

**Supplemental Materials I. Photograph of the samples with wetted particles in aqueous surfactant solution.**



Fig. I.1. Samples with sedimented particles in aqueous surfactant solution.

## Supplemental Materials II. Calculation of main characteristics of C18-derivatized silica particles (pore area, pore volume, pore radius)

The values of pore volume, pore radius and surface area were provided by the manufacturer for underivatized material (bare silica). Also available for C18-derivatized particles were the total carbon content and surface coverage of C18. The nominal diameter of underivatized pores is 93 Å, for a total surface area of underivatized material to be 426 m<sup>2</sup>/g silica. After C18 modification, the material has a total carbon content of 17.84% and a C18 bonding density of 3.04 μmol C18/m<sup>2</sup>.

For underivatized native silica,  $V_{pore}$  is estimated from the surface area ( $A_{pore}$ ) and radius  $R$ :

$$V_{pore} = \frac{A_{pore} R}{2} \quad (\text{II.1})$$

where

$$V_{pore} = \pi R^2 H \quad (\text{II.2})$$

and

$$A_{pore} = 2\pi R H \quad (\text{II.3})$$

assuming cylindrical pores. By substituting the values for total surface area and pore radius, the total pore volume is 0.99 mL/g silica. This value agrees with the estimated 1.00 mL/g silica from the manufacturer specifications.

We will also utilize the following properties of the C18 bonded phase:

- density:  $d_{C18} = 0.79 \text{ g/mL}^{-1}$ ,
- molecular weight:  $MW_{C18} = 311^{-1}$ ,
- number of C atoms of bonded phase:  $N_C = 20^{-1}$ , and

- effective molecular volume:  $MV_{C18} = 494 \text{ \AA}^3$ .

The pore volume for C18-derivatized Luna silica particles was estimated using two methods. The pore radius and surface area for C18-derivatized pore were then calculated.

**Method 1:** using density of C18

For one gram of the C18-derivatized silica particles, the mass of the C18 layer is:

$$mass_{C18} = \%C \frac{MW_{C18}}{12 N_C} \quad (II.4)^1$$

The calculation leads to a value of 0.231 g C18/g C18-silica. By using:

$$V_{C18} = \frac{mass_{C18}}{d_{C18}} \quad (II.5)$$

The volume of bonded phase is 0.293 mL C18/g C18-silica. Considering 1 g of C18-silica particles, the mass of silica is given by:

$$m_{silica} = 1 - mass_{C18} \quad (II.6)$$

which leads to 0.769 g silica/g C18-silica. We convert the volume of underivatized pore expressed as mL/g silica to mL/g C18-silica:

$$V_{underiv\ pore} \left( \frac{mL}{g\ C18-silica} \right) = V_{underiv\ pore} \left( \frac{mL}{g\ silica} \right) m_{silica} \left( \frac{g\ silica}{g\ C18-silica} \right) \quad (II.7)$$

The numerical calculation gives a volume of underivatized pores of 0.761 mL/g C18-silica.

Finally, the pore volume of the C18-derivatized silica is:

$$V_{deriv\ pore} = V_{underiv\ pore} - V_{C18} \quad (II.8)$$

or 0.469 mL/g C18-silica.

**Method 2:** using surface coverage and molecular volume of C18

The volume of bonded phase with respect to the fraction of silica in C18-silica is estimated by:

$$V_{C18} = \text{surface coverage} \cdot \text{surface area} \cdot \text{Avogadro's number} \cdot \text{C18 molecular volume} \quad (\text{II.9})$$

The calculation leads to 0.385 mL C18/g silica.

Similar to method 1 (eq. II.6), we use the mass of silica  $m_{\text{silica}} = 0.769 \text{ g silica/g C18-silica}$  to convert the volume of C18 expressed as mL/g silica to mL/g C18-silica:

$$V_{C18} \left( \frac{\text{mL}}{\text{g C18-silica}} \right) = V_{C18} \left( \frac{\text{mL}}{\text{g silica}} \right) m_{\text{silica}} \left( \frac{\text{g}}{\text{g C18-silica}} \right) \quad (\text{II.10})$$

which leads to 0.296 mL C18/g C18-silica.

