqueous solutions. J Am Chem Soc 1946; 68: 220–8.
[9] Mattoon RW, Stearns RS, Harkins WD. Structure for soap micelles as indicated by a previously unrecognized X-ray diffraction band. J Chem Phys 1947; 15: 209–10.
[10] Harkins WD, Mattoon RW, Corrin ML. Structure of soap micelles indicated by X-rays and interpreted by the theory of molecular orientation. II. The solubilization of hydrocarbons and other oils in aqueous soap solutions. J Colloid Sci 1946; 1: 105–26.
[11] Harkins WD. A cylindrical model for the small soap micelles. J Chem Phys 1948; 16: 156–7.

[12] Adam NK. The structure of surface films on water. J Phys Chem 1925; 29: 87–101.

[13] Hartley GS, Collie B, Samis CS. Transport numbers of paraffin-chain salts in aqueous solution. Part I. Measurement of transport numbers of cetylpyridinium and cetyltrimethylammonium bromides and their interpretation in terms of micelle formation, with some data also for cetane sulphonic acid. Trans Faraday Soc 1936; 32: 795–815.

[14] Hartley GS, Runnicles DF. The determination of the size of paraffin-chain salt micelles from diffusion measurements. Proc R Soc Lond A 1938; 168: 420–40.

[15] Hartley GS. Organized structure in soap solutions. Nature 1949; 163: 767–8.

[16] Corrin ML. Interpretation of X-ray scattering from solutions of long-chain electrolytes on the basis of a spherical micelle. J Chem Phys 1948; 16: 844–5.

[17] Harkins WD. Soap solutions: Salt, alcohol, micelles, rubber. Scientific Monthly 1950; 70: 220–8.

[18] Philippoff W. Colloidal and polyelectrolytes. The micelle and swollen micelle on soap micelles. Discuss Faraday Soc 1951; 11: 96–107.

[19] Vincent B. McBain and the centenary of the micelle. Adv Colloid Interface Sci 2014; 203: 51–4.

[20] Prévost S, Gradzielski M, Zemb T. Self-assembly, phase behavior and structural behavior as observed by scattering for classical and non-classical microemulsions. Adv Colloid Interface Sci 2017; 247: 374–96.

[21] Danino D. Cryo-TEM of soft molecular assemblies. Curr Opin Colloid Interface Sci 2012; 17: 316–29.

[22] Dreiss CA. Wormlike micelles: where do we stand? Recent developments, linear rheology and scattering techniques. Soft Matter 2007; 3: 956–70.

[23] Nicolas-Morgantini L. Giant Micelles and Shampoo. In Giant Micelles. Properties and Applications. Zana R, Kaler EW, eds., CRC Press, 2007; 493–514.

[24] Ezrahi S, Tuval E, Aserin A, Garti N. Daily applications of systems with wormlike micelles. In Giant Micelles. Properties and Applications. Zana R, Kaler EW, eds., CRC Press, 2007; 515–44.

[25] Sullivan PF, Panda MKR, Laffite V. Applications of wormlike micelles in oilfield industry. In Wormlike Micelles. Advances in Systems, Characterization and Applications. Dreiss CA, Feng Y, eds., RSC, 2017; 330–52.

[26] Zakin JL, Maxson AJ, Saeki T, Sullivan PF. Turbulent Drag-reduction Applications of Surfactant Solutions. In Wormlike Micelles. Advances in Systems, Characterization and Applications. Dreiss CA, Feng Y, eds., RSC, 2017; 353–78.

[27] Zemb T, Dubois M, Demé B, Gulik-Krzywicki T. Self-assembly of flat nanodiscs in salt-free catanionic surfactant solutions. Science 1999; 283: 816–9.
[28] Song Y, Dorin RM, Garcia RM, Jiang Y-B, Wang H, Li P, Qui Y, van Swol F, Miller JE, Shelnutt JA. Synthesis of platinum nanowheels using a bicellar template. J Am Chem Soc 2008; 130; 12602–3.

[29] Kralchevsky PA, Danov KD, Anachkov SE, Georgieva GS, Ananthapadmanabhan KP. Extension of the ladder model of self-assembly from cylindrical to disclike surfactant micelles. Curr Opin Colloid Interface Sci 2013; 18: 524–31.

[30] Danino D, Abezgauz L, Portnaya I, Dan N. From discs to ribbons networks: the second critical micelle concentration in nonionic sterol solutions. J Phys Chem Lett 2016; 7: 1434–9.

[31] Anachkov SE, Georgieva GS, Abezgauz L, Danino D, Kralchevsky PA. Viscosity peak due to shape transition from wormlike to disclike micelles: effect of dodecanoic acid. Langmuir 2018; 34: 4897–907.

[32] Rehage H, Hoffmann H. Rheological properties of viscoelastic surfactant systems. J Phys Chem 1988; 92; 4712–9.

[33] Rehage H, Hoffmann H. Viscoelastic surfactant solutions: Model systems for rheological research. Mol Phys 1991; 74: 933–73.

[34] Hoffmann H, Rauscher A, Gradzielski M, Schulz SF. Influence of ionic surfactants on the viscoelastic properties of zwitterionic surfactant solutions. Langmuir 1992; 8: 2140–6.

