Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information of

The Impact of Nonionic Surfactant Additives on the Nonequilibrium Association between Oppositely Charged Polyelectrolytes and Ionic Surfactants

Edit Fegyver and Róbert Mészáros*

Laboratory of Interfaces and Nanosized Systems, Institute of Chemistry, Eötvös Loránd University, 1117 Budapest, Pázmány Péter sétány 1/A, Hungary

The Supplementary Information contains additional experimental details, graphs and tables as discussed in the manuscript text.

Table S1. The critical micelle concentration of SDS, $C_{12}G_2$ and $C_{12}E_6$ as well as of SDS/$C_{12}G_2$ and SDS/$C_{12}E_6$ mixtures determined from different techniques.

	cmc_{SDS} (± 0.1 mM)	$cmc_{\mathrm{C_{12}G_2}}$ (± 0.02 mM)	$cmc_{\mathrm{C_{12}E_6}}$ (± 0.02 mM)	$cmc^{0.8}_{\mathrm{SDS,C12G2}}$ (± 0.05 mM)	$cmc^{0.9}_{\mathrm{SDS,C12E6}}$ (± 0.05 mM)
Surface tension	8.0[a]	0.15[a]	0.07[a]	0.45[b]	0.40[c]
Fluorescence spectroscopy[d]	7.8	0.16	0.07	0.50	0.43

[a] from our surface tension measurements

[b] from ref. 34 of the manuscript

[c] from ref. 33 of the manuscript

[d] based on Figure 1

In Table S1 $cmc^{0.8}_{\mathrm{SDS,C12G2}}$ and $cmc^{0.9}_{\mathrm{SDS,C12E6}}$ designate the sum of the critical concentrations of SDS and $C_{12}G_2$ ($cmc^{0.8}_{\mathrm{SDS,C12G2}} = cmc^{0.8}_{\mathrm{mix,SDS}} + cmc^{0.8}_{\mathrm{mix,C12G2}}$) as well as SDS and $C_{12}E_6$ ($cmc^{0.9}_{\mathrm{SDS,C12E6}} = cmc^{0.9}_{\mathrm{mix,SDS}} + cmc^{0.9}_{\mathrm{mix,C12E6}}$) belonging to the onset of mixed micelle formation where $\frac{cmc^{0.8}_{\mathrm{mix,SDS}}}{cmc^{0.8}_{\mathrm{SDS,C12G2}}} = 0.8$ and $\frac{cmc^{0.9}_{\mathrm{mix,SDS}}}{cmc^{0.9}_{\mathrm{SDS,C12E6}}} = 0.9$, respectively. The mixed *cmc* values were determined from the break point of the surface tension isotherms of SDS/$C_{12}E_6$ (ref. 33) and SDS/$C_{12}G_2$ (ref. 34) mixtures in which the SDS-to-nonionic surfactant ratio was fixed at ($c_{\mathrm{SDS}}/(c_{\mathrm{SDS}} + c_{\mathrm{C12E6}})$)=0.9 and ($c_{\mathrm{SDS}}/(c_{\mathrm{SDS}} + c_{\mathrm{C12G2}})$)=0.8, respectively. On the other hand, $cmc^{0.8}_{\mathrm{SDS,C12G2}}$ and $cmc^{0.9}_{\mathrm{SDS,C12E6}}$ can also be derived on the basis of Figure 1b, from the critical SDS concentrations belonging to the onset of the decreasing I_1/I_3 ratio at 0.10 mM $C_{12}G_2$ (0.4 mM SDS) and 0.04 mM $C_{12}E_6$ concentration (0.39 mM SDS).

Conductivity Measurements

The electrical conductivity (G) of SDS solutions and nonionic surfactant/SDS mixtures (at constant concentration of the nonionic amphiphiles) was measured at 25.0 ± 0.1°C by making use of a Radelkis conductometer. The conductivity values measured at a given composition immediately and 24 hours after the solution preparation were found to be identical within the experimental error.