Finally, the volume of derivatized pore expressed as mL/g C18-silica is:

$$V_{\text{deriv pore}} = V_{\text{underiv pore}} - V_{C18} \quad (\text{II.11})$$

or 0.465 mL C18/g C18-silica.

The pore volume used in this paper for all the calculations represents the average value of methods 1 and 2:

$$V_{\text{deriv pore}} = 0.467 \frac{\text{mL}}{\text{g C18-silica}} = 0.47 \frac{\text{mL}}{\text{g C18-silica}} \quad (\text{II.12})$$

The radius of derivatized pore is calculated by using the volume of derivatized pore and the volume and radius of pore prior to derivatization:

$$V_{\text{underiv pore}} = \pi R_{\text{underiv pore}}^2 H_{\text{underiv pore}} \quad (\text{II.13})$$

$$V_{\text{deriv pore}} = \pi R_{\text{deriv pore}}^2 H_{\text{deriv pore}} \quad (\text{II.14})$$

$$R_{\text{deriv pore}} = R_{\text{underiv pore}} \sqrt{\frac{V_{\text{deriv pore}}}{V_{\text{underiv pore}}}} \quad (\text{II.15})$$

By substituting the values for parameters above,  $R_{underv pore} = 46.5 \text{ \AA}$ ,  $V_{underv pore} = 0.76 \text{ mL/g}$  C18-silica and  $V_{deriv pore} = 0.47 \text{ mL/g}$  C18-silica, a radius of  $36.5 \text{ \AA}$  is obtained for the derivatized pore.

Finally, the surface area is calculated by using the volume and the radius of the derivatized pore:

$$S_{deriv pore} = \frac{2 V_{deriv pore}}{R_{deriv pore}} \quad (\text{II.16})$$

The value calculated is  $256 \text{ m}^2/\text{g}$  C18-silica.

## Supplemental Materials III. Calculation of particle density for Models I, II and III

### 1. General formula for particle density calculation

The total volume of the particles,  $V_{total}$ , is the sum of the C18-silica particles volume  $V_{solid}$  (including volumes of both the silica and the C18 layer) and the pore volume  $V_{pores}$ , which is occupied by air ( $V_{air}$ ), adsorbed SDS ( $V_{SDS\ adsorbed}$ ) and the wetting solution ( $V_{solution}$ ):

$$V_{total} = V_{solid} + V_{pores} = V_{solid} + V_{air} + V_{solution} + V_{SDS\ adsorbed} \quad (III.1)$$

The volumes are calculated with the respective masses ( $m$ ) and densities ( $\rho$ ):

$$\frac{m_{total}}{\rho_{total}} = \frac{m_{solid}}{\rho_{solid}} + V_{pores} \quad (III.2)$$

Sum of the masses gives:

$$\frac{m_{solid} + m_{air} + m_{solution} + m_{SDS\ adsorbed}}{\rho_{total}} = \frac{m_{solid}}{\rho_{solid}} + V_{pores} \quad (III.3)$$

The mass of adsorbed SDS is determined by its number of moles ( $n_{SDS\ adsorbed}$ ):

$$\frac{m_{solid} + \rho_{solution} V_{solution} + n_{SDS\ adsorbed} MW_{SDS}}{\rho_{total}} = \frac{m_{solid}}{\rho_{solid}} + V_{pores} \quad (III.4)$$

The density of a particle modified by SDS and wetting solution is thus:

$$\rho_{total} = \frac{m_{solid} + \rho_{solution} V_{solution} + n_{SDS\ adsorbed} MW_{SDS}}{\frac{m_{solid}}{\rho_{solid}} + V_{pores}} \quad (III.5)$$

$m_{air}$  was neglected because its contribution to the total mass is negligible. For example, for completely dry particles ( $V_{air} = V_{pores}$ ), the mass of air is 0.000561 g per g C18-silica when air density is taken for 20°C and 1 bar (0.001194 g/mL<sup>3</sup>). This means that the percentage contribution of air is < 0.0561% for particles modified by SDS and the wetting solution.