[35] Candau SJ, Khatory A, Lequeux F, Kern F. Rheological behavior of wormlike micelles: Effect of salt content. J Phys IV France 1993; 3: C1-197–C1-209.

[36] Ali AA, Makhloufi R. Linear and nonlinear rheology of an aqueous concentrated system of cetyltrimethylammonium chloride and sodium salicylate. Phys Rev E 1997; 56: 4474–8.

[37] Hartmann V, Cressely R. Linear and non linear rheology of a wormlike micellar system in presence of sodium tosylate. Rheol Acta 1998; 37: 115–21.

[38] Cappelaere E, Cressely R. Influence of NaClO₃ on the rheological behavior of a micellar solution of CPCl. Rheol Acta 2000; 39: 346–53.

[39] Koehler RD, Raghavan SR, Kaler EW. Microstructure and dynamics of wormlike micellar solutions formed by mixing cationic and anionic surfactants. J Phys Chem B 2000; 104; 11035–44.

[40] Candau SJ, Oda R. Linear viscoelasticity of salt-free wormlike micellar solutions. Colloids Surf A 2001; 183–185: 5–14.

[41] Raghavan SR, Fritz G, Kaler EW. Wormlike micelles formed by synergistic self-assembly in mixtures of anionic and cationic surfactants. Langmuir 2002; 18: 3797–803.

[42] Acharya DP, Hattori K, Sakai T, Kunieda H. Phase and rheological behavior of salt-free alkyltrimethylammonium bromide/alkanoyl-N-methylethanolamide/water systems. Langmuir 2003; 19: 9173–8.

[43] Angelesku D, Khan A, Caldararu H. Viscoelastic properties of sodium dodecyl sulfate with aluminum salt in aqueous solution. Langmuir 2003; 19: 9155–61.
Acharya DP, Hossain MK, Feng J, Sakai T, Kunieda H. Phase and rheological behavior of viscoelastic wormlike micellar solutions formed in mixed nonionic surfactant systems. Phys Chem Chem Phys 2004; 6: 1627–31.

Naito N, Acharya DP, Tanimura J, Kunieda H. Rheological behavior of wormlike micellar solutions in mixed nonionic systems of polyoxyethylene phytosterol-polyoxyethylene dodecyl ether. J Oleo Sci 2004; 53: 599–606.

Mitrinova Z, Tcholakova S, Popova Z, Denkov N, Dasgupta BR, Ananthapadmanabhan KP. Efficient control of the rheological and surface properties of surfactant solutions containing C8-C18 fatty acids and cosurfactants. Langmuir 2013; 29: 8255–65.

Parker A, Fieber W. Viscoelasticity of anionic wormlike micelles: Effects of ionic strength and small hydrophobic molecules. Soft Matter 2013; 9: 1203–13.

Kamada M, Shimizu S, Aramaki K. Manipulation of the viscosity behavior of wormlike micellar gels by changing the molecular structure of added perfumes. Colloids Surf A 2014; 458: 110–6.

Yixiu H, Hong Z, Yongqiang W, Yongjin M, Hang W. Rheological investigation on anionic wormlike micelles at high temperature. J Mol Liq 2015; 211: 481–6.

Różańska S. Rheology of wormlike micelles in mixed solutions of cocoamidopropyl betaine and sodium dodecybenzenesulfonate. Colloids Surf A 2015; 482: 394–402.

Zhang Y, Zhou D, Ran H, Dai H, An P, He S. Rheology behaviors of C22-tailed carboxybetaine in high-salinity solution. J Disper Sci Tech 2016; 37: 496–503.

Dai C, Li W, Cui Y, Sun Y, Wu W, Xu Z, Liu Y, Yang Z, Wu X. The effect of functional groups on the sphere-to-wormlike micellar transition in quaternary ammonium surfactant solutions. Colloids Surf A 2016; 500: 32–9.

Zhao M, Gao M, Dai C, Zou C, Yang Z, Wu X, Liu Y, Wu Y, Fang S, Lv W. Investigation of novel triple-responsive wormlike micelles. Langmuir 2017; 33: 4319–27.

Zhai Z, Yan X, Song Z, Shang S, Rao X. Wormlike micelles constructed by a highly water-soluble carboxylate surfactant containing a phenoxy and nonionic surfactant. J Mol Liq 2017; 248: 595–601.

Liu L, Zheng C, Lu H. CO2-responsive wormlike micelles based on sodium oleate and hydrophobic tertiary amines. J Disper Sci Tech 2017; 38: 1824–31.

Wang J, Huang Z, Zheng C, Lu H. CO2/N2-switchable viscoelastic fluids based on a pseudogemini surfactant system. J Disper Sci Tech 2017; 38: 1705–10.

Kamada M, Pierlot C, Molinier V, Aubry J-M, Aramaki K. Rheological properties of wormlike micellar gels formed by novel bio-based isosorbide surfactants. Colloids Surf A 2018; 536: 82–7.

Mitrinova Z, Tcholakova S, Denkov N. Control of surfactant solution rheology using medium-chain cosurfactants. Colloids Surf A 2018; 537: 173–84.

