Impact of poly (ethylene glycol) on the structure and interaction parameters of aqueous micelle systems

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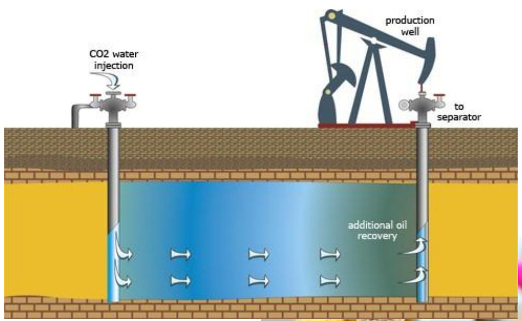
[3]*Wigner Research Centre of Physic, Hungarian Academy of Sciense, Budapest, Hungary*

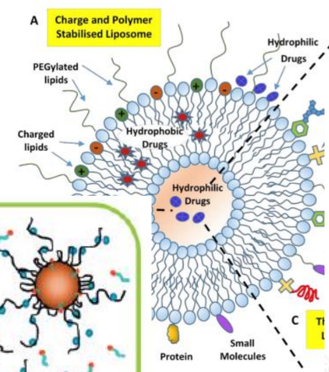
[4]*Institute of Materials Research Helmholtz-Zentrum, Geesthacht, Germany*

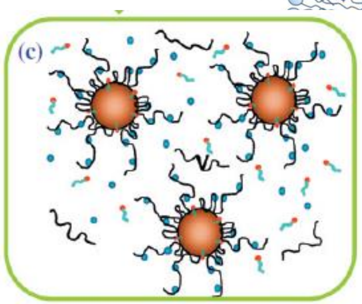
Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

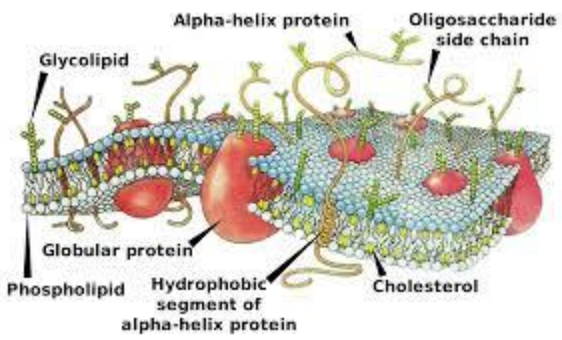
Surfactant-polymer complexation: application and fundamental aspect

- Application in the *pharmaceutics, detergent, enhanced oil recovery industries*
- Important tool for *manipulation of the physical properties of an interface, particularly, steric stabilization* and producing *of drug-delivery systems*
- Serve as a *simplified model for biological binding processes into cell membranes*





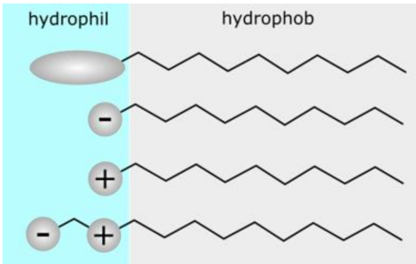


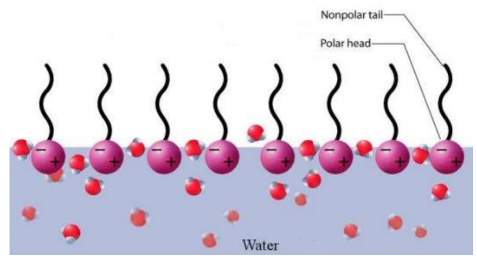


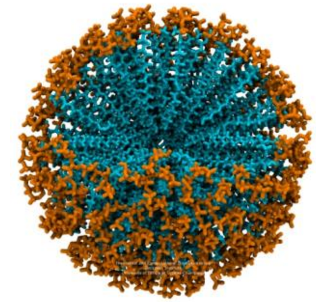
Guzmán E. et al. Polymer–surfactant systems in bulk and at fluid interfaces // *Adv. Coll. Interf. Sci, (2016). 233., 38-64.*

Philip J., Prakash G. G., Jaykumar T., Kalyanasundaram P., Raj B. Stretching and collapse of neutral polymer layers under association with ionic surfactants. // *Phys. rev. let.*, (2002). *89*(26), 268301.

