Supplementary Data

A model for monomer and micellar concentrations in surfactant solutions: Application to conductivity, NMR, diffusion and surface tension data

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Contents

ADDITIONAL FIGURES

References to figures, equations, and citations refer to the main paper.

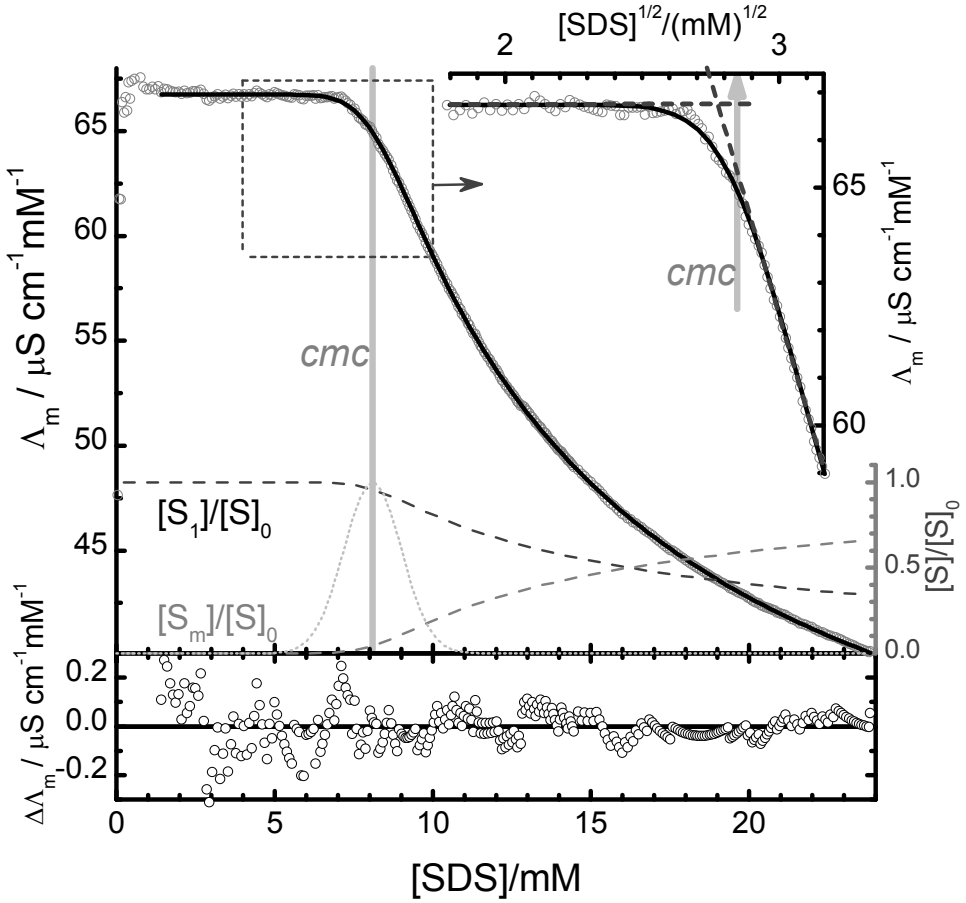

Figure SI1: Molar conductivity $\Lambda_m = (\kappa - \kappa_s)/[S]_0$ of SDS in pure water at 298K (calculated from the conductivities κ in Figure 2). Circles: experimental data. Black line: fit of eq (23) together with model (15) to the data. Dashed grey lines: concentration fractions $[S_1]/[S]_0$ and $[S_m]/[S]_0$ calculated from eqs (15) and (5). Dotted grey line: second derivative of $[S_1]$ (eq (7)). Inset: Plot of the same molar conductivity data vs. the square root of the concentration $[S]_0^{1/2}$ in the reduced interval $[S]_0$ =4-10 mM. Dashed black lines are limiting straight lines. Vertical grey lines: *cmc* as given by the fit. Lower panel: residuals of the fit.

FITTING FUNCTIONS

We provide ready to use fitting functions for Origin Data Analysis Software (OriginLab Corporation, Northampton, MA 01060, USA) as compressed zip-archive. Updated versions can be downloaded from the author's webpage.

The functions were tested with Origin 8.5 SR1.

For use in Origin the zip-archive should be decompressed in a temporal directory and the functions should be added from the *fitting function organizer* to the Origin Fitting functions. (Do not copy them directly to the Origin directory.) We propose to add them to a new category such as "APNModel".

All functions can be used for nonlinear fitting and for calculations in columns or other functions. For calculations the functions should be called as "`nlf_FunctionName(parameters)`", for example: "`nlf_APNModel_S1(cS0,cmc,r)`".

The functions also serve as examples for other data analysis packages. Therefore we describe briefly the main code of each of the functions.