Clinckspoor KJ, Jorge LL, Hoffmann H, Sabadini E. Rheologic and calorimetric study of alkyltrimethylammonium bromide-sodium salicylate wormlike micelles in aqueous binary systems. J Colloid Interface Sci 2018; 515: 198–207.
[60] Clausen TM, Vinson PK, Minter JR, Davis HT, Talmon Y, Miller WG. Viscoelastic micellar solutions: Microscopy and rheology. J Phys Chem 1992; 96: 474–84.

[61] Aswal VK, Goyal PS, Thiagarajan P. Small-angle neutron-scattering and viscosity study of CTAB/NaSal viscoelastic micellar solutions. J Phys Chem B 1998; 102: 2469–73.

[62] Schubert BA, Kaler EW, Wagner NJ. The microstructure and rheology of mixed cationic/anionic wormlike micelles. Langmuir 2003; 19: 4079–89.

[63] Croce V, Cosgrove T, Maitland G, Hughes T, Karlsson G. Rheology, cryogenic transmission electron spectroscopy, and small-angle neutron scattering of highly viscoelastic wormlike micellar solutions. Langmuir 2003; 19: 8536–41.

[64] Acharya DP, Kunieda H, Shiba Y, Aratani K. Phase and rheological behavior of novel gemini-type surfactant systems. J Phys Chem B 2004; 108: 1790–7.

[65] Ziserman L, Abezgauz L, Ramon O, Raghavan SR, Danino D. Origins of the viscosity peak in wormlike micellar solutions: 1. Mixed cationic surfactants. Cryo-transmission electron microscopy study. Langmuir 2009; 25: 10483–9.

[66] Afifi H, Karlsson G, Heenan RK, Dreiss CA. Solubilization of oil or addition of monoglycerides drives the formation of wormlike micelles with an elliptical cross-section in cholesterol-based surfactants: A study by rheology, SANS, and Cryo-TEM. Langmuir 2011; 27: 7480–92.

[67] Lin W, Yang Z, Wang J, Chen T, Shi X. Wormlike micelles with pH-induced rheological property formed by cationic surfactant/anthranilic acid mixed aqueous solution. J Mol Liq 2016; 224 Part A: 333–7.

[68] Georgieva GS, Anachkov SE, Lieberwith I, Koynov K, Kralchevsky PA. Synergistic growth of giant wormlike micelles in ternary mixed surfactant solutions: Effect of octanoic acid. Langmuir 2016; 32: 12885–93.

[69] Lu H, Yang L, Wang B, Huang Z. Switchable spherical-wormlike micelle transition in sodium oleate/N-(3-(dimethylamino)propyl)-octanamide aqueous system induced by carbon dioxide stimuli and pH regulation. J Disper Sci Tech 2016; 37: 159–65.

[70] Zhang J, Wang Y, Xu G, Lin M, Fan T, Yang Z, Dong Z. Formation and rheological behavior of wormlike micelles in a cationic system of fluoroacetic acid and tetradecyldimethylaminoxide. Soft Matter 2017; 13: 670–6.

[71] Morishima K, Sugawara S, Yoshimura T, Shibayama M. Structure and rheology of wormlike micelles formed by fluorocarbon-hydrocarbon-type hybrid gemini surfactant in aqueous solution. Langmuir 2017; 33: 6084–91.

[72] Sun P, Lu F, Wu A, Shi L, Zheng L. Spontaneous wormlike micelles formed in a single-tailed zwitterionic surface-active ionic liquid aqueous solution. Soft Matter 2017; 13: 2543–8.

[73] Kang W, Wang P, Fan H, Yang H, Dai C, Yin X, Zhao Y, Guo S. A pH-responsive wormlike micellar system of a noncovalent interaction-based surfactant with a tunable molecular structure. Soft Matter 2017; 13: 1182–9.
[74] Wang J, Feng Y, Agrawal NR, Raghavan SR. Wormlike micelles versus water-soluble polymers as rheology-modifiers: similarities and differences. Phys Chem Chem Phys 2017; 19: 24458–66.

[75] Wang P, Kang W, Yang H, Zhao Y, Yin X, Zhu Z, Zhang X. The N-allyl substituted effect on wormlike micelles and salt tolerance of a C22-tailed cationic surfactant. Soft Matter 2017; 13: 7425–32.

[76] Wang B, Liu L, Zheng C, Lu H. pH and temperature-responsive wormlike micelles formed by single amine oxide surfactant. J Disper Sci Tech 2018; 39: 539–47.

[77] Chavda S, Danino D, Aswal VK, Singh K, Marangoni DG, Bahadur P. Microstructure and transitions in mixed micelles of cetyltrimethylammonium tosylate and bile salts. Colloids Surf A 2017; 513: 223–33.

[78] Huerta-Marcial ST, Landázuri G, Macías-Balleza ER, Rosales-Rivera LC, Ruso JM, Puig JE, Armando Soltero JF. Effect of the aniline hydrochloride hydrotrope on the microstructure of SDS/water system: Linear rheological behavior. Colloids Surf A 2017; 523: 19–26.