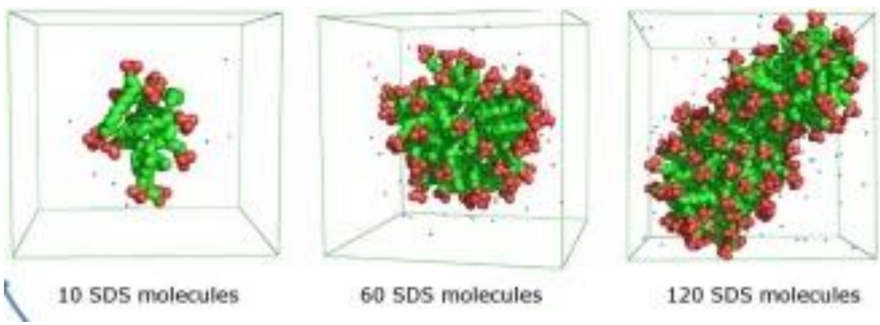
Process of surfactant micellization



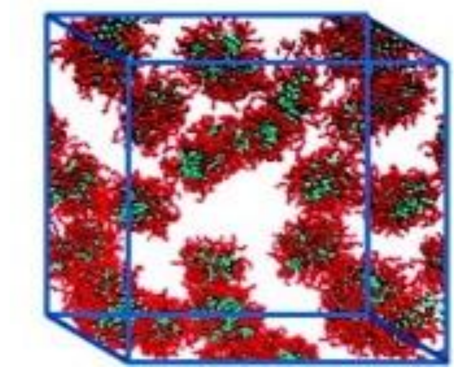


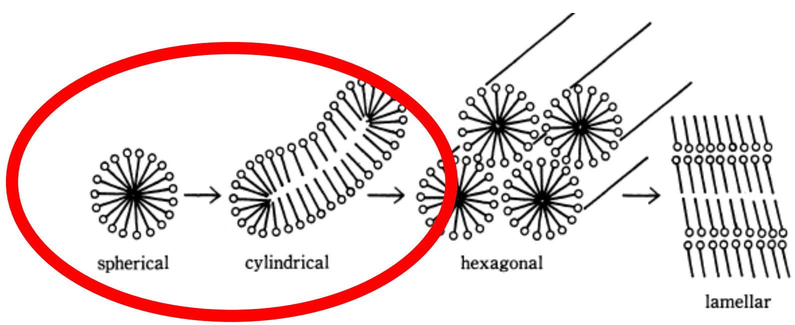


Micelle growth



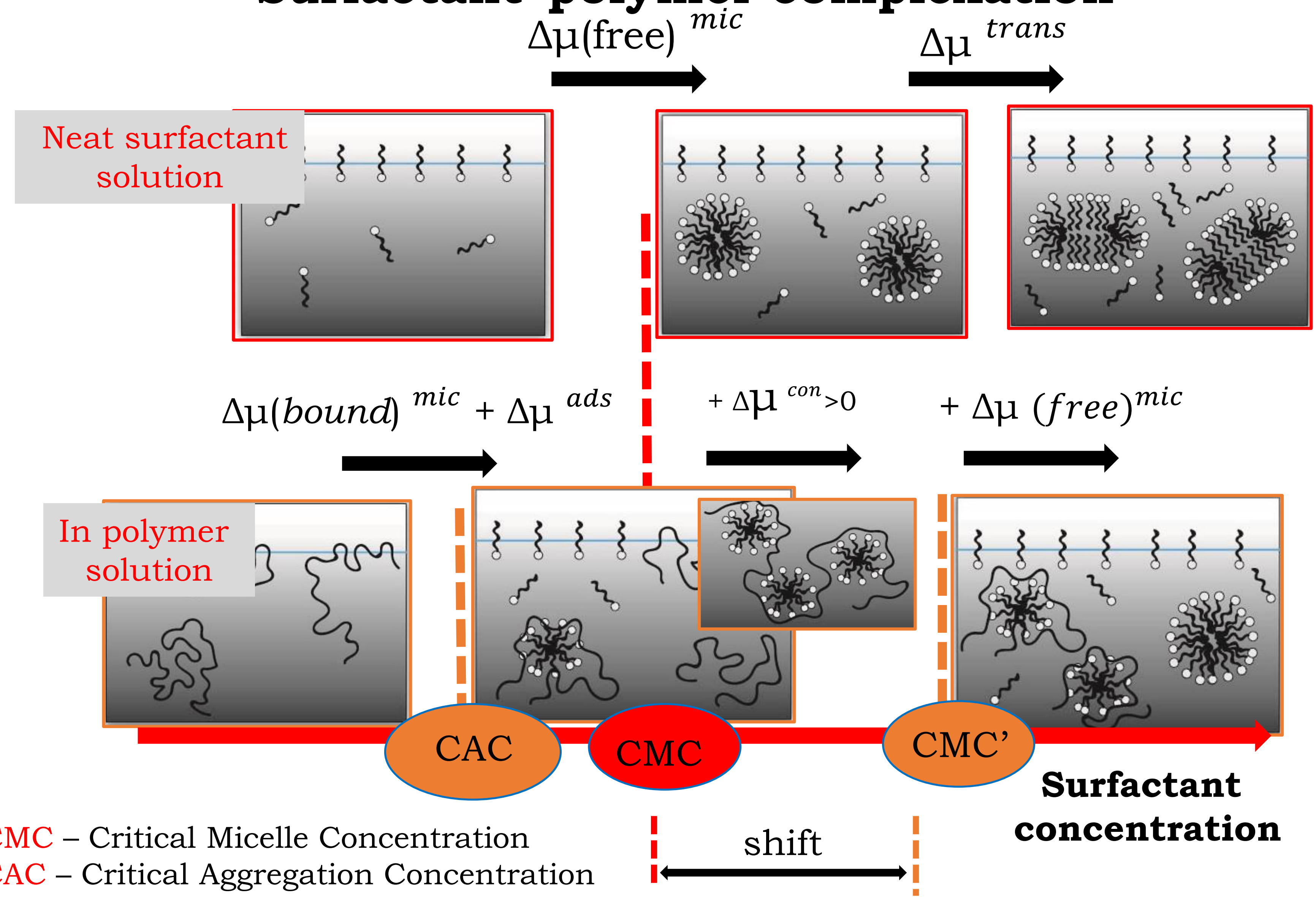
Micellar system





Lebecque S. et al. // J. Mol. Graph. Mod. (2017.), 72, 6-15.

Surfactant–polymer complexation



CMC – Critical Micelle Concentration
CAC – Critical Aggregation Concentration
CMC' – Shifted CMC

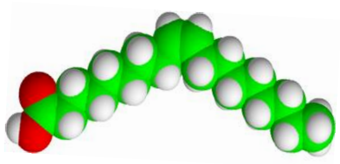
Nikas Y. J., Blankschtein D. / *Langmuir*, (1994) *10*(10), 3512-3528.

Micellar system of surfactants for colloidal stabilization

Anionic surface active agents (surfactants)

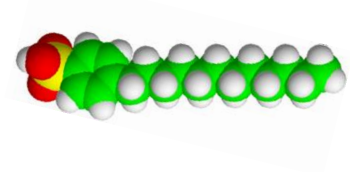
Sodium Oleate (SO)

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COONa$

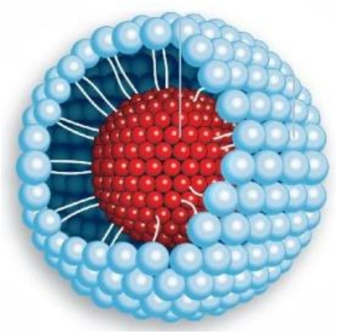


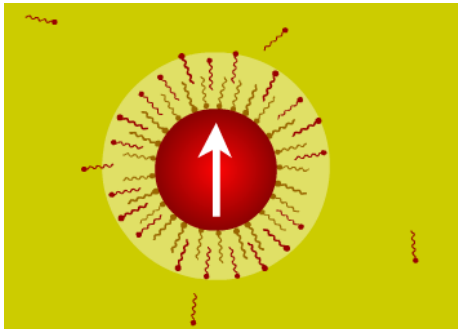
Dodecylbenzene sulfonic acid (DBSA)

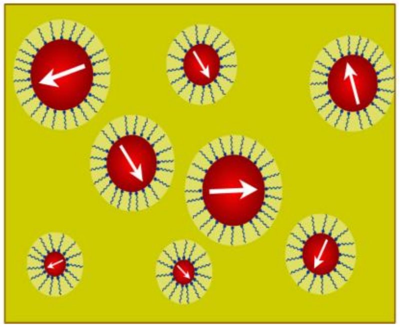
$C_{12}H_{25}C_6H_4SO_3H$



Stabilization of magnetic fluids







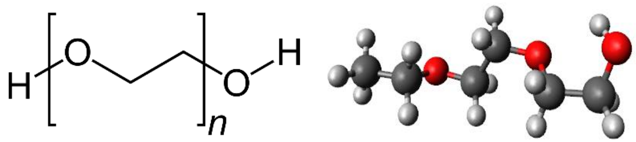
Polar carriers (two stabilization layers) Surfactant excess is required

Avdeev M. V. et al. // J. Coll. Interf. Sci. (2009). 334.(1), 37-41.

Biocompatibility properties of PEGylated colloids. Application for water-based magnetic nanoparticles

Biocompatible polymer

Poly (ethylene glycole) (PEG)

