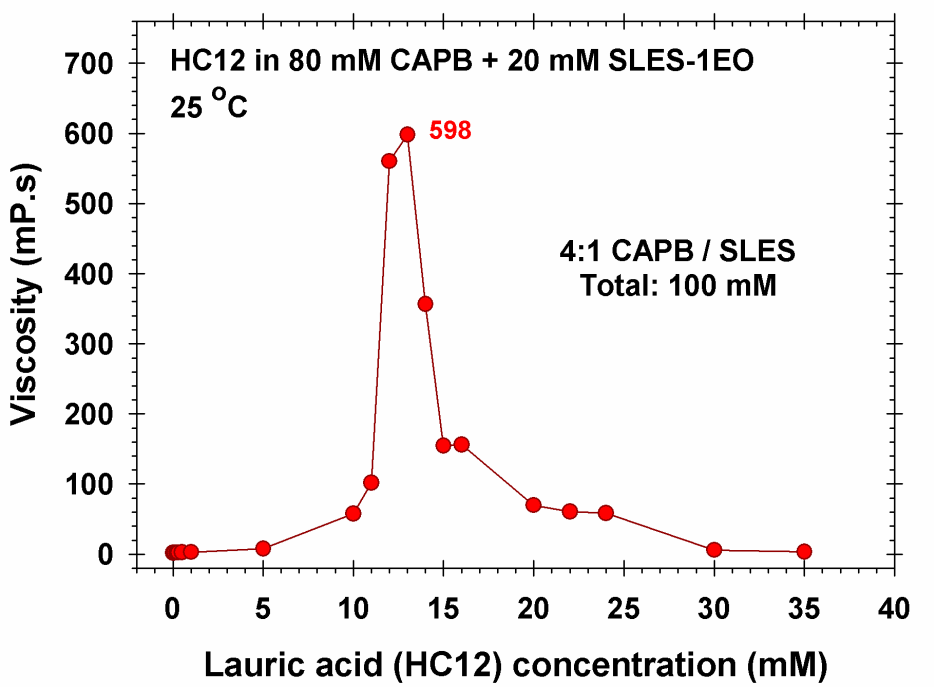
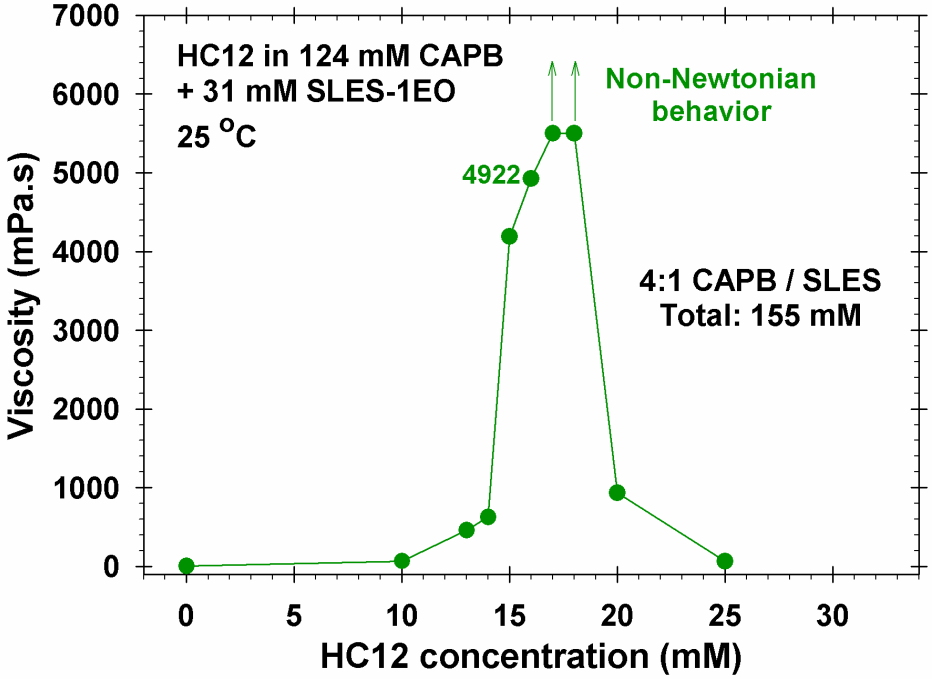
Disclike vs. cylindrical micelles: generalized model of micelle growth and data interpretation

S.E. Anachkov, **P.A. Kralchevsky, K.D. Danov,**
G.S. Georgieva, K.P. Ananthapadmanabhan
Department of Chemical Engineering, Sofia University, Bulgaria
Unilever Research & Development, Trumbull, CT 06611, USA

Motivation: Formulations with Less Surfactant

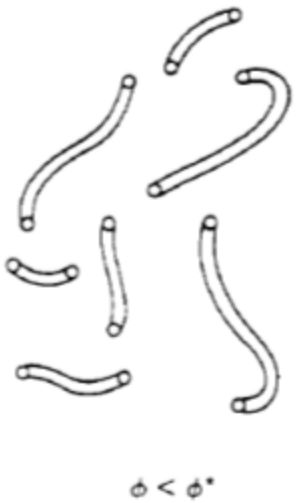
The fact that a relatively small additive of fatty acid to CAPB – SLES mixtures causes the formation of very viscous surfactant solutions (of consistence like that of dense honey) can be used for creation of shampoo-type formulations.