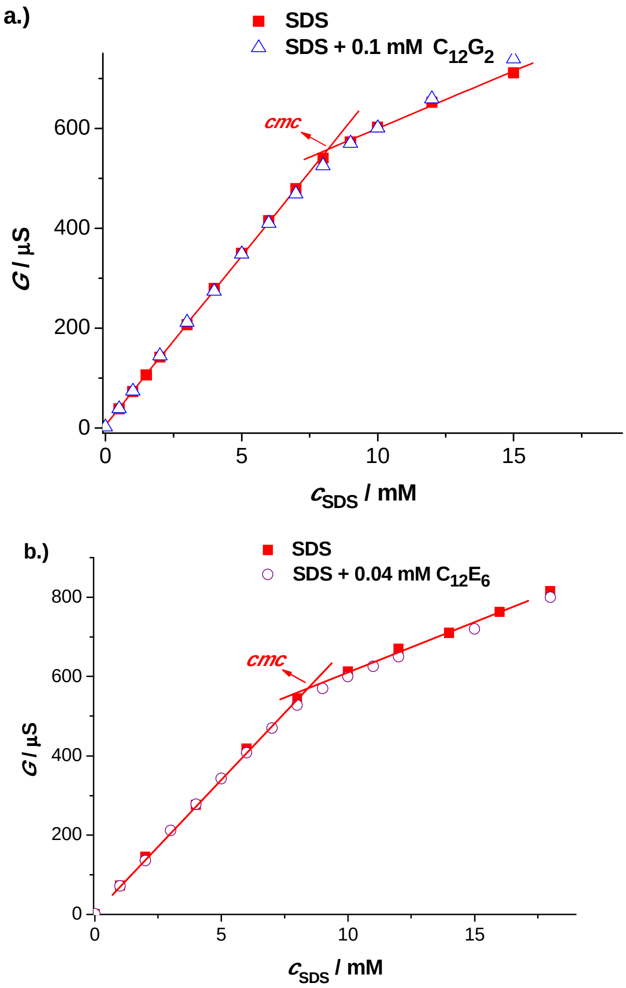

Figure S1. The electrical conductivity (G) as a function of the analytical concentration of SDS in the absence of the nonionic surfactant (red ■) as well as a.) in the presence of 0.10 mM $C_{12}G_2$ (blue △) and b.) 0.04 mM $C_{12}E_6$ (purple ○). The size of the symbols is commensurable with the standard error of the measurements.

According to Figure S1, the measured electrical conductivity values of the SDS solutions and that of the SDS/nonionic surfactant mixtures are indistinguishable within the experimental error in the investigated concentration range of the surfactants.

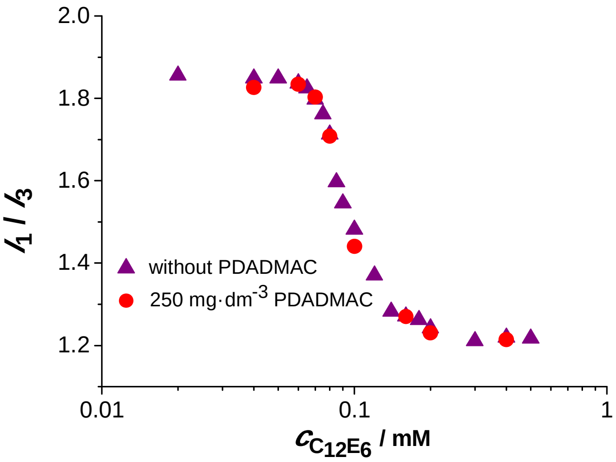

Figure S2. Fluorescence intensity ratio (I_1/I_3) against the $C_{12}E_6$ concentration without polyelectrolyte (purple ▲) and in the presence of 250 mg·dm^{-3} PDADMAC (red ●). The size of the symbols is commensurable with the standard error of the measurements.