The density of C18-derivatized silica particles,  $\rho_{solid}$ , was calculated as:

$$\rho_{solid} = \frac{m_{solid}}{V_{solid}} = \frac{m_{silica} + m_{C18}}{V_{silica} + V_{C18}} = \frac{m_{silica} + m_{C18}}{\frac{m_{silica}}{\rho_{silica}} + \frac{m_{C18}}{\rho_{C18}}} = \frac{1}{\frac{w_{silica}}{\rho_{silica}} + \frac{w_{C18}}{\rho_{C18}}} \quad (III.6)$$

We used  $m_{solid} = 1 \text{ g C18-silica particles}$  and  $m_{silica} = w_{silica} m_{solid} = w_{silica} m_{C18} = w_{C18} m_{solid} = w_{C18}$ , where  $w_{silica}$  and  $w_{C18}$  represent the mass fractions of silica and C18, respectively, in C18-silica particles. In the particles under study,  $w_{silica} = 0.769$ ,  $w_{C18} = 0.231$ ,  $\rho_{silica} = 2.15 \text{ g/mL}$  and  $\rho_{C18} = 0.79 \text{ g/mL}$ . We thus have  $\rho_{solid} = 1.54 \text{ g/mL}$ .

The number of moles of adsorbed SDS is:

$$n_{SDS \text{ adsorbed}} = n_{SDS \text{ adsorbed specific}} \cdot \text{specific surface} \cdot m_{solid}$$

where  $n_{SDS \text{ adsorbed specific}}$  is in  $\text{mol/m}^2$ , specific surface in  $\text{m}^2/\text{g}$  and  $m_{solid}$  in g.

The value of  $n_{SDS \text{ adsorbed specific}}$ ,  $4.2 \times 10^{-6} \text{ mol/m}^2$ , is the maximum surface coverage of SDS molecules on the mesoporous silica.

## 2. Calculation of volumes of all the components inside nanopores in the particle – solution system

The possible components that occupy the nanopores at any moment in time during the adsorption process are: solution, SDS layer adsorbed on the inner wall of nanopores and air.

### 2a. Model I: SDS molecules adsorb as a compact monolayer vertically oriented on the C18 phase of the nanopores.

The SDS coverage is defined with respect to the maximum achievable coverage of a compact SDS monolayer:

$$f = \frac{a}{A} \quad (\text{III.7})$$

where  $a$  is the effective area covered by adsorbed SDS molecules and  $A$  the maximum area that can be covered by adsorbed SDS molecules (pore area).

The pore is considered to be a cylinder with a radius equal to the average radius of C18-derivatized silica particles (see Section II for calculation).

$$a = 2\pi R h \quad (\text{III.8})$$

$$A = 2\pi R H \quad (\text{III.9})$$

where  $R$  is the radius of the cylinder,  $h$  the actual height of the fraction of cylinder that is covered by the adsorbed SDS layer and thus filled by the solution,  $H$  the total height of the cylinder (nanopores) (Fig. III.1).

Thus:

$$f = \frac{h}{H} \quad (\text{III.10})$$

and

$$V_{pore} = \pi R^2 H \quad (\text{III.11})$$

$$V_{solution} = \pi r^2 h = \pi r^2 f H \quad (\text{III.12})$$

$$V_{SDS \text{ max coverage}} = \pi R^2 H - \pi r^2 H = \pi(R^2 - r^2)H \quad (\text{III.13})$$

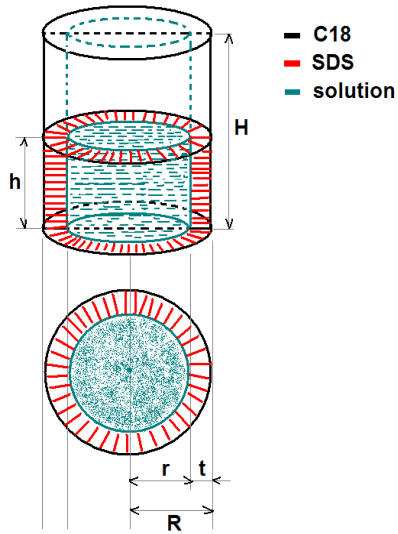


Figure III.1. SDS adsorption as a compact monolayer oriented vertically to surface, guiding solution into the nanopore - *Model I*.