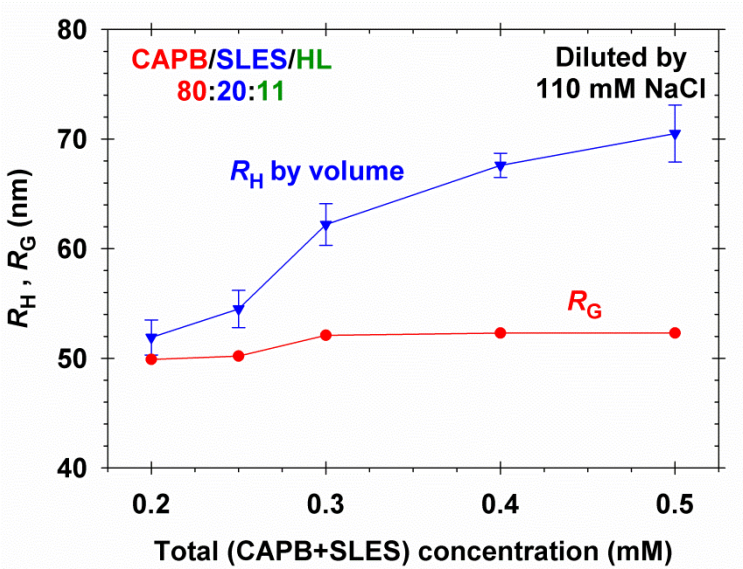




Diluted micellar solutions

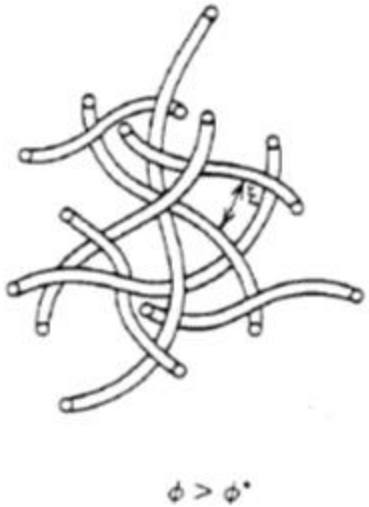
Diluted regime
(no interaction)



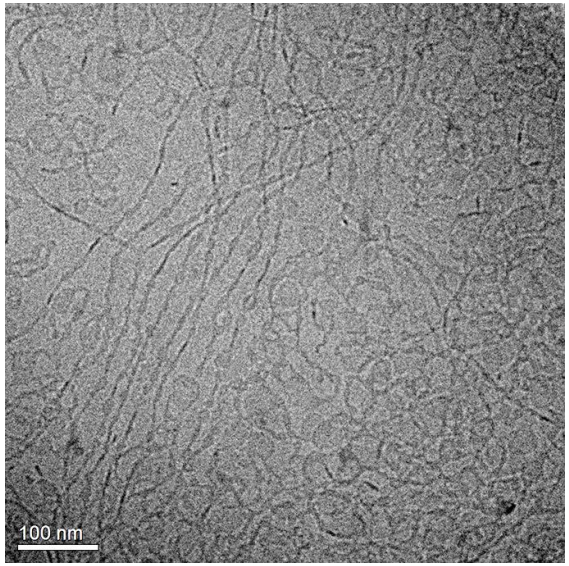


This oral contribution

Concentrated micellar solutions

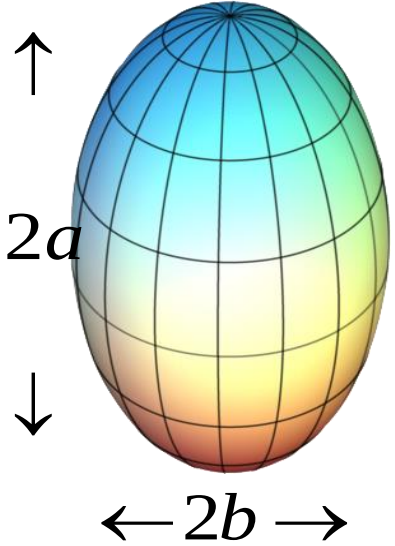


Micelle overlap regime
(interweaved,
non-Newtonian)



Poster P5.6 (Gergana Georgieva)

SLS + DLS Data: The Prolate-Spheroid Model



b **≈ 2.8 nm (length of a CAPB molecule)**

c_t (mM)	$R_{G,exp}$ (nm)	$R_{H,exp}$ (nm)	a (nm)	R_G calculated (nm)
0.20	49.9	51.9	274	122
0.25	50.2	54.5	291	130
0.30	52.1	62.2	342	153
0.35	51.7	68.1	382	171
0.40	52.3	67.6	379	169
0.50	52.3	70.5	398	178