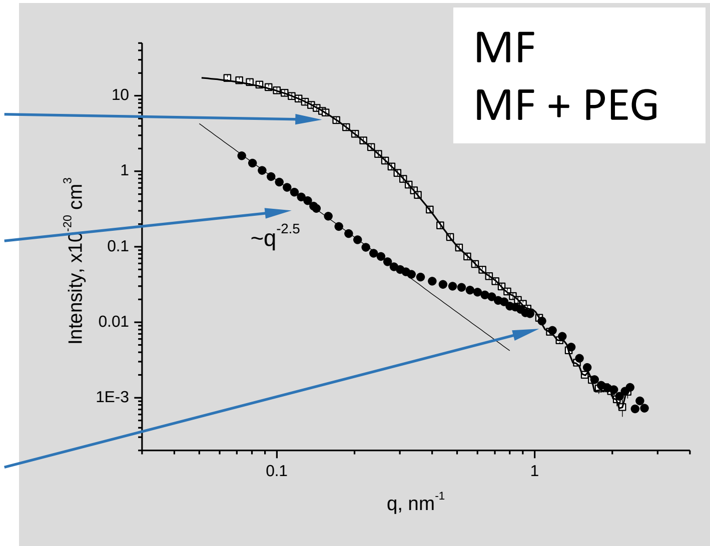


$M_w > 1000$ Da

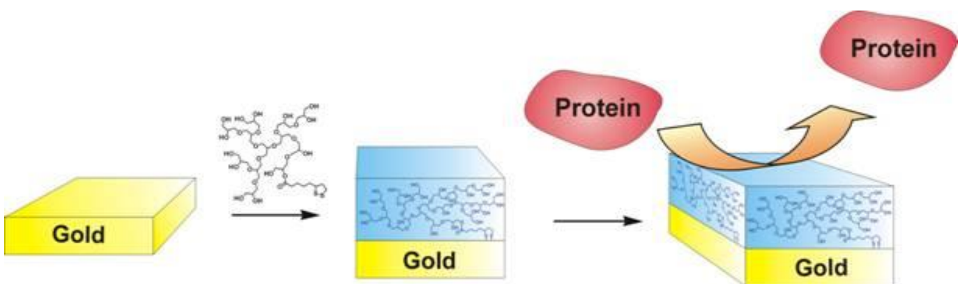
Initial compact aggregates, SO stabilization

Fractal branched aggregates after modification, SO + PEG stabilization

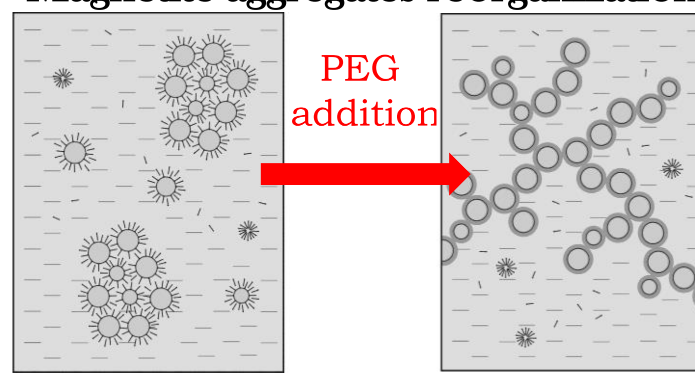
micelles of free surfactant



Protein resistance properties of PEGylated surfaces



Magnetite aggregates reorganization



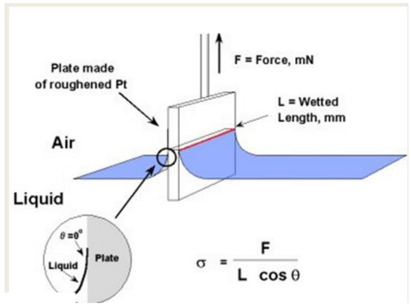
M(SO):M(Fe_3O_4):M(PEG) = ***0.73 : 1 : 2.5***

Structure reorganization of magnetic fluids under PEG addition

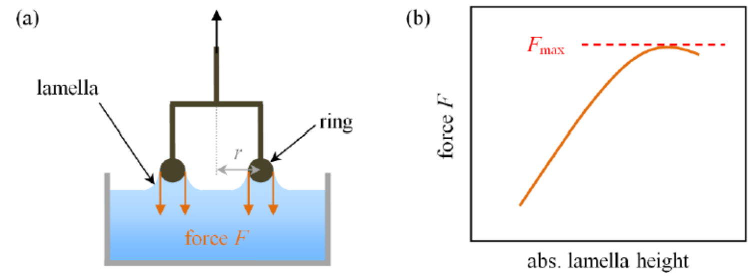
Avdeev M.V., Feoktystov A.V. et.al. // *J. Appl. Cryst.*, (2010) *43*, 959-969.
V.Závišová, M.Koneracká, M.Múčková, et al. // J. Magn. Magn. Mater. 323 (2011) 1408

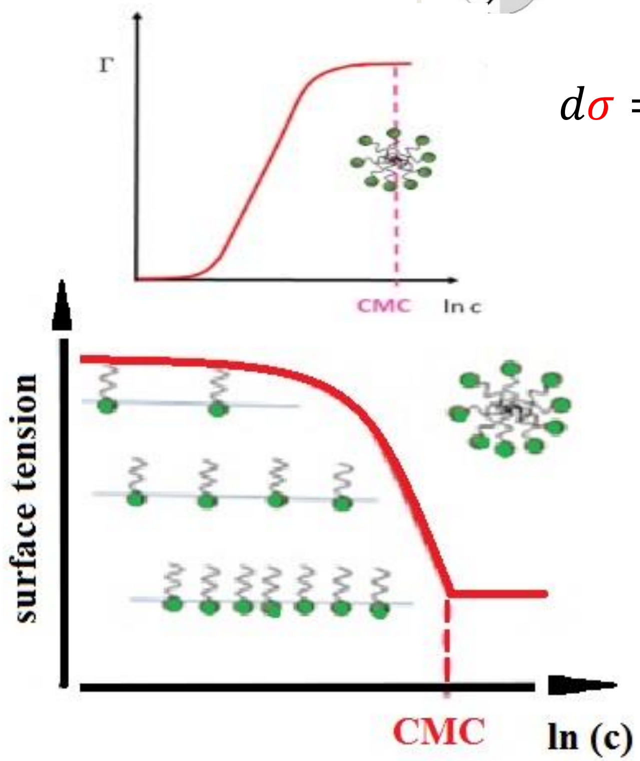
Measurement of surface tension
(force tensiometry method)