Concentration Model

APNModel_S1

Concentration model (equations (14) and (15)) which is used by all other derived properties.
Takes $[S]_0$ and calculates the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width *r*.

$$A = \frac{2}{1+\sqrt{\frac{2}{\pi}}\, r\, e^{-\frac{1}{2r^2}} + \mathrm{erf}\left(\frac{1}{\sqrt{2}\, r}\right)}$$

$$[S_1] = cmc\left[1 - A\frac{1}{2}\left(\sqrt{\frac{2}{\pi}}\, r\, e^{-\frac{(s_0-1)^2}{2r^2}} + (s_0-1)\left(\mathrm{erf}\left(\frac{s_0-1}{\sqrt{2}r}\right)-1\right)\right)\right]$$

```
Function Name = APNModel_S1
Brief Description = APN Model: monomeric surfactant concentration - USC - Al-Soufi
2011
[Independent Variables]
cS0 =
[Dependent Variables]
cS1 =
[Fitting Parameters]
Names = cmc,r
Meanings = cmc,relative transition width
[Formula]
s0 = cS0/cmc;
A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));

cS1=cmc*(1 - (A/2)*( sqrt(2/Pi)*r*exp(-(s0-1)^2/(2*r*r))+(s0-1)*(erf((s0-
1)/(sqrt(2)*r))-1) ));
```

Derived Properties

APNModel_Conductivity

Conductivity of a surfactant solution.
Takes $[S]_0$ and calculates the conductivity κ as function of the cmc, the relative transition width r and the slopes a and b, and the solvent conductivity $c = \kappa_s$.

$$\kappa = a[S_1] + b'[S_m]/n + c = a[S_1] + b[S_m] + c$$

This function needs the function APNModel_S1.

The parameters `cmc,a,b,c` are actively initialized at the beginning of the fit, assuming that the data are sorted with respect to $[S]_0$ (ascending or descending).

```
Function Name = APNModel_Conductivity
Brief Description = APN Model: Electric conductivity - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k =
[Fitting Parameters]
Names = cmc,r,a,b,c
Meanings = cmc,relative transition width,a,b,c
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
k=a* cS1 +b * cSm + c;
```

APNModel_Conductivity_k1

Conductivity of a surfactant solution. Limiting Straight Line 1, below the *cmc*.
Utility Function: Takes $[S]_0$ and calculates the limiting straight line κ_1, below the cmc of the plot of the conductivity κ vs. $[S]_0$ with the parameters `cmc,r,a,b,c` determined with `APNModel_Conductivity`.

$$\kappa_1 = a[S]_0 + c$$

The parameters cmc, r y b are not needed, but included for consistency.

```
Function Name = APNModel_Conductivity_k1
Brief Description = APN Model: Electric conductivity Line 1- USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k1 =
[Fitting Parameters]
Names = cmc,r,a,b,c
Meanings = cmc,relative curvature,a,b,c
[Formula]
k1 = a* cS0 + c;
```

APNModel_Conductivity_k2

Conductivity of a surfactant solution. Limiting Straight Line 1, below the *cmc*.
Utility Function: Takes $[S]_0$ and calculates the limiting straight line κ_2, above the cmc of the plot of the conductivity κ vs. $[S]_0$ with the parameters `cmc,r,a,b,c` determined with `APNModel_Conductivity`.

$$\kappa_2 = a \cdot cmc + b \cdot ([S]_0 - cmc) + c$$

The parameter r is not needed, but included for consistency.

```
Function Name = APNModel_Conductivity_k2
Brief Description = APN Model: Electric conductivity Line 2- USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k2 =
[Fitting Parameters]
Names = cmc,r,a,b,c
Meanings = cmc,relative curvature,a,b,c
[Formula]
k2=a* cmc b*(cS0-cmc)+ c;
```

APNModel_MolarConductivity

Molar conductivity of a surfactant solution.
Takes $[S]_0$ and calculates the molar conductivity (equivalent conductance) as function of the *cmc*, the relative transition width *r* and the slopes a and *b*.

$$\Lambda_m = a[S_1]/[S]_0 + b[S_m]/[S]_0$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_MolarConductivity
Brief Description = APN Model: Electric molar conductivity - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
k =
[Fitting Parameters]
Names = cmc,r,a,b
Meanings = cmc,relative transition width,a,b
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
k=a* cS1/cS0 +b * cSm/cS0;
```

APNModel_SelfDiffusion

Self-diffusion coefficient of a surfactant solution.
Takes $[S]_0$ and calculates the self-diffusion coefficient D_{obs} as function of the *cmc*, the relative transition width *r* and the self-diffusion coefficients of monomeric (D_1) and micellized (D_m) surfactants.

$$D_{obs} = D_1 \cdot \frac{[S_1]}{[S]_0} + D_m \cdot \frac{[S_m]}{[S]_0}$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_SelfDiffusion
Brief Description = APN Model: Self Diffusion Coefficients - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
Dobs =
[Fitting Parameters]
Names = cmc,r,D1,Dm
Meanings = cmc,relative transition width,D1,Dm
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
Dobs = (D1* cS1+Dm *cSm)/cS0;
```