First, *a* is calculated by solving numerically the equation:

$$R_H = \frac{Q}{\ln\left(\frac{a+Q}{b}\right)} \qquad Q = (a^2 - b^2)^{1/2}$$

R_H – experimental volume average

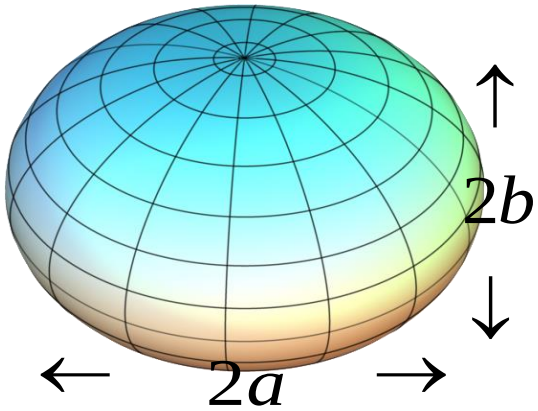
Next, the R_G is calculated from:

$$R_G = \left(\frac{a^2 + 2b^2}{5}\right)^{1/2}$$

Van de Sande, 1985

The calculated R_G is considerably greater than the measured R_G ⇒ the micelles are not prolate-ellipsoids!

SLS + DLS Data: The Oblate-Spheroid Model



$b \approx 2.8$ nm (length of a CAPB molecule)

c_t (mM)	$R_{G,exp}$ (nm)	$R_{H,exp}$ (nm)	a (nm)	R_G calculated (nm)
0.20	49.9	51.9	79.8	50.5
0.25	50.2	54.5	83.8	53.0
0.30	52.1	62.2	95.9	60.7
0.35	51.7	68.1	105.2	66.5
0.40	52.3	67.6	104.4	66.0
0.50	52.3	70.5	109.0	68.9

First, a is calculated from R_H by solving numerically the equation:

$$\frac{Q}{b} = \tan\left(\frac{Q}{R_H}\right) \qquad Q = (a^2 - b^2)^{1/2}$$

R_H – experimental volume average

Next, the R_G is calculated from:

$$R_G = \left(\frac{2a^2 + b^2}{5}\right)^{1/2}$$

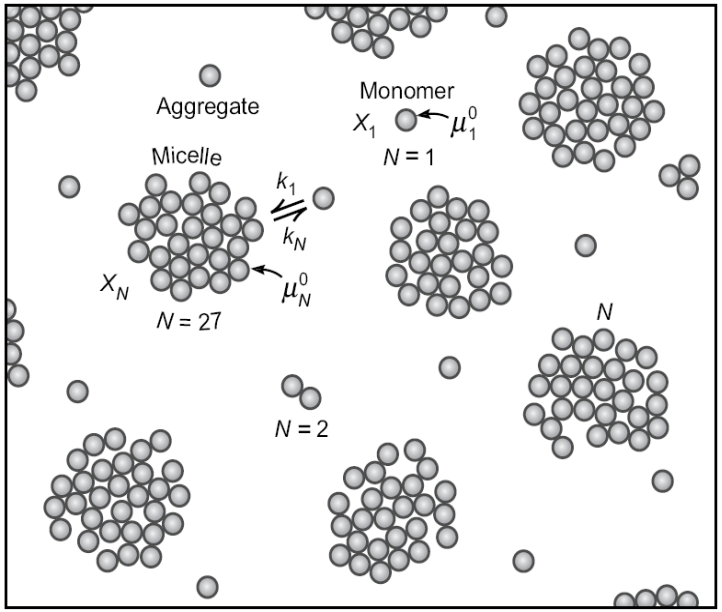
Van de Sande, 1985

Agreement between the calculated and measured R_G

$\Rightarrow$ the micelles are disclike (oblate-ellipsoids)!

Model of Micelle Growth – Single Component

This model is liable to generalization for mixed systems.



Chemical equilibrium between micelles and monomers:

$$n\mu_1 = \mu_n$$

$$n\tilde{\mu}_1 + nkT\ln X_1 = \tilde{\mu}_n + kT\ln X_n$$

***n* – aggregation number of the micelle:**

X_1 and X_n – molar fractions of monomers and *n*-micelles;

$\tilde{\mu}_1, \tilde{\mu}_n$ **– standard chemical potentials;**

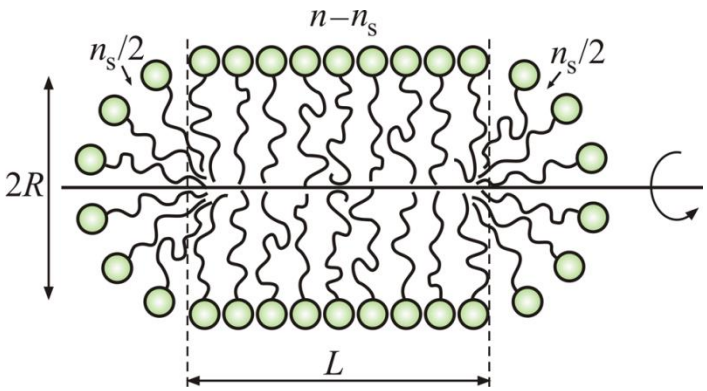
Taking inverse logarithm, we obtain:

$$X_n = X_1^n \exp\left(-\frac{\tilde{\mu}_n - n\tilde{\mu}_1}{kT}\right)$$

The ladder model provides an expression for $\tilde{\mu}_n - n\tilde{\mu}_1$

Ladder Model for Rodlike Micelles: Size Distribution

Missel, P.J.; Mazer, N.A.; Benedek, G.B.; Young, C.Y.; Carey, M.C. *J. Phys. Chem.* 1980, *84*, 1044.



