



## GROWTH OF GIANT MICELLAR AGGREGATES: QUANTITATIVE THEORY VS EXPERIMENTS

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### ABSTRACT

*The concentrated surfactant solutions have a wide application in industry, oil recovery, drug delivery, turbulent drag reduction, etc. The competition between the companies-producers has led to use of new kind of formulations to improve: washing action; skin and eye irritation; stability and durability; biodegradability; tolerance to hard water. Here, we present a review on the state of the art and our contributions to the molecular thermodynamic theory and experiment on the growth of giant micellar aggregates. Despite the considerable advances in theory and computer simulations, agreement with experimental data has been achieved only in isolated cases. Our predictive molecular thermodynamic approach accounts for the different contributions to the micellar scission energy in the case of nonionic, zwitterionic and ionic surfactant solutions and their mixtures. Excellent agreement was achieved between the theoretical model and experimental data for wormlike surfactant micelles at various concentrations of salt and temperatures. At high salt concentrations, the model also predicts loss of chemical equilibrium, which implies a transition to self-assemblies of other morphology or the onset of crystallization and phase separation. The results have applications for the design of new products and nanostructured materials.*

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## 1. INTRODUCTION

At higher concentrations, the molecules in solutions of surface-active substances (surfactants) self-assemble to form giant wormlike and branched micelles [1]. Under certain conditions, the branched micelles assemble into a multi-connected micellar network [2]. The measured significant increase of the solution viscosity (from  $10^{-3}$  to 300 Pa.s) is explained with the formation and growth of wormlike micelles. These aggregates grow in the following three cases: in nonionic surfactant solutions at different temperatures [3]; in ionic surfactant solutions in the presence of salts [4]; in mixed solutions of surfactants that exhibit synergistic mixing [5]. The wide applications of micellar systems and varieties of formulations, from one side, and the strict practical rheological requirements need quantitative predictive models for the self-assembly of molecules in complex solutions.

The fundamental problem in the physical chemistry is how to predict the size of the wormlike micelles on the basis of knowledge for the properties of the constituent molecules and their concentrations. Detailed literature review on the theory of wormlike micelles can be found in Ref. [6]. The majority of papers in this field is aimed at predicting the rheological behavior of micellar solutions at given micelle concentration, size distribution and kinetic parameters, such as the characteristic times of micelle breakage and reptation [7]. There are also studies on computer simulations of wormlike micelles by the Monte

Carlo [8] and molecular dynamics [9] methods. The application of simulation methods is limited because of the large size of the wormlike micelles – typically, their aggregation number ranges from thousand to million molecules.

Another powerful method is the molecular thermodynamic theory, which does not face any micelle-size limitations, and which is able, in principle, to predict micelle aggregation number and length, based on information about the molecular parameters and available experimental data for some collective properties, such as interfacial tension and activity coefficients [10]. The spherocylindrical (rodlike, wormlike) micelles (Fig. 1) are a basic type of self-assemblies formed in surfactant solutions. Their mean mass aggregation number,  $n_M$ , can be estimated from the expression:

$$n_M \approx 2 \left[ (X_S - X_S^0) \exp(E_{sc}) \right]^{1/2} \quad (1)$$

Here:  $k_B$  is the Boltzmann constant;  $T$  is the temperature;  $X_S$  is the total molar fraction of surfactant in the aqueous solution;  $X_S^0$  is the solution's critical micellization concentration (CMC);  $E_{sc}$  is the excess free energy (in  $k_B T$  units) of the molecules in the two spherical micelle endcaps with respect to the cylindrical part of the micelle (Fig. 1). Because the breakage (scission) of a long spherocylindrical micelle to two smaller micelles leads to the formation of

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two new endcaps,  $E_{sc}$  was termed *scission energy* in relation to the reptation-reaction rheological model [7]. Thus, the main goal of the molecular thermodynamic theory is the prediction of  $E_{sc}$ .