The volume of the wetting solution is determined by the pore volume and the volume of SDS at the maximum coverage:

$$V_{solution} = f (V_{pore} - V_{SDS \max coverage}) \quad (III.14)$$

$V_{SDS \max coverage}$  is a function of the pore radius, pore volume and the thickness  $t$  of the SDS adsorbed layer:

$$V_{SDS \max coverage} = \pi(R^2 - r^2) H = \pi(R - r)(R + r) H = \pi t(2R - t) \frac{V_{pore}}{\pi R^2} = \frac{t(2R-t)}{R^2} V_{pore} \quad (III.15)$$

The volumes of the other two components of the nanopore, adsorbed SDS and air above solution, are:

$$V_{SDS} = f V_{SDS \max coverage} \quad (III.16)$$

and

$$V_{air} = V_{pore} - V_{solution} - V_{SDS} \quad (III.17)$$

With these formulas, the volumes can be simulated for each SDS coverage  $f$ .

2b. Model II: SDS molecules adsorb as dispersed individual molecules oriented vertically on the C18 phase of the nanopores; intermolecular space between adsorbed SDS molecules is filled with water.

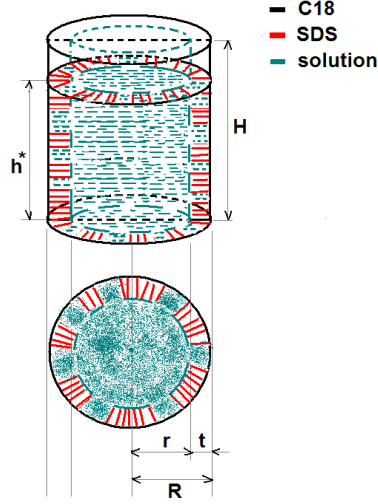


Figure III.2. SDS adsorption as dispersed individual molecules oriented away from surface inducing pore wetting by solution - **Model II**.

The level of solution into the nanopore can be expressed as:

$$h^* = f^* h = f^* f H \quad (\text{III.18})$$

where  $f$  is the SDS coverage as defined in Model I and  $f^*$  is denoted as the “dispersion factor” and reflects the decrease of charge density on the nanopore surface ( $f^* = 1$  means no dispersion and maximum charge density).

The solution will occupy the volume:

$$\begin{aligned} V_{\text{solution}} &= V_{\text{solution in the cylinder}} + V_{\text{interstitial space between adsorbed SDS molecules}} = \\ &f^* f (V_{\text{pore}} - V_{\text{SDS max coverage}}) + f (f^* - 1) V_{\text{SDS max coverage}} = \\ &f (f^* V_{\text{pore}} - V_{\text{SDS max coverage}}) \end{aligned} \quad (\text{III.19})$$

$V_{\text{SDS}}$  and  $V_{\text{air}}$  are calculated using identical formulas as in Model I.

As a general comment for both Models I and II: although the maximum length of expanded C12 tail of SDS, 16.7 Å (based on Tanford formula<sup>4</sup>), is taken into account it is possible that, for a SDS thickness of 11 Å, a fragment of SDS tail penetrates and intercalates into the C18 layer. This situation is favorable in Model II in order to minimize the direct contact of individual unprotected hydrophobic tails with water.

2c. **Model III:** SDS molecules adsorb as dispersed hemisphere-shaped hemimicelles on C18 monolayer; inter-micellar area is wetted with water.