Spherical and bigger cylindrical micelles:
***n* ≥ *n*$_s$**

Different standard chemical potentials of the molecules in the cylindrical part and in the spherical caps:

$$\tilde{\mu}_n = n_s \tilde{\mu}^{(s)} + (n - n_s)\tilde{\mu}^{(c)}$$

$$\tilde{\mu}_n - n\tilde{\mu}_1 = n_s(\tilde{\mu}^{(s)} - \tilde{\mu}^{(c)}) + n(\tilde{\mu}^{(c)} - \tilde{\mu}_1)$$

$$X_n = X_1^n \exp\left(-\frac{\tilde{\mu}_n - n\tilde{\mu}_1}{kT}\right) \quad \Rightarrow \quad X_n = \frac{1}{K}\left(\frac{X_1}{X_B}\right)^n, \quad \frac{X_1}{X_B} < 1$$

$$K = \exp\left(\frac{n_s(\tilde{\mu}^{(s)} - \tilde{\mu}^{(c)})}{kT}\right)$$

$$X_B = \exp\left(\frac{\tilde{\mu}^{(c)} - \tilde{\mu}_1}{kT}\right)$$

Ladder Model: Expression for the Mean Aggregation Number

$$X_n = \frac{1}{K} q^n, \qquad \frac{X_1}{X_B} \equiv q < 1$$

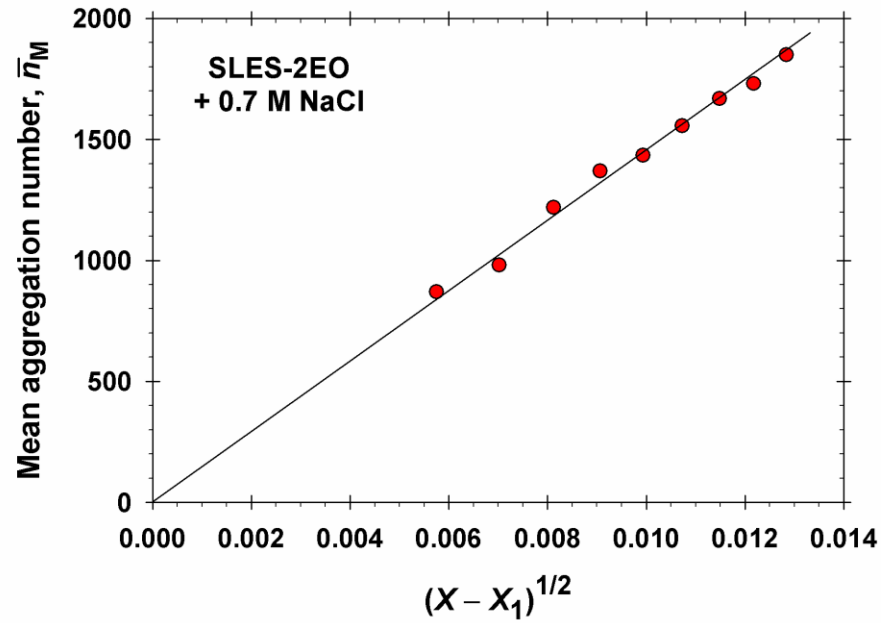
Molar fraction of the surfactant in micelles:

$$X - X_1 = \sum_{n=n_s}^{\infty} n X_n \approx \frac{q^{n_s+1}}{K(1-q)^2} \approx \frac{1}{K\varepsilon^2}$$

$$\boxed{1 - q = \varepsilon} \qquad \boxed{(q \to 1,\ \varepsilon \to 0)}$$

Mean aggregation number by mass:

$$\bar{n}_M \equiv \frac{\sum_{n=n_s}^{\infty} n^2 X_n}{\sum_{n=n_s}^{\infty} n X_n} \approx \frac{2}{\varepsilon} \approx 2[K(X - X_1)]^{1/2}$$



R.G. Alargova, V.P. Ivanova, P.A. Kralchevsky, A. Mehreteab, G. Broze, *Colloids Surf. A* 142 (1998) 201-218.

This square-root dependence is confirmed by the experiment!

Geometrical Relations for micelles of different shape

n_s **is the aggregation number of a spherical micelle;**
R **is the radius of its hydrocarbon core;**
$\bar{v}$ **is the mean volume per hydrocarbon chain in the micelle.**

$$R = \sum_{i=1}^{N} y_i l_i$$

$$\bar{v} = \sum_{i=1}^{N} y_i v_i$$

For a spherical micelle:

$$n_s = \frac{\frac{4}{3}\pi R^3}{\bar{v}}, \qquad a_s = \frac{4\pi R^2}{n_s} = \frac{3\bar{v}}{R}$$