[79] Bernheim-Groswasser A, Wachtel E, Talmon Y. Micellar growth, network formation, and criticality in aqueous solutions of the nonionic surfactant C12E5. Langmuir 2000; 16: 4131–40.

[80] Debye P. Note on light scattering in soap solutions. J Colloid Sci 1948; 3: 407–9.

[81] Debye P. Light scattering in soap solutions. J Phys Chem 1949; 53: 1–8.

[82] Hobbs ME. The effect of salt on the critical concentration, size, and stability of soap micelles. J Phys Chem 1951; 55: 675–83.

[83] Halsey Jr. GD. On the structure of micelles. J Phys Chem 1953; 57: 87–9.

[84] Ooshika Y. A theory of critical micelle concentration of colloidal electrolyte solutions. J Colloid Sci 1954; 9: 254–62.

[85] Reich I. Factors responsible for the stability of detergent micelles. J Phys Chem 1956; 60: 257–62.

[86] Debye P, Anacker EW. Micelle shape from dissymmetry measurements. J Phys Chem 1951; 55: 644–55.

[87] Hoeve CAJ, Benson GC. On the statistical mechanical theory of micelle formation in detergent solutions. J Phys Chem 1957; 61: 1149–58.

[88] Poland DC, Scheraga HA. Hydrophobic bonding and micelle stability; the influence of ionic head groups. J Colloid Interface Sci 1966; 21: 273–83.

[89] Rusanov AI. Refining the ionic surfactant micellization theory based on the law of mass action. Colloid J 2016; 78: 669–73.

[90] Tanford C. Micelle shape and size. J Phys Chem 1972; 76: 3020–4.

[91] Tanford C. Thermodynamics of micelle formation: Prediction of micelle size and size distribution. Proc Natl Acad Sci USA 1974; 71: 1811–5.

[92] Tanford C. The hydrophobic effect and the organization of living matter. Science 1978; 200: 1012–8.
[93] Israelachvili JN, Mitchel DJ, Ninham BW. Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. J Chem Soc Faraday Trans II 1976; 72: 1525–68.

[94] Danov KD, Kralchevsky PA, Ananthapadmanabhan KP. Micelle-monomer equilibria in solutions of ionic surfactants and in ionic-nonionic mixtures. Adv Colloid Interface Sci 2014; 206: 17–45.

[95] Scheraga HA, Backus JK. Flow birefringence in solutions of n-hexadecyltrimethylammonium bromide. J Am Chem Soc 1951; 73: 5108–12.

[96] Mukerjee P. Hydrophobic and electrostatic interactions in ionic micelles. Problems in calculating monomer contributions to the free energy. J Phys Chem 1969; 73: 2054–6.

[97] Mukerjee P. The size distribution of small and large micelles: A multiple equilibrium analysis. J Phys Chem 1972; 76: 565–70.

[98] Ghosh AK, Mukerjee P. Multiple association equilibria in the self-association of methylene blue and other dyes. J Am Chem Soc 1970; 92: 6408–12.

[99] Tausk RJM, Overbeek JThG. Physical chemical studies of short-chain lecithin homologues: IV. A simple model for the influence of salt and the alkyl chain length on the micellar size. Biophys Chem 1974; 2: 175–9.

[100] Missel PJ, Mazer NA, Benedek GB, Young CY, Carey MC. Thermodynamic analysis of the growth of sodium dodecyl sulfate micelles. J Phys Chem 1980; 84: 1044–57.

[101] Anachkov SA, Kralchevsky PA, Danov KD, Georgieva GS, Ananthapadmanabhan KP. Disclike vs. cylindrical micelles: Generalized model of micelle growth and data interpretation. J Colloid Interface Sci 2014; 416: 258–73.

[102] R. Nagarajan R. Evolution of the theory of micellization, In Surfactant Science and Technology. Retrospects and Prospects. Romsted LS, ed., CRC Press, 2014; Ch. 1; 4–52.

[103] Porte G, Appell J, Poggl Y. Experimental investigations on the flexibility of elongated cetylpyridinium bromide micelles. J Phys Chem 1980; 84: 3105–10.

[104] Missel PJ, Mazer NA, Benedek GB, Carey MC. Influence of chain length on the sphere-to-rod transition in alkyl sulfate micelles. J Phys Chem 1983; 87: 1264–77.

[105] Ozeki S, Ikeda S. The sphere-rod transition of micelles of dodecyldimethylammonium bromide in aqueous NaBr solutions, and the effects of counterion binding on the micelle size, shape and structure. Colloid Polymer Sci 1984; 262: 409–17.

[106] Imae T, Kamiya R, Ikeda S. Formation of spherical and rodlike micelles of cetyltrimethylammonium bromide in aqueous NaBr solutions. J Colloid Interface Sci 1985; 108: 215–25.

[107] Malliaris A, Binana-Limbele W, Zana R. Fluorescence probing studies of surfactant aggregation in aqueous solutions of mixed ionic micelles. J Colloid Interface Sci 1986; 110: 114–20.

[108] Imae T, Ikeda S. Sphere-rod transition of micelles of tetradecyltrimethylammonium halides in aqueous sodium halide solutions and flexibility and entanglement of long rodlike micelles. J Phys Chem 1986; 90: 5216–23.