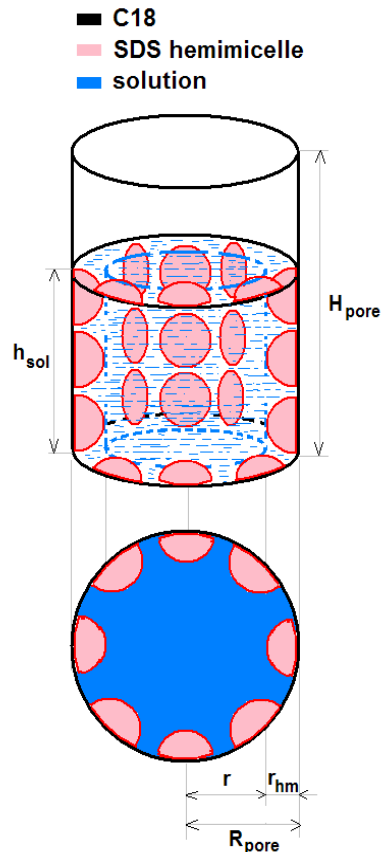


Figure III.3. SDS adsorption as hemispherical hemicelles into nanopore, inducing pore wetting by solution – **Model III**.

Again, this model considers the pore as a cylinder with radius equal to average radius of C18-derivatized silica particles (Section I). The dispersion factor  $f^*$  is defined as the ratio of apparent and effective area of nanopore covered by SDS hemimicelles:

$$f^* = \frac{A_{app\ SDS\ ads}}{A_{eff\ SDS\ ads}} \quad (III.20)$$

where  $A_{app\ SDS\ ads} = 2\pi R_{pore} h_{solution}$  (III.21)

$$A_{eff\ SDS\ ads} = N_{ohm} \times \pi r_{hm}^2 \quad (III.22)$$

and  $N_{ohm}$  is the total number of hemimicelles and is estimated as:

$$N_{ohm} = \frac{n_{SDS\ ads} A_{pore} N_A}{N_{hm}} \quad (III.23)$$

where  $N_{hm}$  is the aggregation number for the hemimicelle,  $n_{SDS\ ads}$  the moles of SDS adsorbed per unit surface,  $A_{pore}$  the total pore area and  $N_A$  the Avogadro's number.

The volume of solution that rises into nanopore during the wetting process is estimated as:

$$V_{solution} = \pi R_{pore}^2 h_{solution} - V_{SDS\ ads\ hm} = \frac{V_{pore}}{H_{pore}} h_{solution} - V_{SDS\ ads\ hm} \quad (III.24)$$

$V_{SDS\ ads\ hm}$ , the volume of SDS adsorbed that contributes to the volume of hemimicelles, is the sum of the volumes of hydrophobic cores and anionic heads. The volume of the hydrophobic core is determined by the actual number of C atoms that participate in hemimicelle formation (see subsection 3). This number is calculated as the difference between the total number of C (12 in case of SDS) and the number of C atoms of hydrophobic tails that intercalate into the C18 layer:

$$V_{SDS\ ads\ hm} = N_{ohm} V_{core\ hm} + N_{ohm} N_{hm} V_{head} = N_{ohm} (V_{core\ hm} + N_{hm} V_{head}) \quad (III.25)$$

in which  $V_{head}$  is the volume of SDS head group.

Because  $A_{pore} = 2\pi R_{pore} H_{pore}$ ,  $\frac{h_{solution}}{H_{pore}} = \frac{A_{app SDS ads}}{A_{pore}}$  (III.26)

Finally:

$$V_{solution} = \frac{A_{app SDS ads}}{A_{pore}} V_{pore} - V_{SDS ads hm} = f^* \frac{A_{eff SDS ads}}{A_{pore}} V_{pore} - V_{SDS ads hm} \quad (III.27)$$

$$V_{air} = V_{pore} - V_{SDS ads} - V_{solution} \quad (III.28)$$

### 3. Calculation of hemimicellar radius

The SDS hemimicelle is considered as a hemisphere with two components: an inner hydrophobic core formed by the hydrophobic tails and a charged shell formed by the anionic sulfate groups (Fig. 5). The hydrophobic core is assumed to be impenetrable to solvent molecules or ions (no holes). This assumption is a reasonable one for the simulation although the solvent molecules do penetrate into the core, especially into the outer-most fraction of the hydrocarbon chains. The number of solvent molecules in the core is low and can be neglected in the volume calculation. On the contrary, depending on the aggregation number and the number of C atoms that participate in the hemimicelle formation, water molecules and counterions can penetrate the charged shell and occupy the space between the sulfate groups.