Likewise we obtain:

$$\boxed{a_d = \frac{\bar{v}}{R}}$$

discoidal

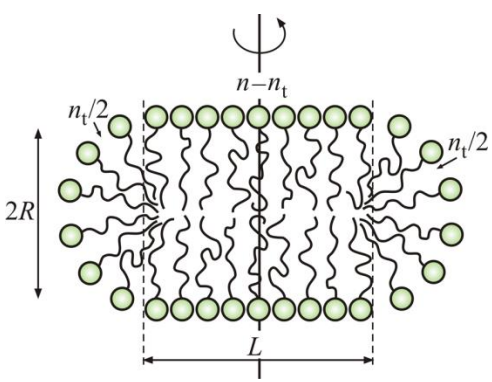
$$\boxed{a_c = \frac{2\bar{v}}{R}}$$

cylindrical

$$\boxed{a_s = \frac{3\bar{v}}{R}}$$

spherical

***L*→∞ = cylinder**



$$\boxed{a_t = \frac{\pi L + 4R}{\pi L + \frac{8}{3}R}\,\frac{2\bar{v}}{R}}$$

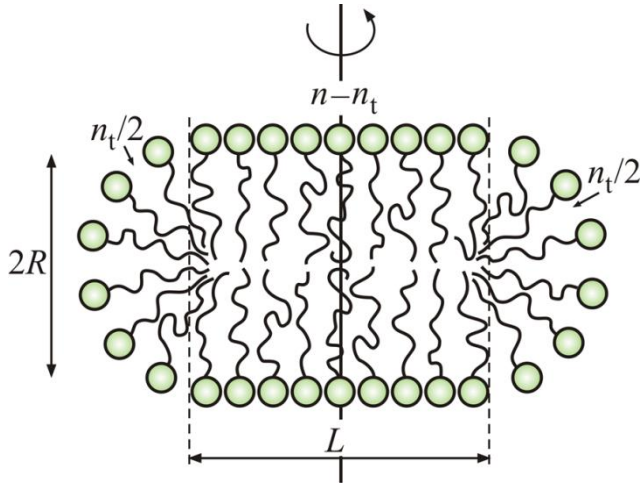
toroidal

***L*→0 = sphere**

$$\frac{2\bar{v}}{R} = a_c \le a_t \le a_s = \frac{3\bar{v}}{R}$$

The area per molecule in the toroidal part is between that for cylinder and sphere

Generalization of the Model to Disclike Micelles

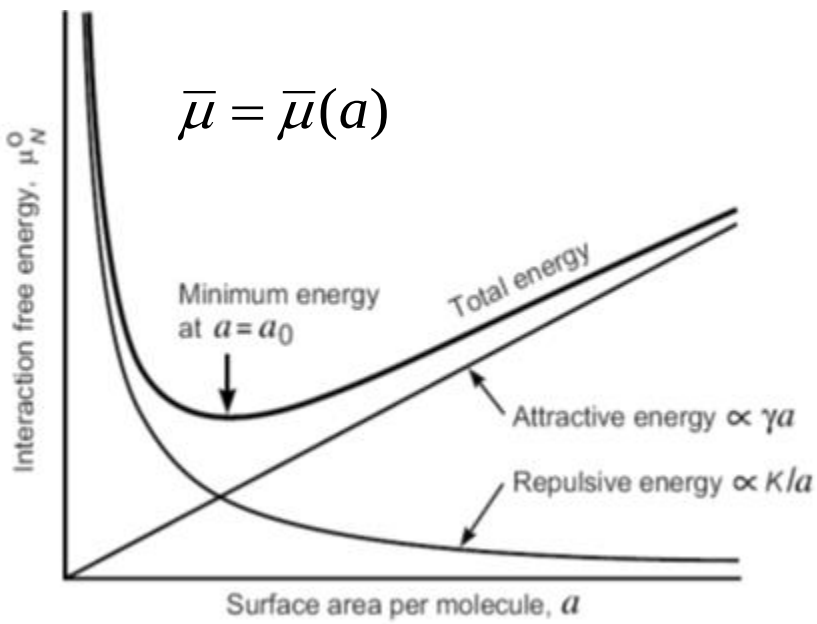


$$\tilde{\mu}_n = \bar{\mu}^{(d)}(n - n_t) + \bar{\mu}^{(t)} n_t$$

$\bar{\mu}^{(d)}$ – **mean standard free energy per molecule in the discoidal part of the micelle**

$\bar{\mu}^{(t)}$, n_t – **for the toroidal part of the micelle (depend on the micelle size!)**

For $L \to 0$ the micelle is transformed into a spherical micelle with $\bar{\mu}^{(s)}$, n_s



$\bar{\mu}^{(s)} = \bar{\mu}(a_s)$ **spherical**

$\bar{\mu}^{(t)} = \bar{\mu}(a_t)$ **toroidal**

$\bar{\mu}^{(c)} = \bar{\mu}(a_c)$ **cylindrical**

$\bar{\mu}^{(d)} = \bar{\mu}(a_d)$ **discoidal**

parts of a micelle

Theoretical model of disclike micelles growth

Extension of the ladder model:

$$\tilde{\mu}_n = \bar{\mu}^{(\mathrm{d})}(n - n_\mathrm{t}) + \bar{\mu}^{(\mathrm{t})} n_\mathrm{t} \approx \bar{\mu}^{(\mathrm{d})} n + \left[\bar{\mu}^{(\mathrm{s})} + \left.\frac{\partial \bar{\mu}}{\partial a}\right|_{a=a_\mathrm{s}} (a_\mathrm{t} - a_\mathrm{s}) - \bar{\mu}^{(\mathrm{d})} \right] n_\mathrm{t}$$