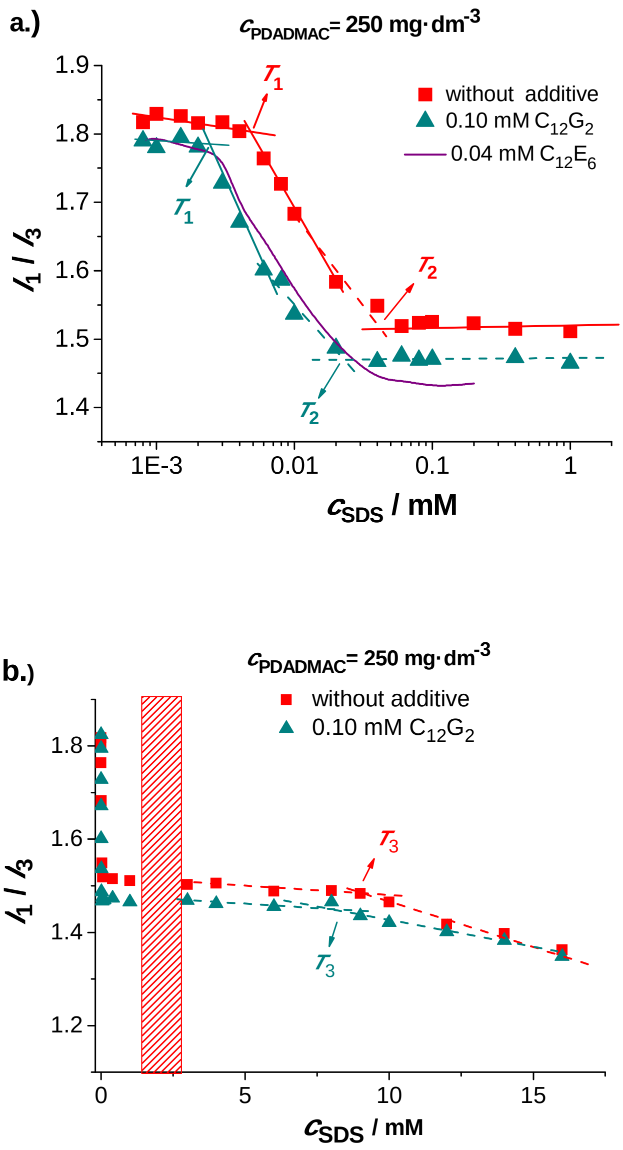

Figure S3. Fluorescence intensity ratio (I_1/I_3) as a function of analytical SDS concentration at 250 mg·dm^{-3} PDADMAC concentration in the absence and presence of nonionic surfactants a.) at low SDS concentrations and b.) in the whole investigated SDS concentration range; without additive (red ■), 0.10 mM $C_{12}G_2$ (turquoise ▲) and 0.04 mM $C_{12}E_6$ (purple –). The mixtures were prepared *via* the stopped-flow mixing protocol. The red striped area denotes the precipitation concentration range in the absence of nonionic additives. For the sake of clarity, not all the data of Figure S3a are replotted in Figure S3b. The size of the symbols is commensurable with the standard error of the fluorescence intensity ratio measurements.

Table S2. Polydispersity indices (P_D) of PDADMAC/SDS/$C_{12}G_2$ systems at 250 mg·dm^{-3} PDADMAC concentration.