According to Tanford<sup>4</sup>, an alkyl chain will occupy a certain volume in the hydrophobic core:

$$v_{chain} = 27.4 + 26.9 n_C \quad (in \text{ \AA}^3) \quad (III.29)$$

As a result, the volume of hemimicelle core becomes:

$$V_{core hm} = v_{chain} N_{hm} = (27.4 + 26.9 n_C) N_{hm} \quad (in \text{ \AA}^3) \quad (III.30)$$

Because hemimicelle is a hemisphere, the volume of hemimicelle core is also:

$$V_{core hm} = \frac{2}{3} \pi r_{core hm}^3 \quad (III.31)$$

The radius of the hemimicelle core is a function of its aggregation number and the number of C atoms participating in the hemimicelle formation:

$$r_{core\ hm} = \sqrt[3]{\frac{3N_{hm} (27.4 + 26.9 n_C)}{2\pi}} \quad (\text{in } \text{\AA}) \quad (\text{III.32})$$

Finally, the hemimicelle radius represents the sum of radius of hemimicelle core and diameter of anionic head group:

$$r_{hm} = r_{core\ hm} + d_{SDS\ head} \quad (\text{III.33})$$

The diameter of sulfate group is estimated based on Bruce *et al*<sup>5</sup>. Specifically, the radius of SDS head can be considered as the distance from S atom to the neighbor water O minus the radius of water:

$$d_{SDS\ head} = 2 r_{SDS\ head} = 2 (l_{S-O} - r_{H_2O}) \quad (\text{III.34})$$

The values 3.8 Å for distance between S and O and 1.4 Å for radius of water molecule lead to a diameter of 4.8 Å for SDS head.

**Supplemental Materials IV. Calculation of particle density for Model III when formation of a vapor film between water and the wall of hydrophobic nanopore is assumed.**

The particle density is calculated in the same way as in the previous section (eq. III.5). The mass of the gas-like fluid that separates water from the hydrophobic wall is neglected due to its insignificant contribution comparing to the other terms in the equation (similar to neglecting mass of air due to its contribution to the total mass). The overall particle density will decrease comparing to no-vapor film situation because of the smaller volume of solution that rises into nanopore during the wetting process. Thus, the volume of the vapor film  $V_{gp}$  is subtracted from the term  $V_{solution}$  (calculated as in eq. III.27).  $V_{gp}$  is estimated as:

$$V_{gp} = (f^* - 1)A_{eff\ SDS\ ads} t_{gp} \quad (IV.1)$$

where  $t_{gp}$  represent the average thickness of the vapor film between water and the wall of hydrophobic nanopore (Figure IV.1).

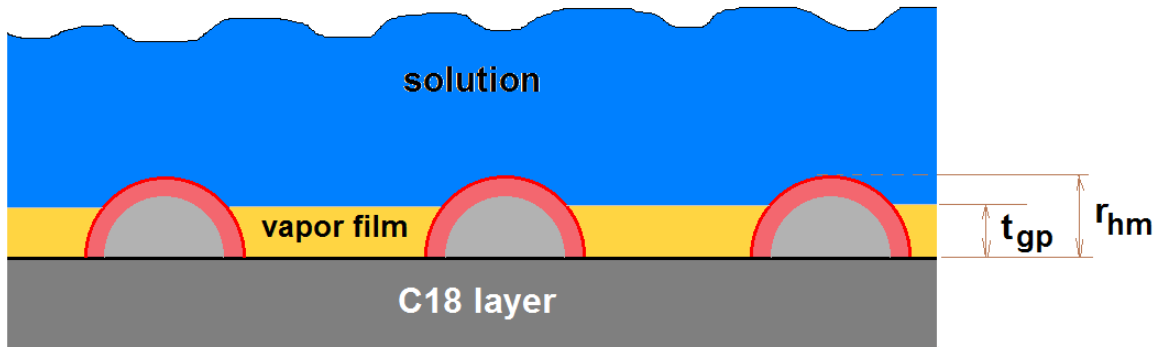


Fig. IV.1. Formation of a vapor film between water (non-wetting liquid) and the C18 layer (hydrophobic surface) in the inter-hemimicelle area.