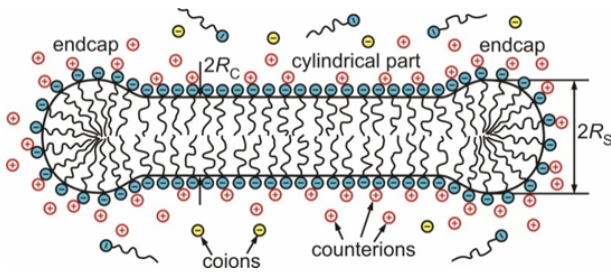


Fig. 1. Sketch of a spherocylindrical micelle from anionic surfactant;  $R_c$  and  $R_s$  are the radii of the micellar hydrocarbon core in the regions of the cylindrical part and the endcaps

For the simplest case of single component spherocylindrical micelles,  $E_{sc}$  can be expressed in the following form:

$$E_{sc} = n_s(f_s - f_c)/(k_B T) \quad (2)$$

Here:  $n_s$  is the total aggregation number of the two micelle endcaps (with shapes of truncated spheres);  $f_s$  and  $f_c$  are the free energies per molecule in the endcaps and in the cylindrical part of the micelle, respectively (Fig. 1). For wormlike micelles,  $E_{sc}$  typically varies in the range 15–30 and  $n_s$  – in the range 60–120. Consequently, the difference  $(f_s - f_c)$  varies in the range  $0.125$ – $0.5 k_B T$ . In other words, to calculate correctly  $n_M$ , the molecular thermodynamic theory has to predict  $(f_s - f_c)$  within accuracy better than  $0.01 k_B T$ , i.e.,  $f_s$  and  $f_c$  have to be very accurately predicted. This is the main difficulty with the molecular thermodynamics of micelle growth.

In this article, we present our contribution in the field of growth of giant micellar aggregates and new theoretical and experimental results related to the crucial effect of electrostatic interactions between ionic and zwitterionic surfactant molecules on the size of their mixed micelles.

## 2. FREE ENERGY OF SURFACTANT MOLECULES IN MICELLES

Generally, the free energy per molecule,  $f_x$  ( $x = s, c$ ), incorporated in the endcaps and in the cylindrical part of the spherocylindrical micelle contains six contributions:

$$f_x = (f_\sigma + f_{hs} + f_{conf} + f_{el} + f_{dip} + f_{d-c})_x \quad (3)$$

For a given molecule, their values are different because of the different confined space in spherical and cylindrical media. Thus, they depend also on the radii  $R_s$  and  $R_c$ .

**Interfacial tension component,  $f_\sigma$ .** This component is equal to the interfacial tension,  $\sigma$ , multiplied by the bare area per surfactant molecule in the considered environment at the boundary between the micelle hydrocarbon core and the outer water phase. The interfacial tension is calculated using the generalized Tolman equation [6,11].

**Headgroups steric repulsion component,  $f_{hs}$ .** The repulsion between surfactant headgroups at the micelle surface has been taken into account using the repulsion term in the two-dimensional multicomponent equation of van der Waals [11].

**Chain-conformation component of free energy,  $f_{conf}$ .** This contribution to the micelle free energy describes the variety of conformations of surfactant hydrocarbon chains

in the finite space of the micelle interior. We derived the generalized version of the Semenov expression for the chain-conformation free energy per molecule in Refs. [11,12].

**Electrostatic free energy,  $f_{el}$ .** In the case of ionic surfactant in the presence of salt, the electrostatic component of the free energy is calculated from the solution of the Poisson-Boltzmann equation for all ionic species in the respective geometry [13,14]. The counterion binding effect and the ionic species activity coefficients are included in calculations. We proved [13], that  $f_{el}$  is equal to the micellar surface charge density multiplied by the surface electrostatic potential added with the electrostatic surface pressure (the contribution of the electric double layer to the surface pressure).

**Dipole free energy,  $f_{dip}$ .** From the viewpoint of the electrostatic interactions, the zwitterionic surfactant polar head is modeled as a dipole with dipole length  $d$  and area per molecule  $a_d$ . This component of the free energy includes the electrostatic interaction between dipoles in the vicinity of the micellar hydrocarbon core [15]. The effect of the micellar curvature and dielectric properties of the continuum media on the decrease of the dipole electrostatic interaction energy is well illustrated in Ref. [15].