APNModel_NMRChemicalShifts

NMR Chemical Shifts of a surfactant solution.
Takes $[S]_0$ and calculates the NMR Chemical Shifts as function of the *cmc*, the relative transition width *r* and the chemical shifts of monomeric (d_1) and micellized (d_m) surfactants.

$$\delta_{obs} = \delta_1 \cdot \frac{[S_1]}{[S]_0} + \delta_m \cdot \frac{[S_m]}{[S]_0}$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_NMRChemicalShifts
Brief Description = APN Model: NMR Chemical Shifts - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
Dobs =
[Fitting Parameters]
Names = cmc,r,d1,dm
Meanings = cmc,relative transition width,d1,dm
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
cSm= cS0 - cS1;
dobs = (d1* cS1+dm *cSm)/(cS1+cSm);
```

APNModel_SurfaceTensionSzyszkowski

Surface Tension (Szyszkowski Equation) of a surfactant solution.

Takes $[S]_0$ and calculates the Surface Tension γ (g) using the Szyszkowski Equation as function of the *cmc*, the relative transition width *r* , the adsorption equilibrium constant K_{ad} , the surface tension of the solvent γ_0 (*g0*), and the constant $a = R \cdot T / \omega$, being ω the cross sectional area of the surfactant molecule at the surface per mol.

$$\gamma = \gamma_0 - a \ln(1 + K_{ad} \cdot [S_1])$$

This function needs the function APNModel_S1.

```
Function Name = APNModel_SurfaceTensionSzyszkowski
Brief Description = APN Model: Surface Tension (Szyszkowski Equation) - USC - Al-
Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
g =
[Fitting Parameters]
Names = cmc,r,a,Kad,g0
Meanings = cmc,relative transition width,(R T)/omega,adsorption equlibrium
constant,g0
[Formula]
cS1= nlf_APNModel_S1(cS0,cmc,r);
g=g0 - a* ln(1+ Kad*cS1);
```

Utility functions

APNModel_d2S1

First derivative of the monomeric surfactant concentration (equation (10)).
Takes $[S]_0$ and calculates the first derivative $[S_1]'$ (gradient) of the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width *r*.

$$A = \frac{2}{1+\sqrt{\frac{2}{\pi}}\, r\, e^{-\frac{1}{2r^2}} + \mathrm{erf}\left(\frac{1}{\sqrt{2}\, r}\right)} \qquad [S_1]' = \frac{d[S_1]}{d[S]_0} = \frac{A}{2}\left(1 - \mathrm{erf}\left(\frac{s_0 - 1}{\sqrt{2}r}\right)\right)$$

```
Function Name = APNModel_d2S1
Brief Description = APN Model: first derivative of monomeric surfactant
concentration - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
d1S1 =
[Fitting Parameters]
Names = cmc,r
Meanings = cmc,relative transition width
[Formula]
s0 = cS0/cmc;
A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));
d1S1=(A/2)*(1-erf((s0-1)/(Sqrt(2)*r)));
```

APNModel_d2S1

Second derivative of the monomeric surfactant concentration (equation (7)).
Takes $[S]_0$ and calculates the second derivative $[S_1]''$ (curvature) of the monomeric concentration $[S_1]$ as function of the *cmc* and the relative transition width *r*.

$$A = \frac{2}{1+\sqrt{\frac{2}{\pi}}\, r\, e^{-\frac{1}{2r^2}} + \mathrm{erf}\left(\frac{1}{\sqrt{2}\, r}\right)} \qquad [S_1]'' = \frac{d^2[S_1]}{ds_0^2} = -\frac{A}{cmc}\frac{1}{\sqrt{2\pi}r} e^{-\frac{(s_0-1)^2}{2r^2}}$$

```
Function Name = APNModel_d2S1
Brief Description = APN Model: second derivative of monomeric surfactant
concentration - USC - Al-Soufi 2011
[Independent Variables]
cS0 =
[Dependent Variables]
d2S1 =
[Fitting Parameters]
Names = cmc,r
Meanings = cmc,relative transition width
[Formula]
s0 = cS0/cmc;
A=2/(1+sqrt(2/Pi)*r*exp(-1/(2*r*r))+erf(1/Sqrt(2)/r));
d2S1=-(A/(cmc*sqrt(2*Pi)*r))*exp(-(s0-1)^2/(2*r*r));
```