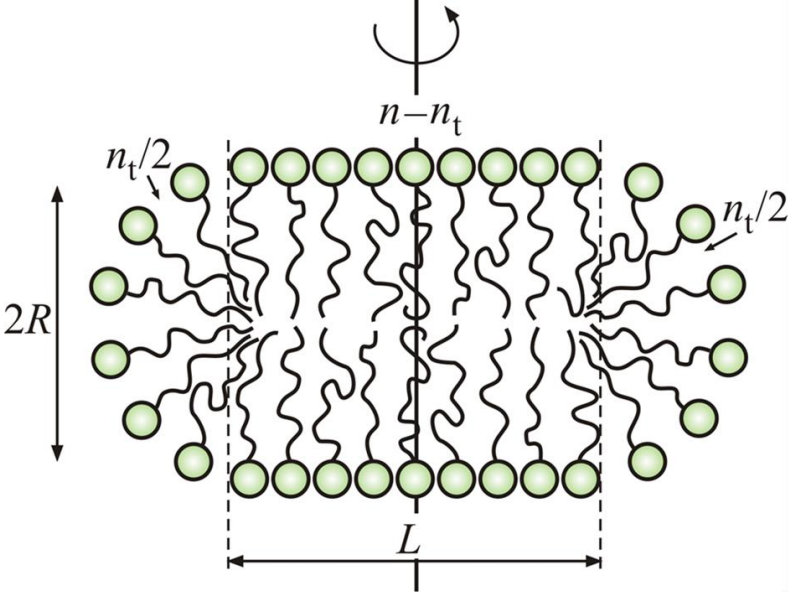
Linear estimate of the derivative:

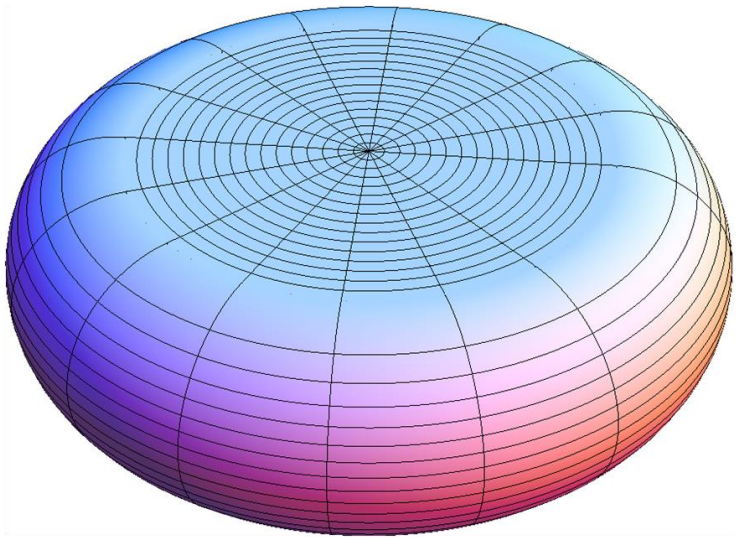
$$\left.\frac{\partial \bar{\mu}}{\partial a}\right|_{a=a_\mathrm{s}} \approx \frac{\bar{\mu}^{(\mathrm{s})} - \bar{\mu}^{(\mathrm{c})}}{a_\mathrm{s} - a_\mathrm{c}} = (\bar{\mu}^{(\mathrm{s})} - \bar{\mu}^{(\mathrm{c})}) \frac{R}{\bar{v}}$$

Micelle size distribution:

$$X_n = \frac{1}{K} \exp\left(-\varepsilon n - \frac{3\pi}{8} n_\mathrm{s} p x \right), \quad \frac{\bar{X}_1}{X_\mathrm{B}} = \exp(-\varepsilon), \quad p = \frac{\bar{\mu}^{(\mathrm{c})} - \bar{\mu}^{(\mathrm{d})}}{kT}$$

$$K = \exp\left(\frac{n_\mathrm{s}(\bar{\mu}^{(\mathrm{s})} - \bar{\mu}^{(\mathrm{d})})}{kT} \right), \quad X_\mathrm{B} = \exp\left(\frac{\bar{\mu}^{(\mathrm{d})} - \bar{\mu}^{(1)}}{kT} \right), \quad x = \frac{L}{R}$$





Parametric equations for n_N and n_M concentration dependences:

$$K(X-X_1)=\left(\frac{3n_s}{8}\right)^2\exp(-n_s\varepsilon)\left(\frac{32}{9n_s}+J_1\right)$$

$$\bar{n}_N=\frac{3n_s}{8}\left(\frac{32}{9n_s}+J_1\right)/\left(\frac{4}{3n_s}+J_0\right)$$