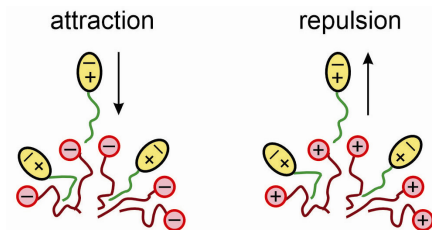


Fig. 2. Sketch of a zwitterionic molecule closed to a charged mixed micelle; the dipole-charge electrostatic interaction energy can be positive or negative

**Dipole-charge free energy,  $f_{d-c}$ .** The zwitterionic dipole interacts with the electrostatic field in the electric double layer (Fig. 2) and the obtained expression for  $f_{d-c}$  reads:

$$f_{d-c}/(k_B T) = \pm 4\pi z_c z_d L_B d / a_d \quad (3)$$

Here:  $L_B$  is the Bjerrum length;  $z_c$  is the charge number of the ionic surfactant;  $z_d$  is the charge number of the dipole charges. The sign of  $f_{d-c}$  depends on the orientation of the zwitterionic dipole moment, so that this component corresponds to attraction or repulsion (Fig. 2) in the case of mixed ionic and zwitterionic micellar solutions.

The numerical calculations include minimization of the total free energy for spherocylindrical geometry of micellar aggregates (Fig. 1) under geometrical restrictions – the radii of spherical and cylindrical parts of the micelle hydrocarbon core must be smaller than the extended length of the surfactant hydrocarbon tail. As a result, the most probable radii  $R_s$  and  $R_c$ , number of molecules  $n_s$ , and the components of the free energy are obtained. Note that there are no adjustable parameters.

## 3. THEORY VS EXPERIMENTS

**Nonionic surfactant micelles.** Fig. 3 summarizes experimental data for the scission energy of wormlike micelles in the case of polyoxyethylene alkyl ethers,  $C_n E_m$ , with  $n$  carbon atoms and  $m$  ethylene-oxide groups [6]. The solid lines show the calculated values of  $E_{sc}$  from the

proposed model. The agreement between theory and experiments is excellent.

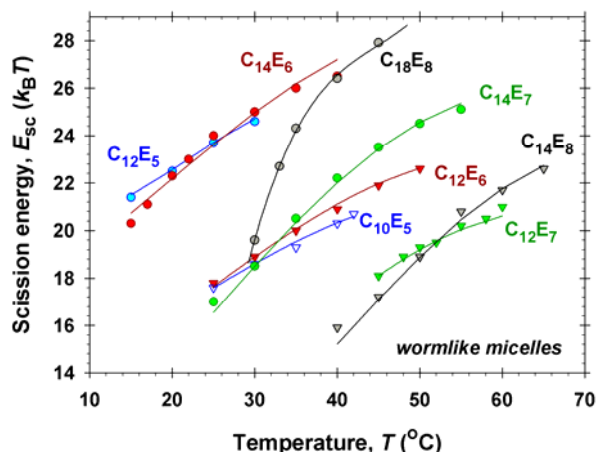


Fig. 3. Dependence of the scission energy of  $C_nE_m$  micelles on temperature. Solid lines show the theoretical predictions

The following conclusions can be drawn. The increase in temperature leads to a considerable increase in the aggregate size for all kinds of  $C_nE_m$ . Oppositely, the increase of the size of surfactant polar head (number of ethylene-oxide groups) decreases the values of the scission energy. As should be, the longer the surfactant hydrocarbon tail is, the larger the mean aggregation number and viscosities are.

*Mixed micelles from nonionic surfactants.* The surfactant mixtures consist of molecules with different alkyl chain lengths and/or different polar heads. Thus, it is nontrivial to guess preliminary what will be the result of mixing (ideal, synergistic or antagonistic mixing).

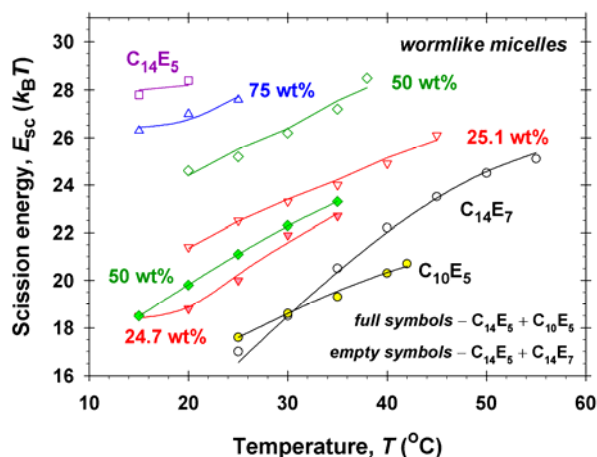


Fig. 4. Experimental data vs theoretical predictions for the dependence of  $E_{sc}$  for wormlike micelles in mixed solutions of  $C_{14}E_5 + C_{10}E_5$  and  $C_{14}E_5 + C_{14}E_7$  at different temperatures and weight fractions of  $C_{14}E_5$