SDS concentration (mM)	$C_{12}G_2$ concentration (mM)	P_D
0	0	0.39
1	0	0.35
3	0	0.19
4	0	0.19
5	0	0.17
7	0	0.19
SDS concentration (mM)	$C_{12}G_2$ concentration (mM)	P_D
0	0.30	0.37
1	0.30	0.34
3	0.30	0.18
4	0.30	0.20
5	0.30	0.19
7	0.30	0.20
SDS concentration (mM)	$C_{12}G_2$ concentration (mM)	P_D
0	0.60	0.38
1	0.60	0.34
3	0.60	0.16
4	0.60	0.17
5	0.60	0.18
7	0.60	0.19
SDS concentration (mM)	$C_{12}G_2$ concentration (mM)	P_D
0	0.80	0.35
1	0.80	0.31
3	0.80	0.19
4	0.80	0.20

5	0.80	0.19
7	0.80	0.20

The apparent diffusion coefficient (D_{app}) of the polyelectrolyte/surfactant complexes in the presence and absence of nonionic surfactants was derived from the first cumulant, $\overline{\Gamma}(q)$

$$D_{app}(q) = \frac{\overline{\Gamma}(q)}{q^2} \tag{1}$$

where q is the scattering vector ($q = (4\pi n/\lambda_o)\cdot\sin(\theta/2)$, n is the refractive index of the solution, and λ_o is the wavelength of the incident light). The apparent mean hydrodynamic diameter (d_H) of the complexes was calculated from D_{app} based on the Einstein-Stokes relation:

$$D_{app} = \frac{k_\mathrm{B}T}{3\pi\eta d_\mathrm{H}} \tag{2}$$

where k_B is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the medium. The polydispersity index (P_D) was determined from the second cumulant (Γ_2) according to the following formula:

$$P_D = \frac{\sqrt{\left\langle D_\mathrm{app}{}^2\right\rangle - \left\langle D_\mathrm{app}\right\rangle^2}}{\left\langle D_\mathrm{app}\right\rangle} = \sqrt{\frac{\Gamma_2}{\overline{\Gamma}^2}} \tag{3}$$

where $\left\langle D_\mathrm{app}\right\rangle$ and $\left\langle D_\mathrm{app}{}^2\right\rangle$ denote the expected values of the apparent diffusion coefficient and its square, respectively.