Wilhelme plate method



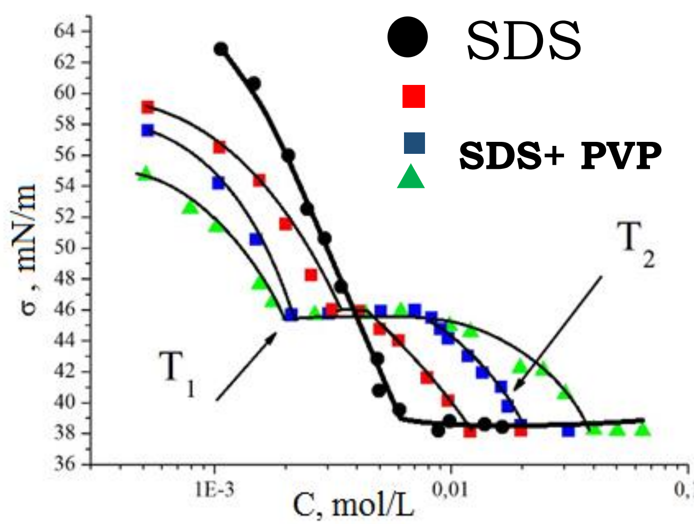
Du Nouy ring method





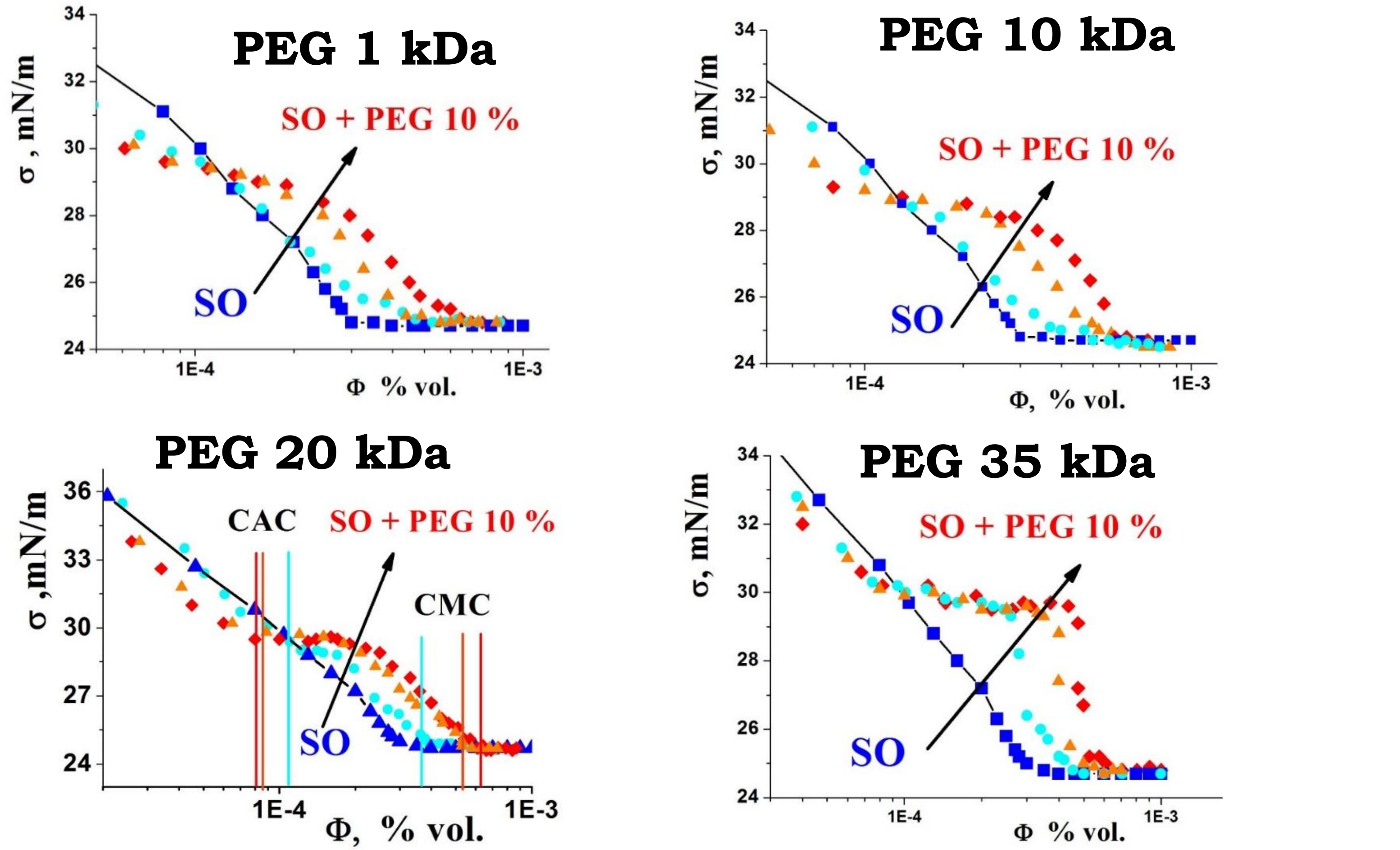
$$d\sigma = -\sum \Gamma_i d\mu_i$$

$$\Gamma_i = \Gamma_\infty \frac{K_s S_i}{1 + K_s S_i}$$



Lunkenheimer K., Wantke K. D. //Coll. Poly. Sci. (1981). 259(3). 354-366.

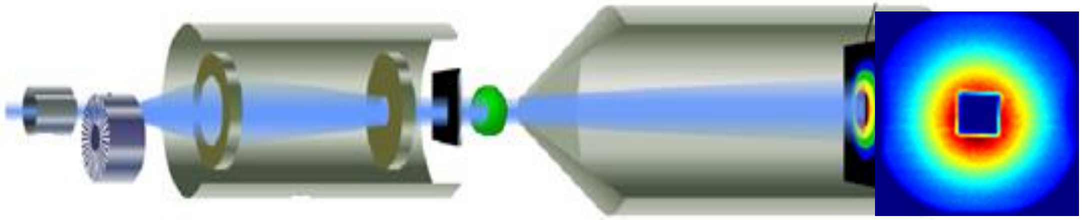
Polymer – surfactant interaction phenomena detecting by surface tension

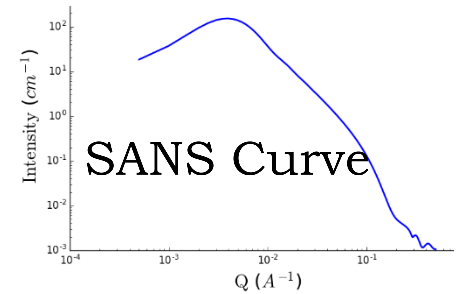


Phenomena of surfactant-polymer complexes formation in aqueous solution of DBSA and SO surfactant with PEG addition was observed

Artykulnyi O.P., et.al // J. Surf. Invest.-X-RAY+ , (2018), in press

Small Angle Neutron Scattering (SANS) method





Decoupling approximation

$$I(q)=nV^2(\Delta\rho)^2P(q)S(q) \qquad I(q) = n(\Delta\rho)^2 P(q)\left(1+\beta(q)\left[\overline{S}(q)-1\right]\right)$$

$$P(q) = \langle |F(q)|^2 \rangle = \frac{1}{V}\int_0^1 |V_c(\rho_m-\rho_s)\,|\,\frac{3j_1(u)}{u}^2\, d\cos\alpha$$

$\overline{S}(q)$ - *Hayterr – Penfold RMSA structure factor of macroion*

$N_{agg} = \frac{4/3\pi ab^2}{v_{chain}}$ - *number of aggregation*

$$U(r) = \left[\frac{Z}{4\pi\varepsilon_0\varepsilon(1+\kappa d)}\right]\left(\frac{\exp[-\kappa(r-d)]}{r}\right)$$

$\gamma = \frac{a}{b}$ – *axial ratio of ellipsoid*

$\kappa = \left[\frac{2(C_{\text{ккм}}+0.5\alpha C)e^2}{\varepsilon\varepsilon_0 k_Б T}\right]^{\frac{1}{2}}$ – *Debye length*

$\alpha = \frac{Z}{N_{agg}}$ - *degree of ionization and charge*

$\Psi = \frac{Z}{\varepsilon\varepsilon_0 d(2+\kappa d)}$ - *surface potential*

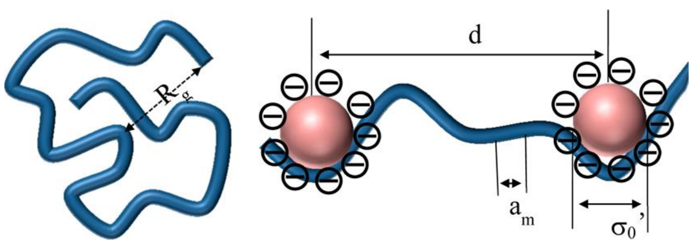
Pedersen J. S. // Adv. Coll. Interf. Sci. (1997) 70, 171-210.