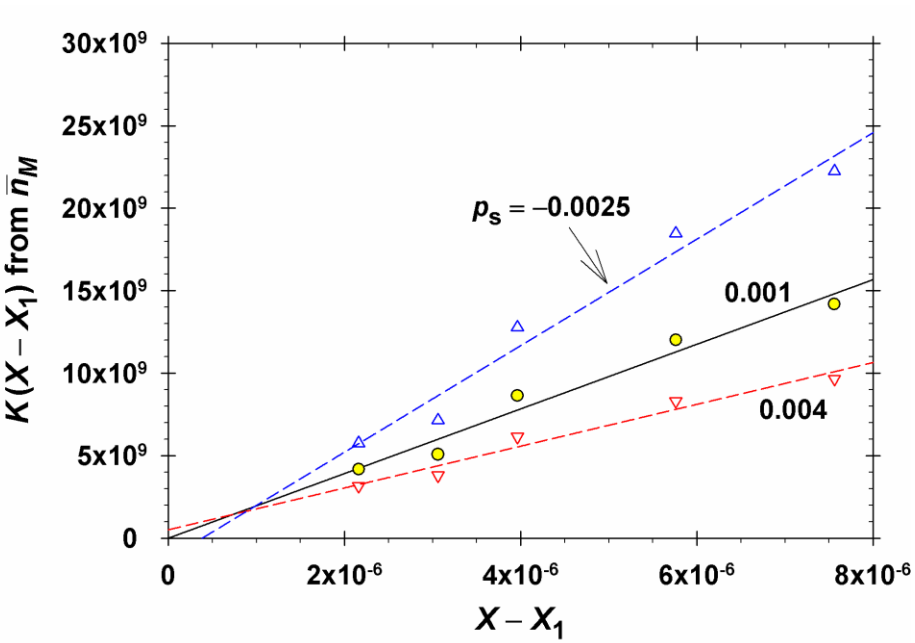
$$\bar{n}_M=\frac{3n_s}{8}\left(\frac{256}{27n_s}+J_2\right)/\left(\frac{32}{9n_s}+J_1\right)$$

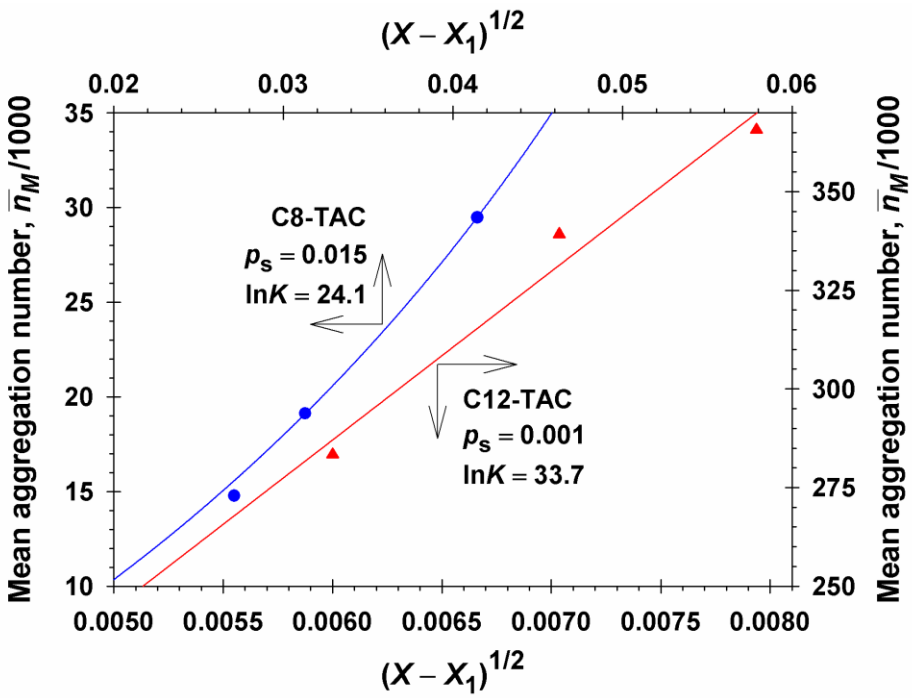
$$J_k\equiv\int_0^\infty\left(x^2+\pi x+\frac{8}{3}\right)^k(2x+\pi)\exp[F(x)]\,\mathrm{d}x,\quad F(x)=-\frac{3n_s}{8}\left[\varepsilon x^2+\pi(p+\varepsilon)x\right]$$

For $p > 0$, J_0, J_1, J_2 attain their maximum values at $\varepsilon \to 0$.

Data interpretation of disclike micelles growth

Anachkov, Kralchevsky, Danov, et al., *J. Colloid Interface Sci*. 416 (2014) 258–273.