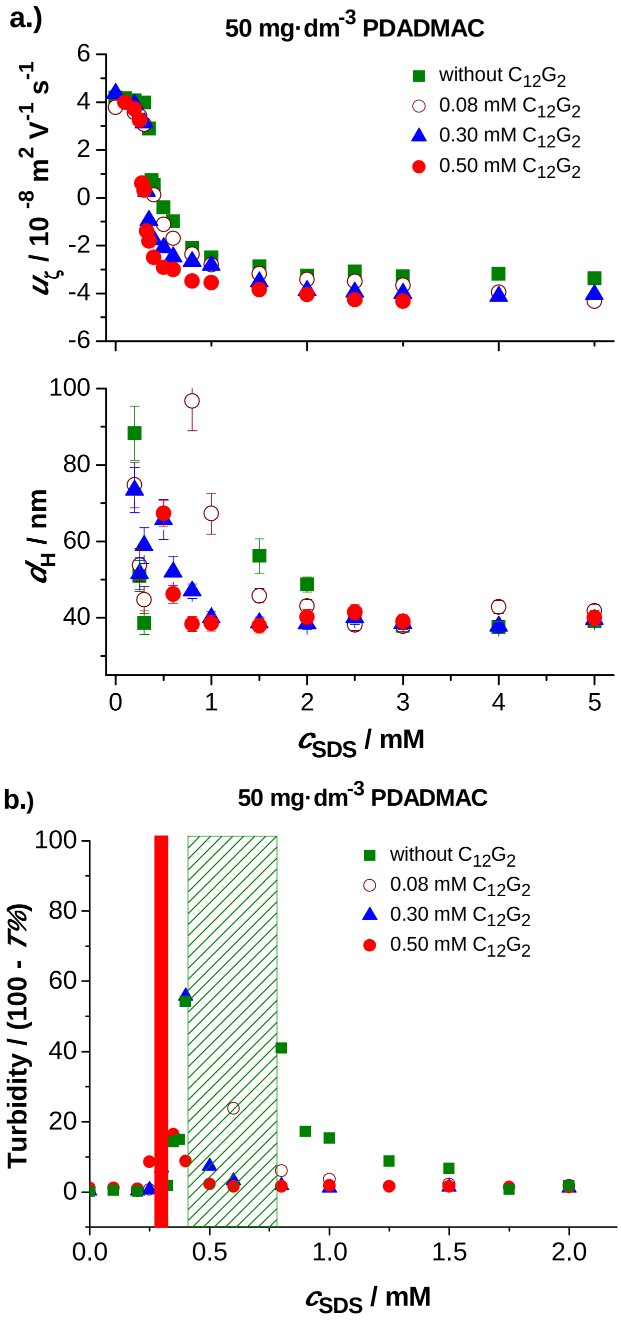

Figure S4. a.) Mean electrophoretic mobility (u_ζ) and apparent mean hydrodynamic diameter (d_H) of the complexes of PDADMAC, SDS and $C_{12}G_2$, b.) turbidity (100-*T*%) of the systems against the analytical SDS concentration at 50 mg·dm^{-3} PDADMAC concentration. The mixtures were prepared *via* the stopped-flow mixing protocol. The different symbols denote various fixed concentrations of the sugar surfactant: 0 mM (green ■), 0.08 mM (brown ○), 0.30 mM (blue ▲) and 0.50 mM (red ●) $C_{12}G_2$. The red area as well as the green striped area indicates the precipitation composition range at c_{C12G2} = 0.50 mM and in the absence of dodecyl maltoside, respectively. The size of the symbols is commensurable with the standard error of the measurements except for the DLS data, where the estimated standard deviation of the d_H values is denoted by error bars.