Polymers and surfactant-polymer complexes

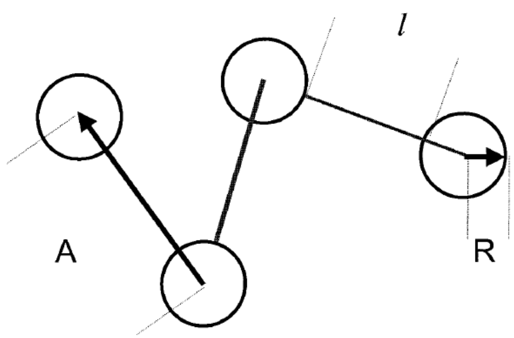
$$P(q) = \frac{2[e^{-x} - (1-x)]}{x^2}$$ - *Gauss coil polymer form factor*

$$I(q) = I(0)\left[P(q) - \frac{A}{I(0)}P(q)^2\right] + \mathrm{B}$$ – *polymer with self-avoid interaction*

$$P(q) = \frac{K}{4\pi L_B \alpha^2}\frac{(q^2 + k^2)}{1 + R_0(q^2 + k^2)[q^2 - (12hC/a_m^2)]}$$ - *Polyelectrolyte model*



$$I(q) = I_{Polymer}(q) + I_{micelles}(q)$$

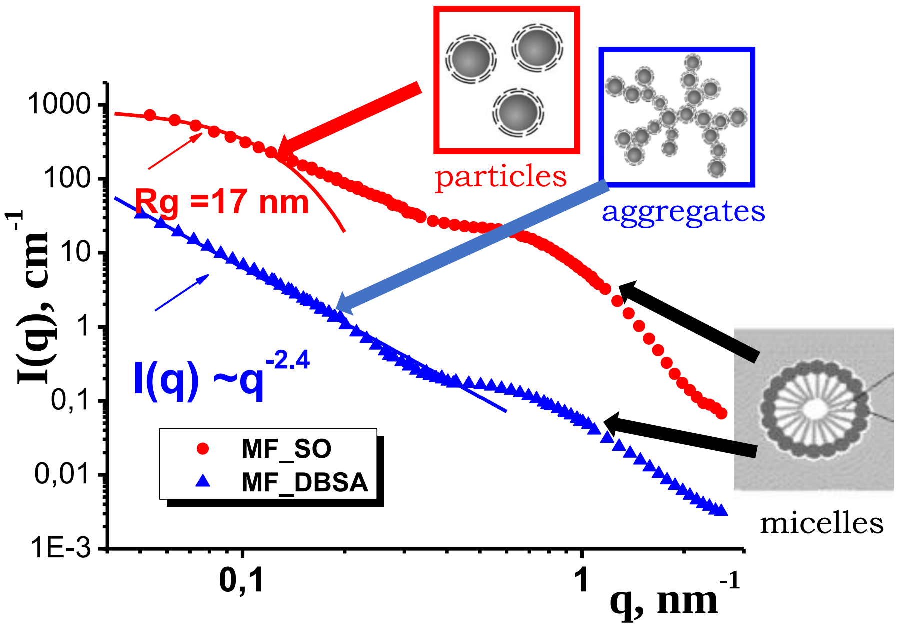


$$P(q) = \frac{I_m + I_l + I_{ml}}{(Mm_r + Nm_s)}$$ - *Pearl-necklace model*

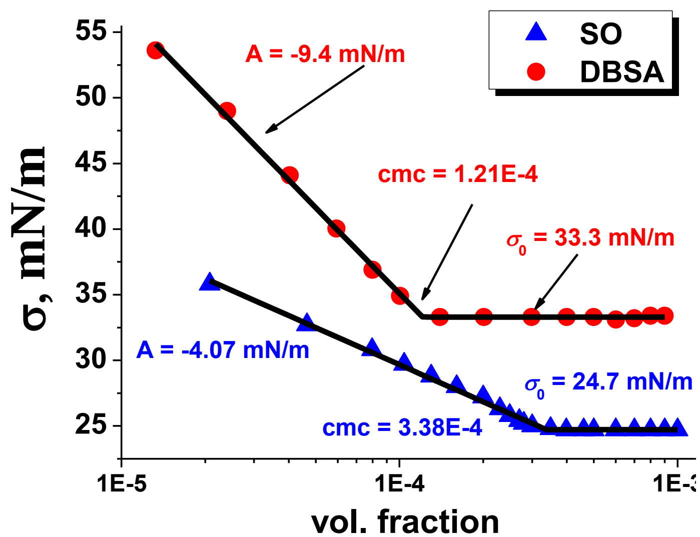
Schweins R. Huber K. // Macromol. Symp. – WILEY-VCH Verlag, (2004). 211.(1) 25-42.

Fajalia A. I. Tsianou M. // J. Phys. Chem. B. (2014). 118.(36) 10725-10739.

Impact of surfactant on the structure of aqueous ferrofluid systems



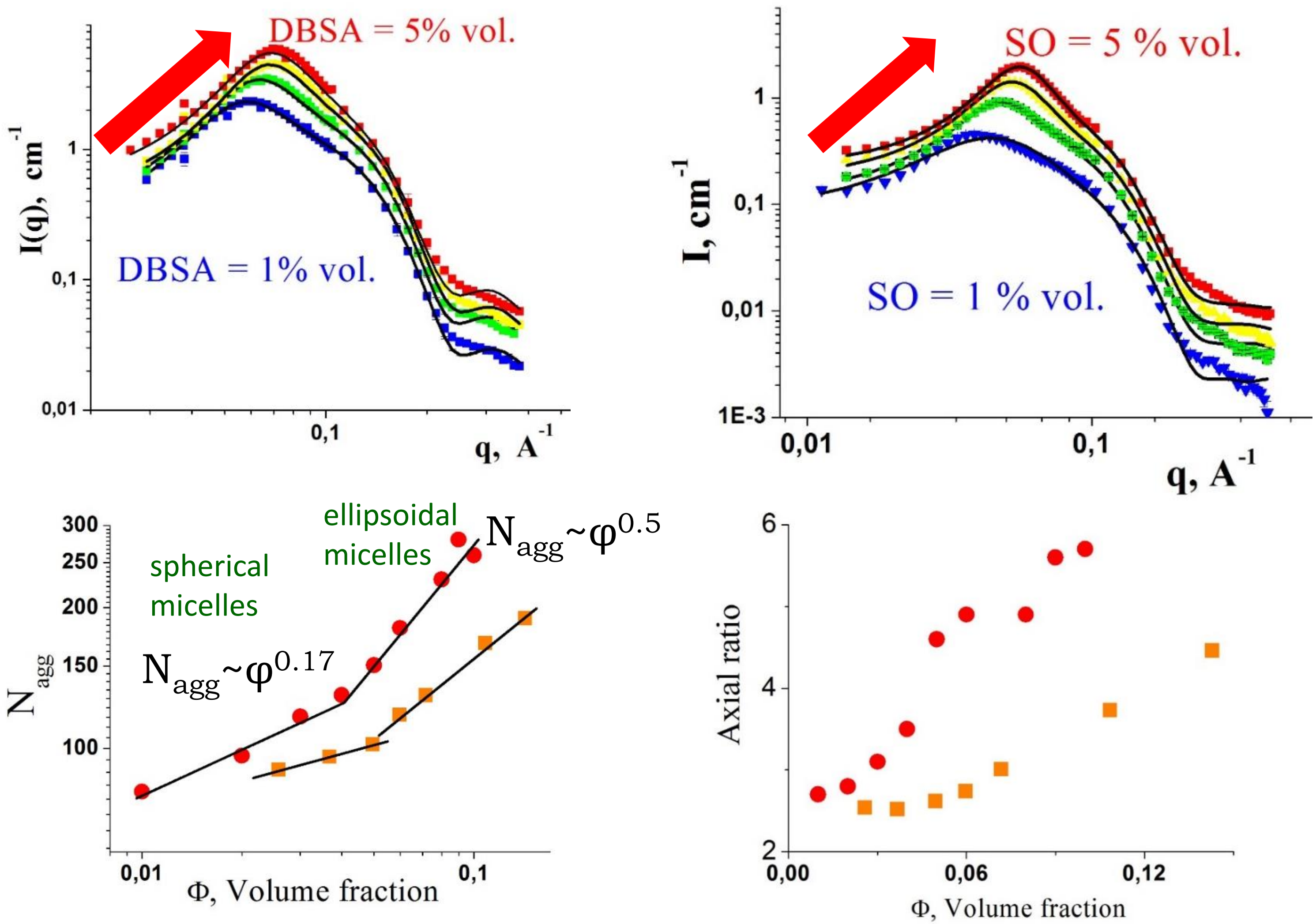
The aggregates of different size and type were observed