In Fig. 4, the points are the experimental data for the micelle growth parameter,  $E_{sc}$ , versus temperature [11], whereas the solid lines represent the prediction of the theory for the respective composition of the surfactant mixture denoted in the figure. For both systems, identical alkyl chain  $C_{14}E_5 + C_{14}E_7$  and identical headgroups  $C_{14}E_5 + C_{10}E_5$ , there is an excellent agreement between theory and experiment. For example, the scission energies of  $C_{10}E_5$  micelles and  $C_{14}E_7$  micelles at 30 °C are equal (Fig. 4) and one expects to have similar values for mixed

solutions with  $C_{14}E_5$  at 30 °C. In contrast, the curves corresponding to almost equidistant weight fractions of  $C_{14}E_5$  are far from being equidistant. This irregular behavior is related to the strong deviations from ideal mixing.

*Ionic surfactant solutions in the presence of salts.* The addition of salts considerably affects the formation and size of ionic surfactant micelles [1]. The comparison between the theory and experiments in the case of ionic surfactants is shown in Fig. 5 for: anionic surfactants – sodium undecyl (SUS), dodecyl (SDS), and tridecyl (STS) sulfate; cationic surfactants – dodecyl (DDAB), tetradecyl (TTAB), cetyl (CTAB) trimethylammonium bromides and respective chlorides (DDAC and CTAC) [14]. The added salts are NaCl and NaBr and the temperature is 30 °C for CTAB and 25 °C for the other surfactants.

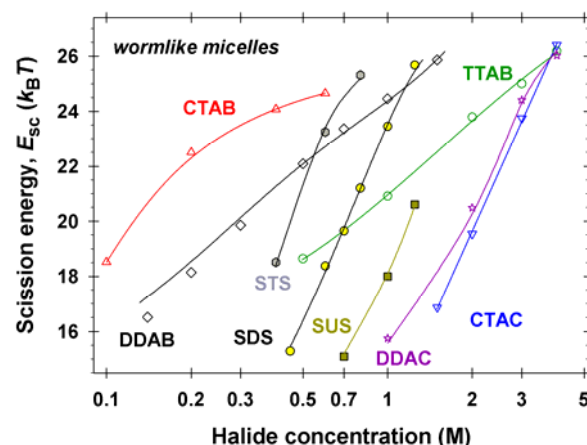


Fig. 5. Dependence of the micelle growth parameter of ionic surfactants on the added salt concentration: experimental data vs theoretical predictions.

The addition of NaCl to anionic SUS, SDS, and STS solutions sharply increases the scission energy and the longer the surfactant tail is the lower amount of salt is needed. The counterion binding effect is well pronounced for cationic surfactants. The energy of counterion binding of  $Br^-$  ions is higher than that of  $Cl^-$  ions, which explains the shift of the experimental data for DDAB compared to DDAC and for CTAB compared to CTAC. One sees that more than 10 times larger concentration of added NaCl (compared to NaBr) is needed to produce the same degree of micellar growth for the studied cationic surfactants (Fig. 5). Experimental results show that CTAB micelles are rodlike for concentrations of added salt lower than 0.2 M and wormlike at higher concentrations. The excellent agreement between the theoretical calculations and experimental data for all concentrations means that the theory predicts correctly the mean aggregation number and length of both rodlike and wormlike micellar aggregates.

*Zwitterionic surfactant solutions.* The importance of the dipole component of the interaction free energy,  $f_{dip}$ , is illustrated in Fig. 6 in the case of dodecyl (DDAO) and tetradecyl (TDAO) dimethylamine oxide micellar solutions [15]. The solid lines in Fig. 6 represent the results from the developed molecular thermodynamic theory.

The molecular dynamics simulations of the structural properties of DDAO and TDAO micelles show that the micelles are generally elongated ellipsoids. It is remarkable that the mean mass aggregation number increases only to 115 with the rise of DDAO concentration up to 1.3 M and

to 320 with the rise of TDAO concentration up to 60 mM. The agreement between theory and experiments proves the validity of the theoretical approach not only for giant micelles but also for small micellar aggregates. For comparison, the mean mass aggregation numbers of  $C_{12}E_5$  versus surfactant concentration are included in Fig. 6 (see Fig. 3 for  $E_{sc}$  of  $C_{12}E_5$  at  $T = 25$  °C). One sees that for 100 mM surfactant concentration, the aggregation number of  $C_{12}E_5$  micelles is more than 150 times greater than that of DDAO – both surfactants have identical hydrocarbon tails.