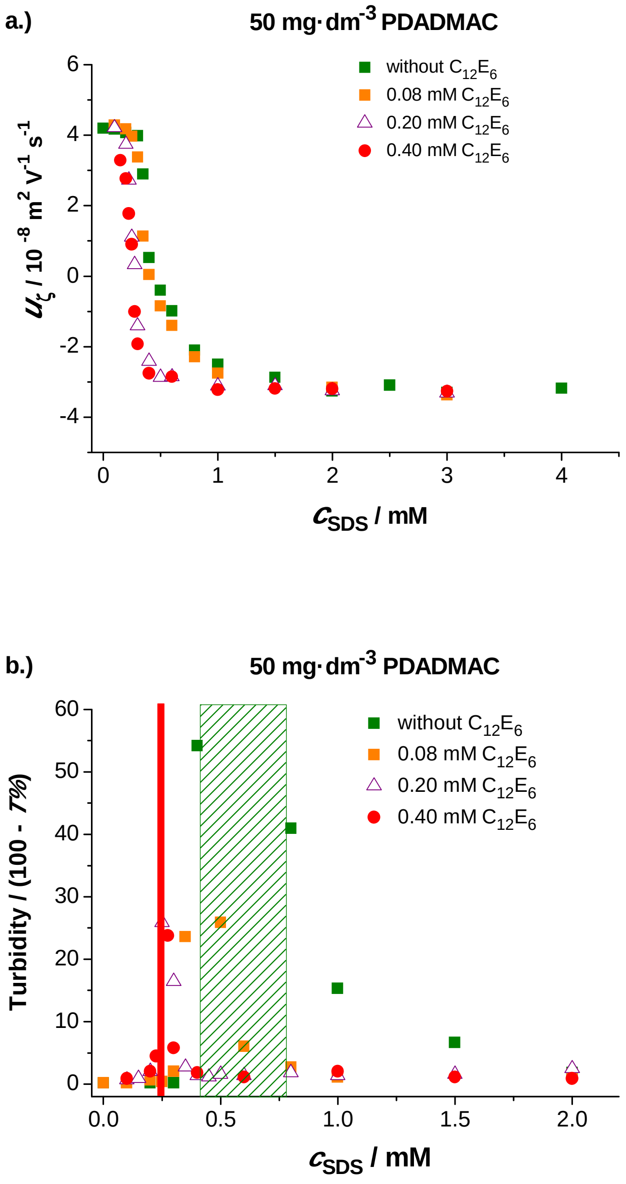

Figure S5. a.) Mean electrophoretic mobility (u_ζ) of the complexes of PDADMAC, SDS and $C_{12}E_6$, b.) turbidity (100-*T*%) of the systems against the analytical SDS concentration at 50 mg·dm^{-3} PDADMAC concentration. The mixtures were prepared *via* the stopped-flow mixing protocol. The different symbols denote various fixed concentrations of the nonionic surfactant: 0 mM (green ■), 0.08 mM (orange ■), 0.20 mM (purple △), and 0.40 mM (red ●) $C_{12}E_6$. The red area as well as the green striped area indicates the precipitation composition range at c_{C12E6} = 0.40 mM and in the absence of $C_{12}E_6$, respectively. The size of the symbols is commensurable with the standard error of the measurements.

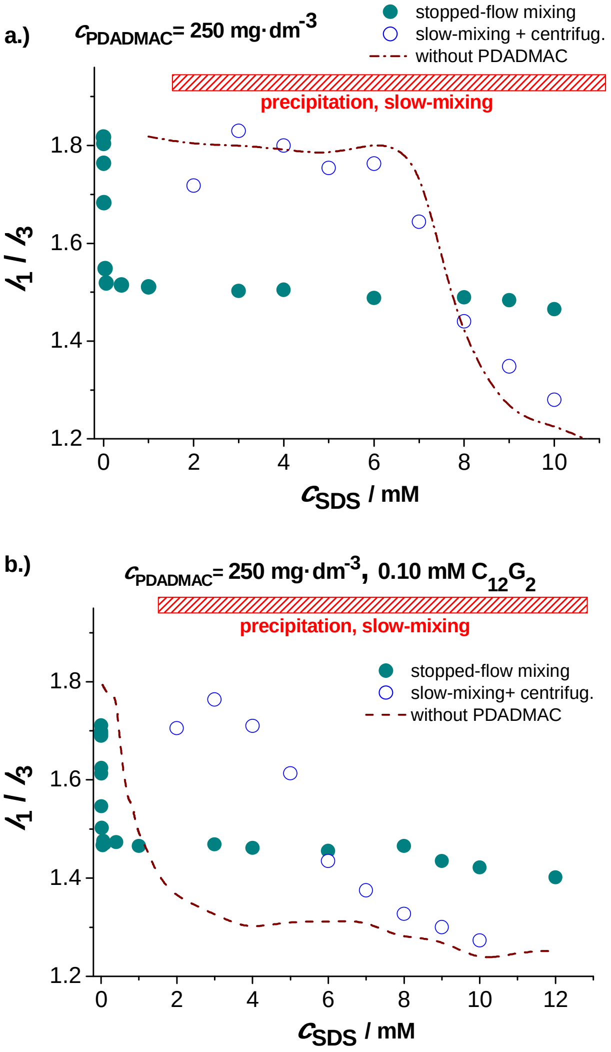

Figure S6. Fluorescence intensity ratio (I_1/I_3) against the analytical SDS concentration at 250 mg·dm^{-3} PDADMAC concentration a.) in the absence and b.) in the presence of $C_{12}G_2$ (0.10 mM). Two types of preparation protocols were used: stopped-flow mixing (turquoise ●) – the pyrene was solubilized in the mixtures after their preparation; slow-mixing and centrifugation (blue ○) – the pyrene probe was added to the supernatant phase after centrifugation. The red striped area belongs to the precipitation concentration range of the mixtures made by slow-mixing. The I_1/I_3 ratio was also measured for SDS/$C_{12}G_2$ mixtures at c_{C12G2} = 0.10 mM in the absence of PDADMAC (---). The size of the symbols is commensurable with the standard error of the I_1/I_3 ratio determination.