significantly different critical micelle concentrations (CMC) parameter

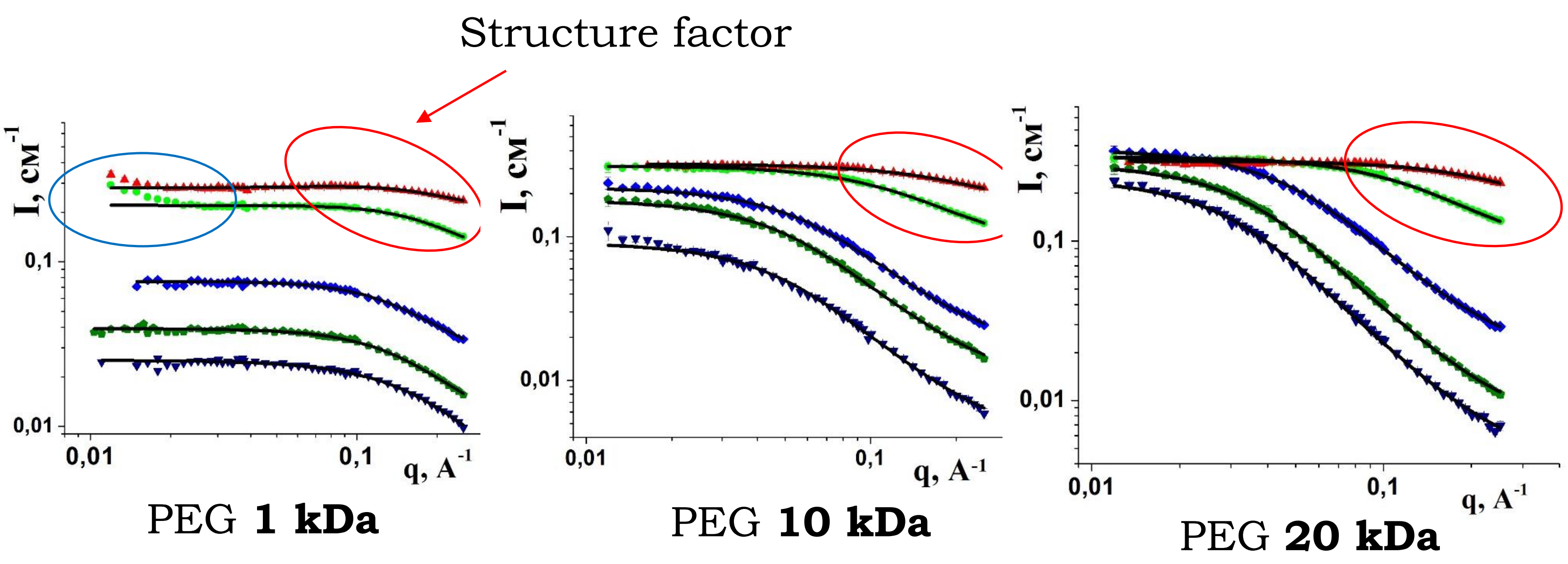
Petrenko V.I., Artykulnyi O.P. et al. // *Coll. Surf. A*. – (2018) 541, 222-226 .

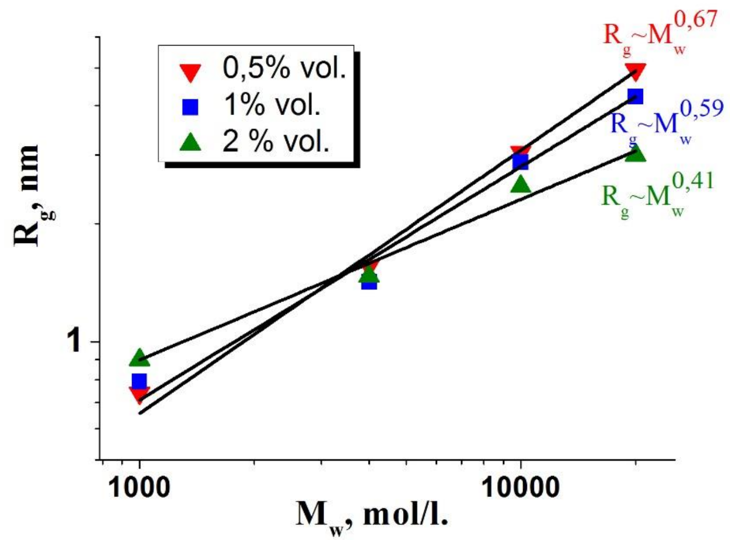
Aqueous solution of SO, DBSA: SANS data



The transition of micelles from spherical to ellipsoidal morphology is detected. SO and DBSA based micelles differ in size

SANS data of PEG aqueous solution



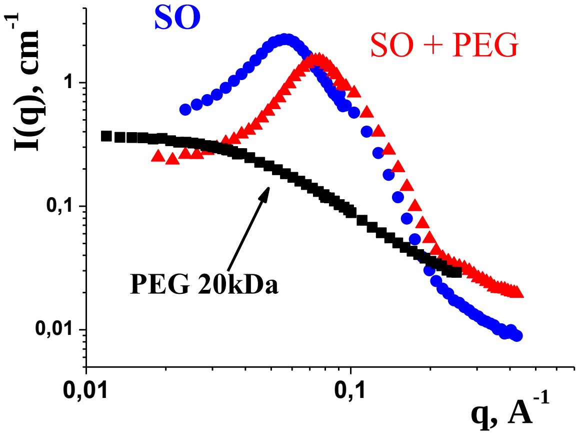


$$P(q) = \frac{2[e^{-x} - (1-x)]}{x^2}$$

$$I(q) = I(0)\left[P(q) - \frac{A}{I(0)}P(q)^2\right] + B$$

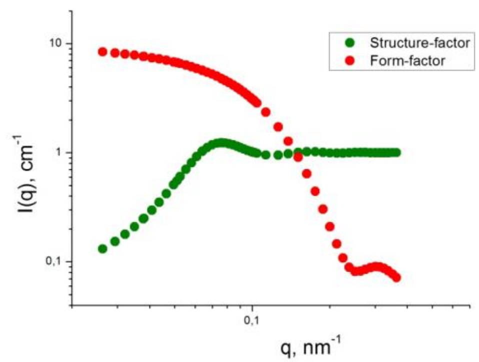
The structure of the polymer coil of PEG is studied (*radius of gyration Rg*), the effect of the structural factor for concentrations of more than 3 vol. % is detected (*second virial coefficient A*)