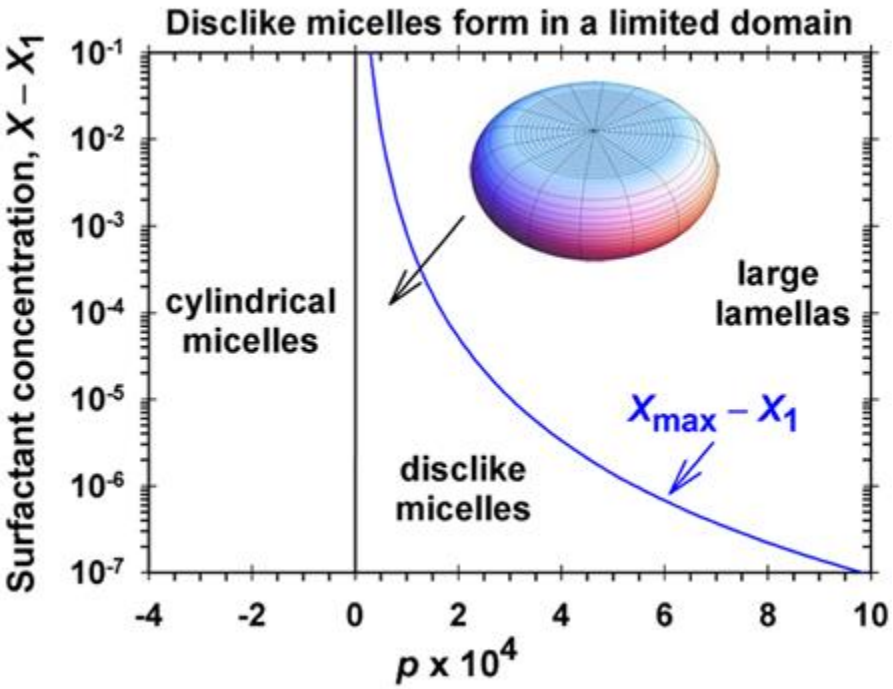


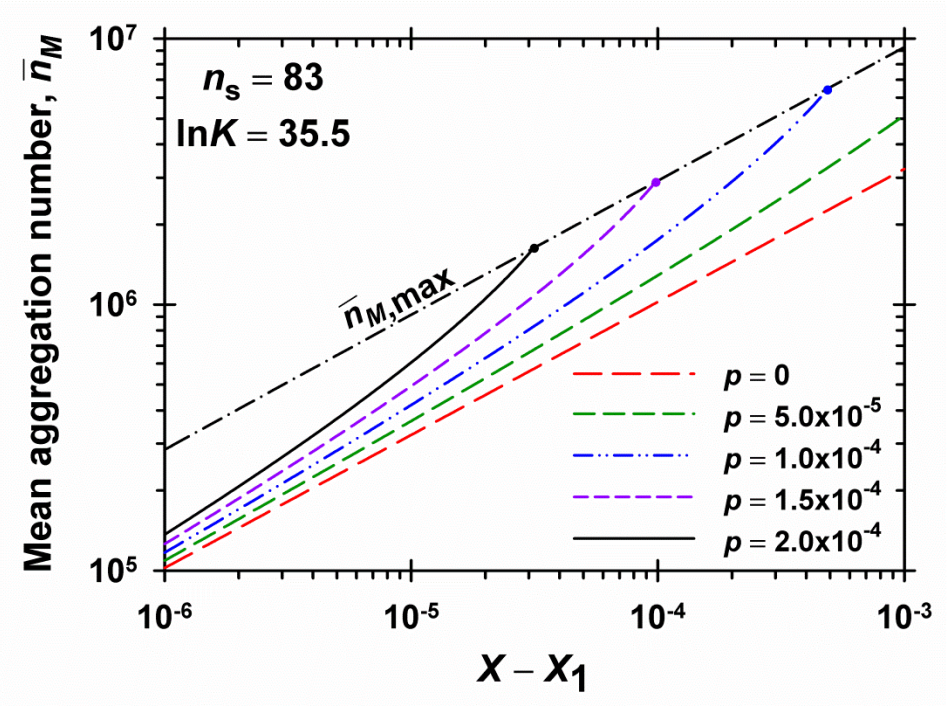
The numerical procedure is applied for the analysis of our experimental data.

Matsuoka, Yonekawa, et. al, Colloid Polym. Sci. 285 (2006) 323–330.

Predictions of the theory of growth of disclike micelles

Anachkov, Kralchevsky, Danov, et al., *J. Colloid Interface Sci*. 416 (2014) 258–273.





Disclike micelles appear only at $p > 0$, but this leads to a rise of the micelle peripheral energy with the increase of the disc diameter, which in turns limits the micelle growth.

The region with disclike micelles appears to be a relatively narrow band of width characterized by the ratio:

$$\bar{n}_{M,\max} / \bar{n}_M \Big|_{p=0} \approx 5/\sqrt{3} \approx 2.89$$

Summary and Conclusions

- **We developed a theoretical model describing the growth of disclike surfactant micelles. It predicts the concentration dependences of n_N and n_M.**
- **Central role in the theory plays the dimensionless difference, p, between the chemical potentials of a surfactant molecule in cylindrical, μ_c, and discoidal, μ_d, environment.**
- **For $p < 0$, cylindrical micelles are energetically favorable.**
- **For $p > 0$ disclike micelles are formed, but their growth is limited due to the rise of their positive peripheral energy. Hence, disclike micelles can be observed in a limited concentration range.**

Acknowledgements

Cryo-TEM experiments and stimulating discussions:

Prof. Dr. Dganit Danino

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Action CM1101

Unilever

European Union

ЕСФ
България

SEVENTH FRAMEWORK PROGRAMME

CAPACITIES
BeyondEverest project

Project BG051PO001-3.3.06-0040
"Establishment of interdisciplinary teams of young scientists in the field of fundamental and applied research relevant to medical practice"

The project is implemented with financial support of the operative program "Human Resources Development" financed by the European Social Fund of the European Union. Sofia University "St. Kliment Ohridski"– Faculty of Medicine bears full responsibility for the content of this document and in no circumstances can be regarded as official position of the European Union or the Bulgarian Ministry of Education and Science.

Thank you for the attention!