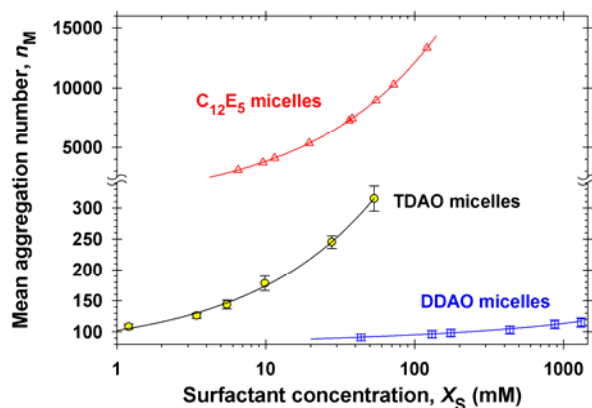


Fig. 6. Comparison of the mean aggregation numbers,  $n_M$ , of zwitterionic (DDAO and TDAO) and nonionic ( $C_{12}E_5$ ) micelles

**Mixed ionic and zwitterionic surfactants.** The thumb rule for practical applications is that the mixtures of zwitterionic and ionic surfactants at a given ratio obey huge synergistic effect – wormlike micelles are formed and the viscosity of the solutions increases orders of magnitude.

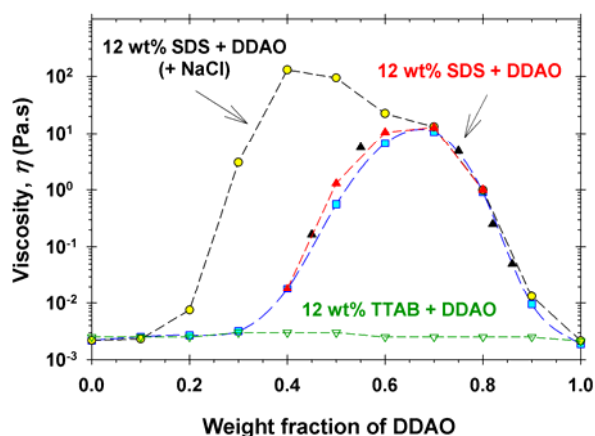


Fig. 7. Viscosity of mixed anionic and zwitterionic surfactant solutions at 12 wt% concentration vs DDAO weight fraction.

Fig. 7 summarizes experimental data for the viscosity of 12 wt% SDS+DDAO mixed solutions measured for different weight fractions of zwitterionic surfactant. The solutions with the individual surfactants are water like. Without added NaCl, the maximum of the viscosity is measured for weight fraction 0.7 and at the maximum, the viscosity increases 5000 times. The presence of NaCl shifts the position of maximum to weight fraction 0.4, where the viscosity increases more than 50000 times. The chemical structures of SDS and DDAO correspond to the electrostatic dipole-charge attraction interactions of the DDAO dipoles (see Fig. 2). In the case of cationic surfactant TTAB, the electrostatic dipole-charge interactions are repulsive (Fig. 2). As a result: the viscosity

of TTAB+DDAO mixed solutions is very low (2 mPa.s); it does not depend on the DDAO weight fraction; the micellar aggregates are small for all weight fractions. Hence, for mixed zwitterionic and ionic surfactant solutions, the dipole-charge interaction component of the free energy plays an important role for the micellar growth and the formation of giant micellar aggregates.

#### 4. CONCLUSIONS

The molecular thermodynamic theory is a powerful approach for a predictive modeling of the critical micelle concentrations, micelle size and growth of the micellar aggregates in surfactant solutions. From the knowledge of the physicochemical properties of individual molecules and the types of interaction between them, it provides information on the CMC, size and shape of the most probable micellar aggregates for ionic and nonionic surfactants and their mixtures with and without added salt and for zwitterionic surfactants. The present theory can be further extended to describe the synergistic mixing of ionic and zwitterionic surfactants. The obtained results could be of practical interest for development of new formulations and nanostructure materials.

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