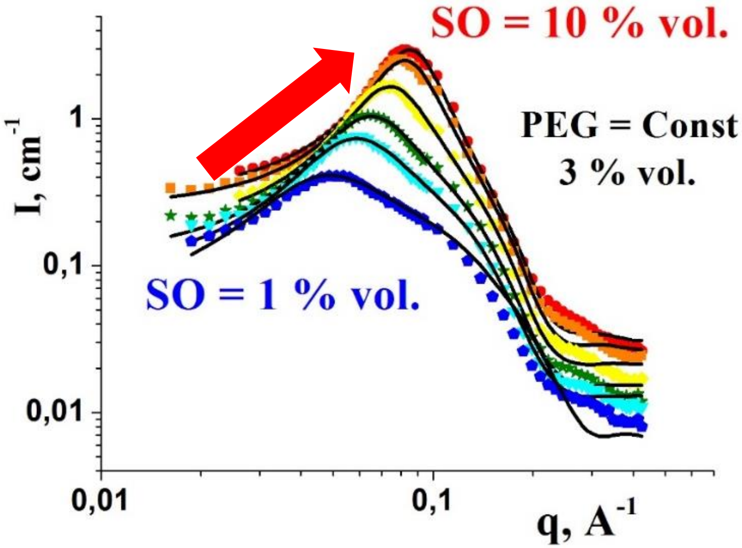
Mixed surfactant – polymer aqueous solution

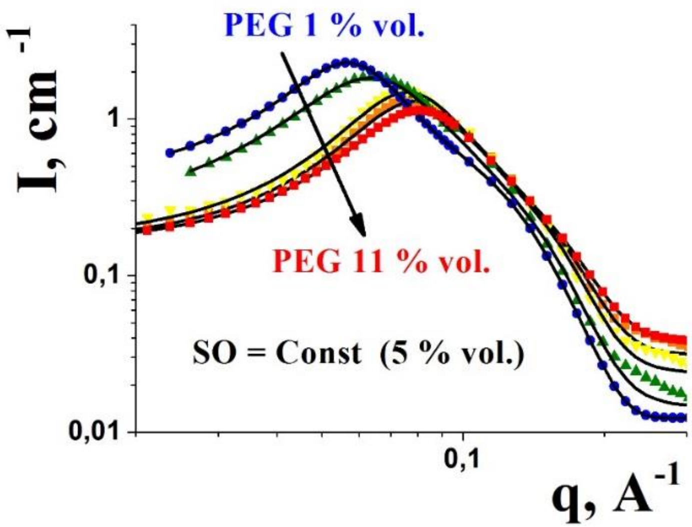


$I(SO) + I(PEG) \neq I(SO + PEG)$

Polymer reorganizes the structure of the micellar system, which leads to qualitative changes in the scattering curve

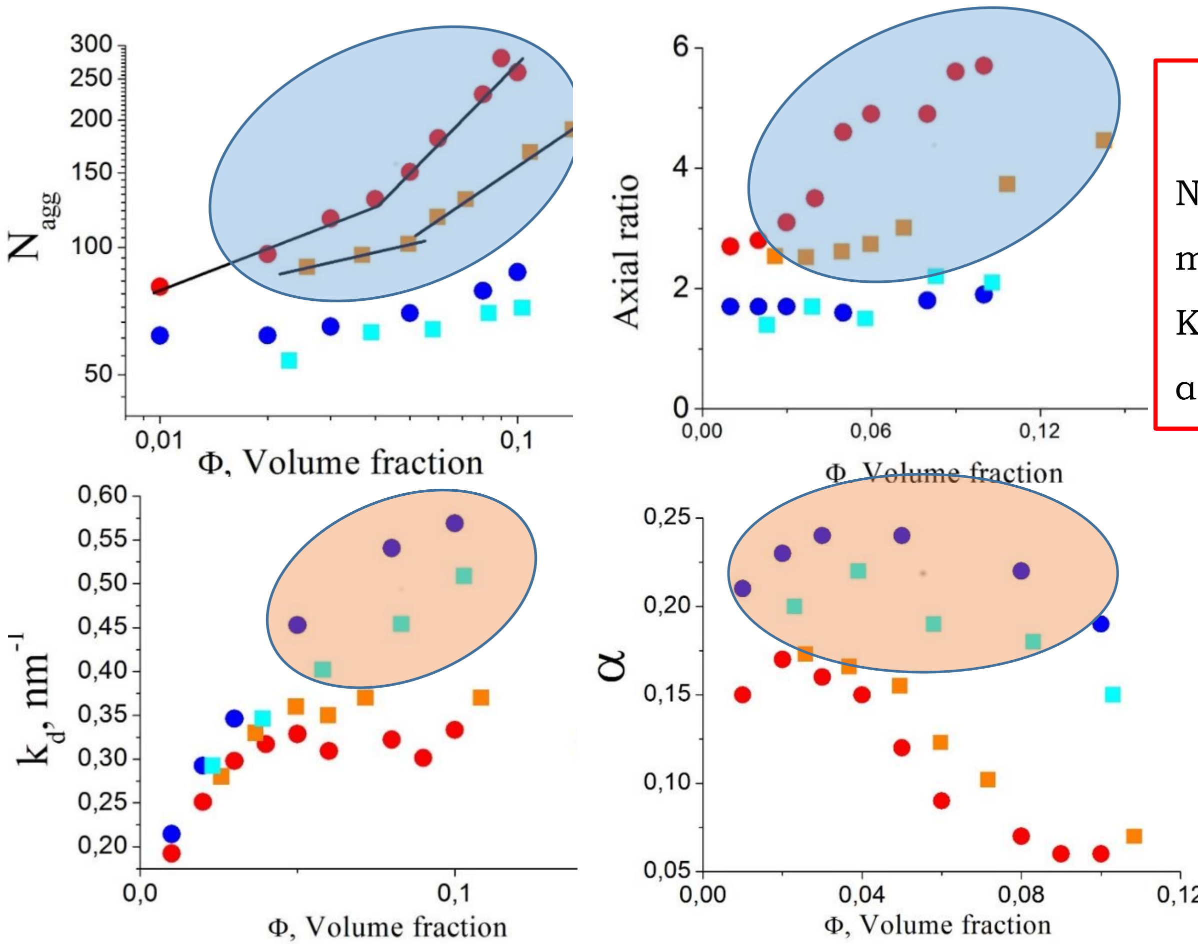






Petrenko V. I., Avdeev M. V., Garamus V. M., Bulavin L. A., Kopcansky P. // (2015). *Coll. Surf. A, 480*, 191-196.