$r_{hm}$  – hemimicelle radius;  $t_{gp}$  – thickness of the vapor film

We calculated the extent of particle density decrease for several types of SDS hemimicelles. We chose two representative combinations *aggregation number – number of C atoms intercalated into C18 layer* out of the hemimicelles that obey the steric constraint in Fig. 7B (hemimicelle radius < 11.7 Å). Thus, we selected the hemimicelle with aggregation number 7 and ten C atoms intercalated into C18 layer, denoted as hemimicelle “7-10” and the hemimicelle with aggregation number 4 and seven C atoms intercalated into C18 layer, denoted as hemimicelle “4-7”. The hemimicelle “7-10” represents one of the structures with a charge density close to the bulk SDS micelles in solution, whereas the combination “4-7” corresponds to hemimicelles with lower charge density. We used 5.6 Å as the thickness of the vapor film.<sup>6</sup>

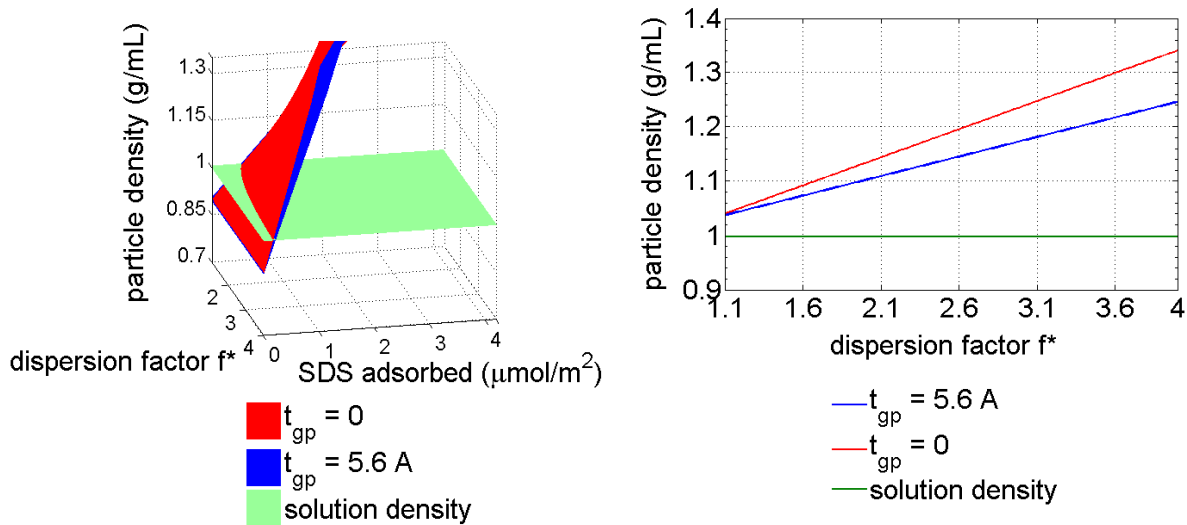


Fig. IV.2. A - Particle density as a function of the amount of SDS adsorbed and dispersion factor  $f^*$  for adsorbed hemimicelles with aggregation number 7 and ten C atoms of the SDS tails intercalating into the C18 layer; B - particle density along the entire range of dispersion factor  $f^*$  for SDS coverage  $0.73 \mu\text{mol}/\text{m}^2$ .



Figure IV.2.A shows comparatively the particle density as function of the dispersion factor  $f^*$  and SDS coverage for both situations, namely no-vapor film model versus the formation of the vapor film, when hemimicelles “7-10” are formed on nanopores wall. Figure IV.2.B presents the 2D cross-sections through the particle density surfaces at experimental coverage  $0.73 \mu\text{mol}/\text{m}^2$ .