51
[109] Imae T. Ikeda S. Characteristics of rodlike micelles of cetyltrimethylammonium chloride in aqueous NaCl solutions: Their flexibility and the scaling law in dilute and semidilute regimes. Colloid Polymer Sci 1987; 265: 1090–8.

[110] Missel PJ, Mazer NA, Carey MC, Benedek GB. Influence of alkali-metal counterion identity on the sphere-to-rod transition in alkyl sulfate micelles. J Phys Chem 1989; 93: 8354–66.

[111] Nguyen D, Bertrand GL. Calorimetric observations of the sphere-rod transition of sodium dodecyl sulfate: Effects of electrolytes and nonelectrolytes at 25 °C. J Phys Chem 1992; 96: 1994–8.

[112] Alargova R, Petkov J, Petsev D, Ivanov IB, Broze G, Mehreteab A. Light scattering study of sodium dodecyl polyoxyethylene-2-sulfate micelles in the presence of multivalent counterions. Langmuir 1995; 11: 1530–36.

[113] Alargova RG, Danov KD, Petkov JT, Kralchevsky PA, Broze G, Mehreteab A. Sphere-to-rod transition in the shape of anionic surfactant micelles determined by surface tension measurements. Langmuir 1997; 13: 5544–51.

[114] Alargova RG, Danov KD, Kralchevsky PA, Broze G, Mehreteab A. Growth of giant rodlike micelles of ionic surfactants in the presence of Al3+ counterions. Langmuir 1998; 14: 4036–49.

[115] Alargova RG, Ivanova VP, Kralchevsky PA, Mehreteab A, Broze G. Growth of rod-like micelles in anionic surfactant solutions in the presence of Ca2+ counterions. Colloids Surf A 1998; 142: 201–18.

[116] Fujio K, Mitsui T, Kurumizawa H, Tanaka Y, Uzu Y. Solubilization of water-insoluble dye in aqueous NaBr solutions of alkylpyridinium bromides and its relation to micellar size and shape. Colloid Polymer Sci 2004; 282: 223–9.

[117] Christov NC, Denkov ND, Kralchevsky PA, Ananthapadmanabhan KP, Lips A. Synergistic sphere-to-rod micelle transition in mixed solutions of sodium dodecyl sulfate and cocoamidopropyl betaine. Langmuir 2004; 20: 565–71.

[118] Varade D, Joshi T, Aswal VK, Goyal PS, Hassan PA, Bahadur P. Effect of salt on the micelles of cetyl pyridinium chloride. Colloids Surf A 2005; 259: 95–101.

[119] Thomas HG, Lomakin A, Blankschtein D, Benedek GB. Growth of mixed nonionic micelles. Langmuir 1997; 13: 209–18.

[120] Menge U, Lang P, Findenegg GH. From oil-swollen wormlike micelles to microemulsion droplets: A static light scattering study of the L1 phase of the system water + C12E5 + decane. J Phys Chem B 1999; 103: 5768–74.

[121] Menge U, Lang P, Findenegg GH. Influence of temperature and oil-to-surfactant ratio on micellar growth in aqueous solutions of C12E5 with decane. Colloids Surf A 2000; 163: 81–90.

[122] Menge U, Lang P, Findenegg GH, Strunz P. Structural transition of oil swollen cylindrical micelles of C12E5 in water studied by SANS. J Phys Chem B 2003; 107; 1316–20.
Yoshimura S, Shirai S, Einaga Y. Light-scattering characterization of the wormlike micelles of hexaoxyethylene dodecyl C_{12}E_6 and hexaoxyethylene tetradecyl C_{14}E_6 ethers in dilute aqueous solution. J Phys Chem B 2004; 108: 15477–87.

Hamada N, Einaga Y. Effect of hydrophobic chain length on the characteristics of the micelles of octaoxyethylene tetradecyl C_{14}E_8, hexadecyl C_{16}E_8, and octadecyl C_{18}E_8 ethers. J Phys Chem B 2005; 109: 6990–8.

Shirai S, Einaga Y. Wormlike micelles of polyoxyethylene dodecyl C_{12}E_j and heptaoxyethylene alkyl C_jE_7 ethers. Hydrophobic and hydrophilic chain length dependence of the micellar characteristics. Polym J 2005; 37: 913–24.

Einaga Y, Kusumoto A, Noda A. Effects of hydrophobic chain length on the micelles of heptaoxyethylene hexadecyl C_{16}E_7 and octadecyl C_{18}E_7 ethers. Polym J 2005; 37: 368–75.

Imanishi K, Einaga Y. Effects of hydrophilic chain length on the characteristics of the micelles of pentaoxyethylene n-decyl C_{10}E_5 and hexaoxyethylene n-decyl C_{10}E_6 ethers. J Phys Chem B 2005; 109: 7574–81.

Shirai S, Yoshimura S, Einaga Y. Intrinsic viscosity of polyoxyethylene alkyl ether C_jE_j micelles. Polym J 2006; 38: 37–43.

Imanishi K, Einaga Y. Wormlike micelles of polyoxyethylene alkyl ether mixtures C_{10}E_5+C_{14}E_5 and C_{14}E_5+C_{14}E_7: Hydrophobic and hydrophilic chain length dependence of the micellar characteristics. J Phys Chem B 2007; 111: 62–73.