Concentration dependences of structure parameters in micellar system



Structure parameters

N_{agg} – number of aggregation

major to minor ellipsoid axis ratio

K_d – inverse screen length

α – degree of ionization

SO ●

DBSA ■

SO + PEG ●

DBSA + PEG ■

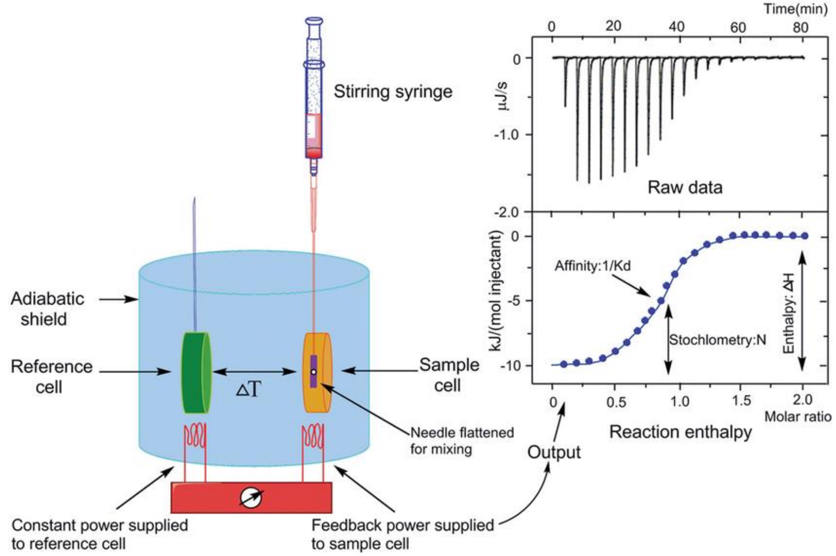
Addition of PEG leads to:

- *Decrease size of micelles and change of the shape*
- *Decrease intermicellear electrostatic interaction (increasing Debye length)*

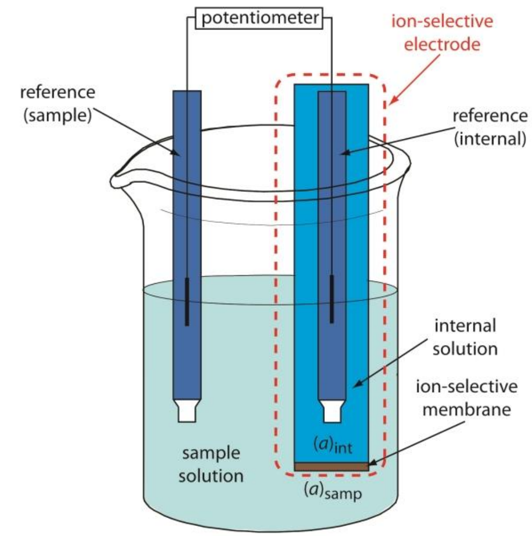
Further research: experimental methods and theoretical models

Isothermal Titration Calorymetry

- Determination of PEG-surfactants binding properties from isothermal titration calorimetry (ITC) thermograms and electromotive forse (EmF) binding isoterms



Isothermal titration calorimety (*ITC*) is a method to measure the energy, related to the formation of physical interactions and chemical bonds.



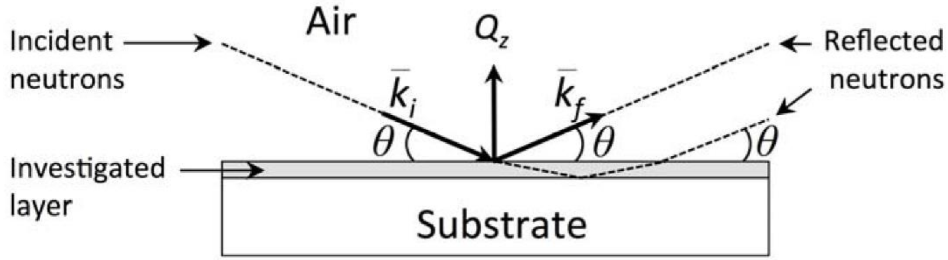
Surfactant-ion selective electrodes (*SISEs*) are usually used for determination of monomeric surfactant concentration in solution with almost no pretreatment

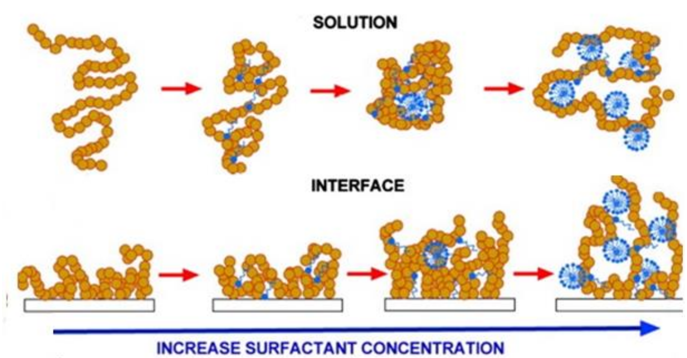
Mészáros R., Varga I., Gilányi T. / *J. Phys. Chemi. B*, (2005). *109*(28), 13538-13544.

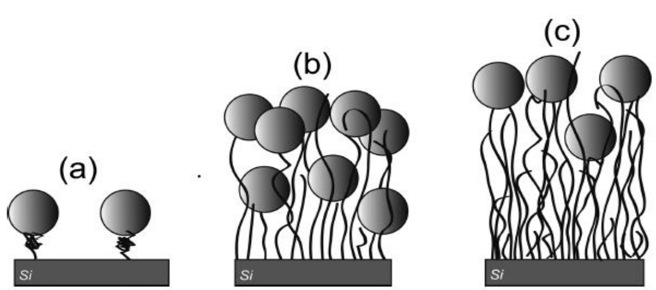
Dai S., Tam K. C. // *J. Phys. Chem. B*, (2001). *105*(44), 10759-10763.

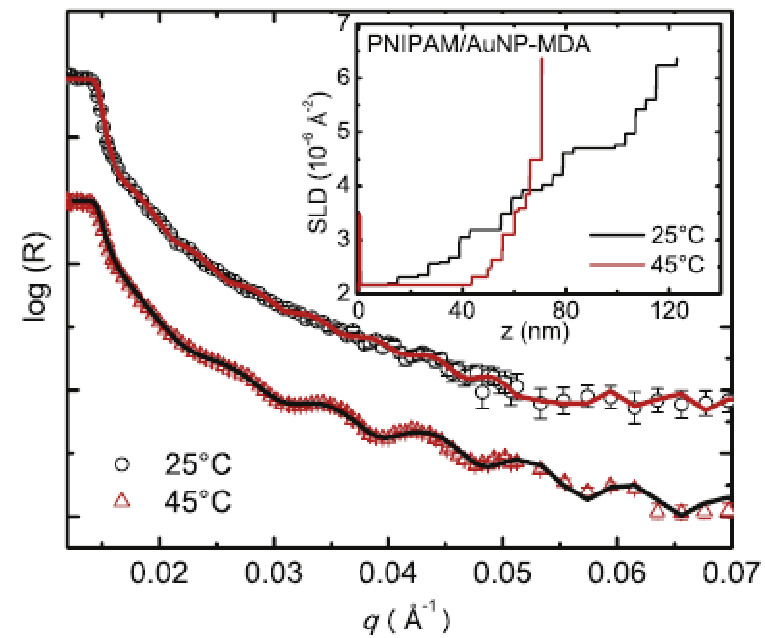
neutron reflectometry,

setting and carrying out of the experiment on the study of surfactant-polymer complexation in dense polymer brush system.









Christau S., Mölle T., Brose F., Genzer J., Soltwedel O., von Klitzing R. /*Polymer*, (2016). *98*, 454-463.

THANK FOR YOUR ATTENTION !