Similarly, the cross-sections through the particle density surfaces at experimental coverage  $0.73 \mu\text{mol}/\text{m}^2$  corresponding to formation of hemimicelles “4-7” is shown in fig. IV.3.

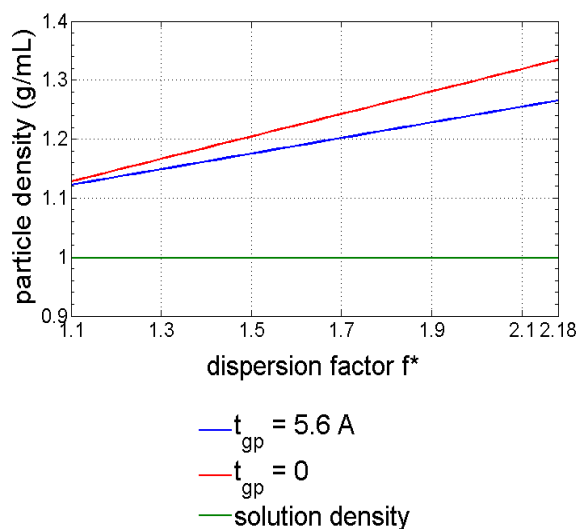


Fig. IV.3. Particle density along the entire range of dispersion factor  $f^*$  for the experimental SDS coverage  $0.73 \mu\text{mol}/\text{m}^2$  when SDS adsorbs as hemimicelles with aggregation number 4 and seven C atoms of the SDS tails intercalating into the C18 layer.

Table IV.1 shows the decrease in the overall density of the particles with nanopores completely filled (maximum dispersion factor  $f^*$ ) and SDS coverage of  $0.73 \mu\text{mol}/\text{m}^2$  when the formation of a  $5.6 \text{ \AA}$  vapor film is assumed.

Table IV.1. The decrease in particle density when the formation of a 5.6 Å vapor film between water and nanopore's wall is assumed.

Type hemimicelle	Thickness vapor film (Å)	particle density (g/mL)	Dispersion factor $f^*$	Volume solution (mL/g part.)	Volume SDS adsorbed (mL/g part.)	Volume vapor film (mL/g part.)
"7-10"	0	1.341	4	0.450	0.015	0
	5.6	1.246		0.343		0.106
		<b>density decrease (%)</b>		<b>volume decrease (%)</b>		
		<b>7.1</b>		<b>23.7</b>		
Type hemimicelle	Thickness vapor film (Å)	particle density (g/mL)	Dispersion factor $f^*$	Volume solution (mL/g part.)	Volume SDS adsorbed (mL/g part.)	Volume vapor film (mL/g part.)
"4-7"	0	1.334	2.18	0.442	0.024	0
	5.6	1.265		0.365		0.077
		<b>density decrease (%)</b>		<b>volume decrease (%)</b>		
		<b>5.1</b>		<b>17.4</b>		

## References

- (1) Gritti, F.; Guiochon, G. *Journal of Chromatography A* **2007**, *1176*, 107.
- (2) Rustamov, I.; Farcas, T.; Ahmed, F.; Chan, F.; LoBrutto, R.; McNair, H. M.; Kazakevich, Y. V. *Journal of Chromatography A* **2001**, *913*, 49.
- (3) *CRC Handbook of Chemistry and Physics* 89th ed.; Lide, D. R., Ed., 2008-2009.
- (4) Tanford, C. *Journal of Physical Chemistry* **1972**, *76*, 3020.
- (5) Bruce, C. D.; Berkowitz, M. L.; Perera, L.; Forbes, M. D. E. *Journal of Physical Chemistry B* **2002**, *106*, 3788.
- (6) Helmy, R.; Kazakevich, Y.; Ni, C. Y.; Fadeev, A. Y. *Journal of the American Chemical Society* **2005**, *127*, 12446.