Miyake M, Einaga Y. Characteristics of wormlike pentaoxyethylene decyl ether C_{10}E_5 micelles containing n-dodecanol. J Phys Chem B 2007; 111: 535–42.

Einaga Y, Wormlike micelles of polyoxyethylene alkyl ethers C_jE_j. Polym J 2009; 41: 157–73.

Focher B, Savelli G, Torri G, Vecchio G, McKenzie DC, Nicoli DF, Bunton CA. Micelles of 1-alkyl glucoside and maltoside: Anomeric effects on structure and induced charity. Chem Phys Lett 1989; 158: 491–4.

Nagarajan R, Ruckenstein E. Thermodynamics of amphiphilic aggregation into micelles and vesicles. In Mittal KL, ed. Micellization, Solubilization and Microemulsions, Vol. 1. New York: Plenum Press; 1977: 133–49.

Nagarajan R. Are large micelles rigid or flexible? A reinterpretation of viscosity data for micellar solutions. J Colloid Interface Sci 1982; 90: 477–86.

Nagarajan R. Self-assembly of bola amphiphiles. Chem Eng Comm 1987; 55: 251–73.

Nagarajan R, Ruckenstein E. Theory of surfactant self-assembly: A predictive molecular thermodynamic approach. Langmuir 1991; 7: 2934–69.

Nagarajan R. Micellization of binary surfactant mixtures. Theory. In Holland PM, Rubingh DN, eds. Mixed Surfactant Systems, Vol. 501. Washington: ACS Symposium Series; 1992: 54–95.

Nagarajan R. Modeling solution entropy in the theory of micellization. Colloids Surf A 1993; 71: 39–64.
[139] Nagarajan R, Ruckenstein E. Self-assembled systems. In Sengers JV, Kayser RF, Peters CJ, White Jr HF, eds. Equations of State for Fluids and Fluid Mixtures. Amsterdam: Elsevier Science; 2000: 589–749.

[140] Nagarajan R. Molecular packing parameter and surfactant self-assembly: The neglected role of the surfactant tail. Langmuir 2002; 18: 31–8.

[141] Nagarajan R. Theory of micelle formation. Quantitative approach to predicting the micellar properties from surfactant molecular structure. In Esumi H, Ueno M, eds. Structure-Performance Relationships in Surfactants. New York: Marcel Dekker; 2003: 1–110.

[142] Nagarajan R. Molecular thermodynamics of giant micelles. In Zana R, Kaler E, eds. Giant Micelles. Properties and Applications. New York: Taylor and Francis; 2007: 1–40.

[143] Puvvada S, Blankschtein D. Molecular-thermodynamic approach to predict micellization, phase behavior and phase separation of micellar solutions. I. Application to nonionic surfactants. J Chem Phys 1990; 92: 3710–24.

[144] Puvvada S, Blankschtein D. Theoretical and experimental investigation of micellar properties of aqueous solutions containing binary mixtures of nonionic surfactants. J Phys Chem 1992; 96: 5579–92.

[145] Puvvada S, Blankschtein D. Thermodynamic description of micellization, phase-behavior, and phase-separation of aqueous-solutions of surfactant mixtures. J Phys Chem 1992; 96: 5567–79.

[146] Naor A, Puvvada S, Blankschtein D. An analytical expression for the free-energy of micellization. J Phys Chem 1992; 96: 7830–2.

[147] Yuet PK, Blankschtein D. Molecular-thermodynamic modeling of mixed cationic/anionic vesicles. Langmuir 1996; 12: 3802–18.

[148] Zoeller N, Lue L, Blankschtein D. Statistical-thermodynamic framework to model nonionic micellar solutions. Langmuir 1997; 13: 5258–75.

[149] Shiloach A, Blankschtein D. Predicting micellar solution properties of binary surfactant mixtures. Langmuir 1998; 14: 1618–36.

[150] Srinivasan V, Blankschtein D. Effect of counterion binding on micellar solution behavior: 1. Molecular-thermodynamic theory of micellization of ionic surfactants. Langmuir 2003; 19: 9932–45.

[151] Srinivasan V, Blankschtein D. Effect of counterion binding on micellar solution behavior: 2. Prediction of micellar solution properties of ionic surfactant-electrolyte systems. Langmuir 2003; 19: 9946–61.

[152] Srinivasan V, Blankschtein D. Prediction of conformational characteristics and micellar solution properties of fluorocarbon surfactants. Langmuir 2005; 21: 1647–60.

[153] Semenov AN. Contribution to the theory of microphase layering in block-copolymer melts. Sov Phys JETP 1985; 61: 733–42.

[154] Ben-Shaul A, Szleifer I, Gelbart WM. Statistical thermodynamics of amphiphile chains in micelles. Proc Natl Acad Sci USA 1984; 81: 4601–5.

[155] Gruen DWR. A model for the chains in amphiphilic aggregates. 1. Comparison with a molecular dynamics simulation of a bilayer. J Phys Chem 1985; 89: 146–53.
[156] Gruen DWR. A model for the chains in amphiphilic aggregates. 2. Thermodynamic and experimental comparison for aggregates with different shape and size. J Phys Chem 1985; 89: 153–63.

[157] Ben-Shaul A, Gelbart WM. Theory of chain packing in amphiphilic aggregates. Ann Rev Phys Chem 1985; 36: 179–211.

[158] Ben-Shaul A, Szleifer I, Gelbart WM. Chain organization and thermodynamics in micelles and bilayers. I. Theory. J Chem Phys 1985; 83: 3597–611.

[159] Szleifer I, Ben-Shaul A, Gelbart WM. Chain organization and thermodynamics in micelles and bilayers. II. Model calculations. J Chem Phys 1985; 83; 3612–20.

[160] Szleifer I, Ben-Shaul A, Gelbart WM. Chain statistics in micelles and bilayers: Effects of surface roughness and internal energy. J Chem Phys 1986; 85: 5345–58.

[161] Szleifer I, Ben-Shaul A, Gelbart WM. Statistical thermodynamics of molecular organization in mixed micelles and bilayers. J Chem Phys 1987; 86; 7094–109.

[162] May S, Ben-Shaul A. Molecular theory of the sphere-to-rod transition and the second CMC in aqueous micellar solutions. J Phys Chem B 2001; 105: 630–40.

[163] May S, Ben-Shaul A. Molecular packing in cylindrical micelles. In Zana R, Kaler E, eds. Giant Micelles. Properties and Applications. New York: Taylor and Francis; 2007: 41–79.

[164] Moreira L, Firoozabadi A. Molecular thermodynamic modeling of specific ion effects on micellization of ionic surfactants. Langmuir 2010; 26: 15177–91.

[165] Lukanov B, Firoozabadi A. Specific ion effects on the self-assembly of ionic surfactants: A molecular thermodynamic theory of micellization with dispersion forces. Langmuir 2014; 34: 6373–83.

[166] Koroleva SV, Victorov AI. Modeling of the effects of ionic specificity on the onset and growth of ionic micelles in a solution of simple slats. Langmuir 2014; 30: 3387–96.

[167] Karaborni S, Esselink K, Hilbers P, Smit B, Karthauser J, Van Os N, Zana R. Simulating the self-assembly of Gemini surfactants. Science 1994; 266: 254–6.

[168] Maiti P K, Lansac Y, Glaser MA, Clark N A, Rouault Y. Self-assembly in surfactant oligomers: A coarse-grained description through molecular dynamics simulations. Langmuir 2002; 18: 1908–18.

[169] Arai N, Yasuoka K, Masubuchi Y. Spontaneous self-assembly process for threadlike micelles. J Chem Phys 2007; 126: 244905.

[170] Stephenson BC, Goldsipe A, Beers KJ, Blankschtein D. Quantifying the hydrophobic effect. 1. A computer simulation-molecular-thermodynamic model for the self-assembly of hydrophobic and amphiphilic solutes in aqueous solution. J Phys Chem 2007; 111: 1025–44.

[171] Stephenson BC, Goldsipe A, Beers KJ, Blankschtein D. Quantifying the hydrophobic effect. 2. A computer simulation-molecular-thermodynamic model for the micellization of nonionic surfactants in aqueous solution. J Phys Chem 2007; 111: 1045–62.

[172] Stephenson BC, Beers KJ, Blankschtein D. Quantifying the hydrophobic effect. 3. A computer simulation-molecular-thermodynamic model for the micellization of ionic and zwitterionic surfactants in aqueous solution. J Phys Chem 2007; 111: 1063–75.
[173] Wu R, Deng M, Kong B, Yang X. Coarse-grained molecular dynamics simulation of ammonium surfactant self-assemblies: Micelles and vesicles. J Phys Chem B 2009; 113: 15010–6.

[174] Sangwai AV, Sureshkumar R. Coarse-grained molecular dynamics simulations of the sphere to rod transition in surfactant micelles. Langmuir 2011; 27: 6628–38.

[175] Sangwai AV, Sureshkumar R. Binary interactions and salt-induced coalescence of spherical micelles of cationic surfactants from molecular dynamics simulations. Langmuir 2012; 28: 1127–35.

[176] Chng C-P. Effect of simulation temperature on phospholipid bilayer-vesicle transition studied by coarse-grained molecular dynamics simulations. Soft Matter 2013; 9: 7294–301.

[177] Ladanyi BM. Computer simulation studies of counterion effects on the properties of surfactant systems. Curr Opin Colloid Interface Sci 2013; 18: 15–25.

[178] Li Z, Wang P, Yan Y, Wang R, Zhang J, Dai C, Hu S. Tuning and designing the self-assembly of surfactants: The magic of carbon nanotube arrays. J Phys Chem Lett 2013; 4: 3962–6.

[179] Janke JJ, Bennett WFD, Tieleman, DP. Oleic acid phase behavior from molecular dynamics simulations. Langmuir 2014; 30: 10661–7.

[180] Li Z, Wang P, Liu B, Wang Y, Zhang J, Yan Y, Ma Y. Unusual, photo-induced self-assembly of azobenzene-containing amphiphiles. Soft Matter 2014; 10: 8758–64.

[181] Dhakal, S.; Sureshkumar, R. Topology, length scales, and energetics of surfactant micelles. J Chem Phys 2015; 143: 024905.

[182] Sambasivam A, Sangwai AV, Sureshkumar R. Self-assembly of nanoparticle-surfactant complexes with rodlike micelles: A molecular dynamics study. Langmuir 2016; 32: 1214–9.

[183] Wang P, Pei S, Wang M, Yan Y, Sun X, Zhang J. Study on the transformation from linear to branched wormlike micelles: An insight from molecular dynamics simulation. J Colloid Interface Sci 2017; 494: 47–53.

[184] Wang P, Tan J, Pei S, Wang J, Zhang Y, Sun X, Zhang J. Dual effects of cationic surfactant on the wormlike micelle formation of catanionic surfactants mixtures: An experiment and simulation study. Colloids Surf A 2017; 529: 95–101.

[185] Groot RD, Warren PB. Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. J Chem Phys 1997; 107: 4423–35.

[186] Johnston MA, Swope WC, Jordan KE, Warren PB, Noro MG, Bray DJ, Anderson RL. Toward a standard protocol for micelle simulation. J Phys Chem B, 2016; 120: 6337–51.

[187] Anderson RL, Bray DJ, Ferrante AS, Noro MG, Stott IP, Warren PB. Dissipative particle dynamics: Systematic parametrization using water-octanol partition coefficients. J Chem Phys 2017; 147: 094503.

[188] Israelachvili JN. Intermolecular and Surface Forces, 3rd ed. Amsterdam: Academic Press; 2011.

[189] Sato T. Scattering theory for threadlike micellar solutions. Langmuir 2004; 20: 1095–9.
[190] Claesson PM, Kjellander, R, Stenius P, Christenson HK. Direct measurement of
temperature-dependent interactions between non-ionic surfactant layers. J Chem Soc,
Faraday Trans 1, 1986; 82: 2735–46.
[191] Tanford C. The Hydrophobic Effect. The Formation of Micelles and Biological
Membranes, 2nd ed. New York: Wiley; 1980.
[192] Tolman RC. Consideration of the Gibbs theory of surface tension. J Chem Phys 1948;
16: 758–74.
[193] Tolman RC. The superficial density of matter at a liquid-vapor boundary. J Chem Phys
1949; 17: 118–27.
[194] Tolman RC. The effect of droplet size on surface tension. J Chem Phys 1949; 17: 333–7.
[195] Aveyard R, Haydon DA. Thermodynamic properties of aliphatic hydrocarbon/water
interfaces. Trans Faraday Soc 1965; 61: 2255–61.
[196] Gillap WR, Weiner ND, Gibaldi M. Interfacial properties of hydrocarbons. J Am Oil
Chem Soc 1967; 44: 71–3.
[197] Gurkov TD, Kralchevsky PA, Ivanov IB. The van der Waals component of the
interfacial bending moment: 2. Model development and numerical results. Colloids Surf
1991; 56: 119–48.
[198] Kralchevsky PA, Danov KD, Broze G, Mehreteab A. Thermodynamics of ionic
surfactant adsorption with account for the counterion binding: effect of salts of various
valency. Langmuir 1999; 15: 2351–65.
[199] Kralchevsky PA, Danov KD, Kolev VL, Broze G, Mehreteab A. Effect of nonionic
admixtures on the adsorption of ionic surfactants at fluid interfaces. 1. Sodium dodecyl
sulfate and dodecanol. Langmuir 2003; 19: 5004–18.
[200] Danov KD, Kralchevska SD, Kralchevsky PA, Ananthapadmanabhan KP, Lips A.
Mixed solutions of anionic and zwitterionic surfactant (betaine): surface–tension
isotherms, adsorption, and relaxation kinetics. Langmuir 2004; 20: 5445–53.
[201] Danov KD, Kralchevsky PA, Ananthapadmanabhan KP, Lips A. Interpretation of
surface-tension isotherms of n-alkanoic (fatty) acids by means of the van der Waals
model. J Colloid Interface Sci 2006; 300: 809–13.
[202] Ivanova VI, Stanimirova RD, Danov KD, Kralchevsky PA, Petkov JT. Sulfonated
methyl esters, linear alkylbenzene sulfonates and their mixed solutions: Micellization
and effects of Ca^{2+} ions. Colloids Surf A, 2017; 519: 87–97.
[203] Dill KA, Flory PJ. Interphases of chain molecules: Monolayers and lipid bilayer
membranes. Proc Natl Acad Sci USA 1980; 77: 3115–9.
[204] Dill KA, Flory PJ. Molecular organization in micelles and vesicles. Proc Natl Acad Sci
USA 1981; 78: 676–80.
[205] Dill KA, Koppel DE, Cantor RS, Dill JD, Bendedouch D, Chen S-H. Molecular
conformation in surfactant micelles. Nature 1984; 309: 42–5.
[206] Flory PJ. Principles of Polymer Chemistry. Ithaca, NY: Cornell University Press; 1962.
[207] Chakrabarti A. Solution of the generalized Abel integral equation. J Integral Equ Appl
2008; 20: 1–11.