

## Supporting Information

Complexation Between Sodium Poly(styrene sulfonate) and Alkyltrimethylammonium  
Bromides in the Presence of Dodecyl Maltoside

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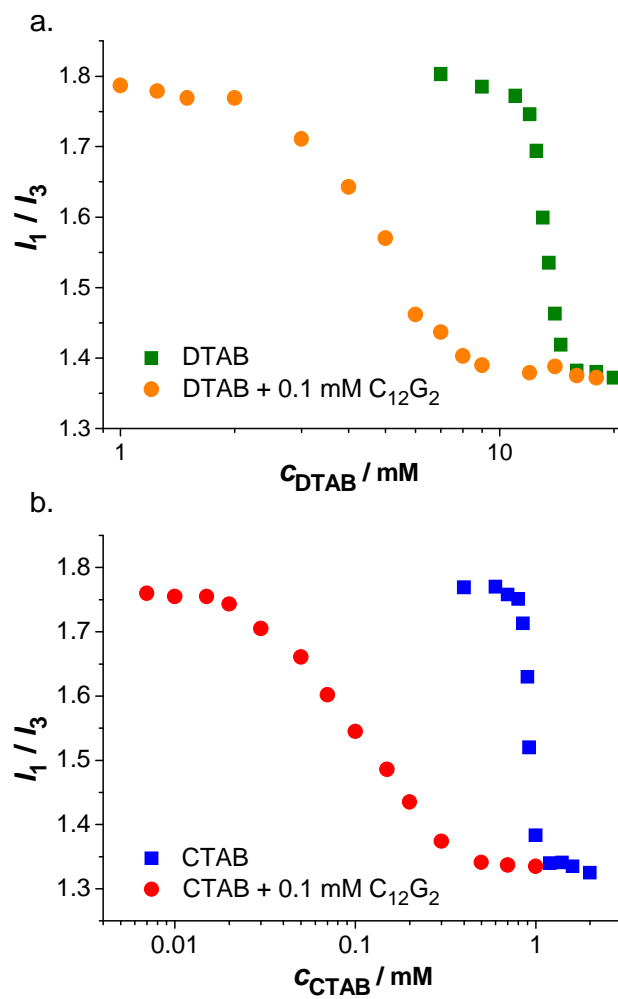
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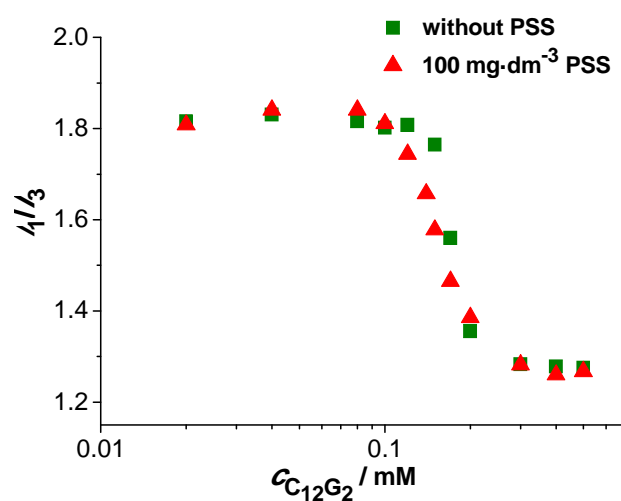
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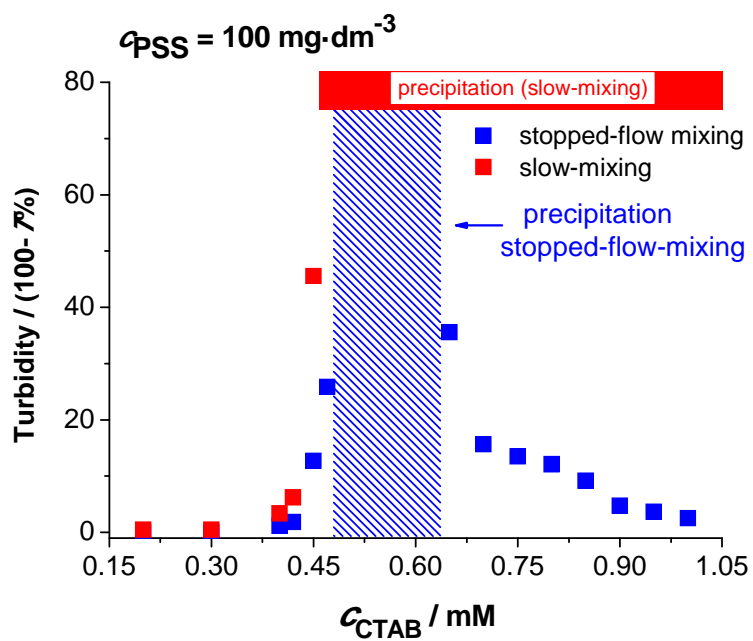
This document contains additional experimental details and graphs as discussed in the manuscript text.



**Figure S1.** Fluorescent  $I_1/I_3$  ratio against a) the DTAB concentration without (green ■) and with 0.1 mM  $\text{C}_{12}\text{G}_2$  (orange ●), b) the CTAB concentration in the absence (blue ■) and presence of 0.1 mM  $\text{C}_{12}\text{G}_2$  (red ●). The mixtures were prepared by the stopped-flow mixing protocols.



**Figure S2.** Fluorescence  $I_1/I_3$  ratio versus the  $C_{12}G_2$  concentration without (green ■) and with  $100 \text{ mg} \cdot \text{dm}^{-3}$  PSS (red ▲). The mixtures were prepared by the stopped-flow mixing protocols.



**Figure S3.** Turbidity of the PSS/CTAB systems against the CTAB concentration at constant  $100 \text{ mg} \cdot \text{dm}^{-3}$  PSS obtained via application of the stopped-flow mixing (blue ■) and slow-mixing (red ■) protocols.

### Slow-mixing



**Immediately** after mixing



**1 week** after mixing

### Stopped-flow mixing



**Immediately** after mixing



**1 week** after mixing

**Figure S4.** Photos of PSS/CTAB/C<sub>12</sub>G<sub>2</sub> mixtures taken immediately and 1 week after mixing. The mixtures were prepared by slow-mixing (top row) and stopped-flow mixing (bottom row). The systems contain 100 mg·dm<sup>-3</sup> PSS and 0.3 mM C<sub>12</sub>G<sub>2</sub>, the CTAB concentration varies from left to right as follows: 0.6, 0.8, 1.0, 1.2 mM. The visual appearance and the turbidity of the mixtures prepared by stopped-flow mixing have not been changed for months.

### Binding isotherm measurements

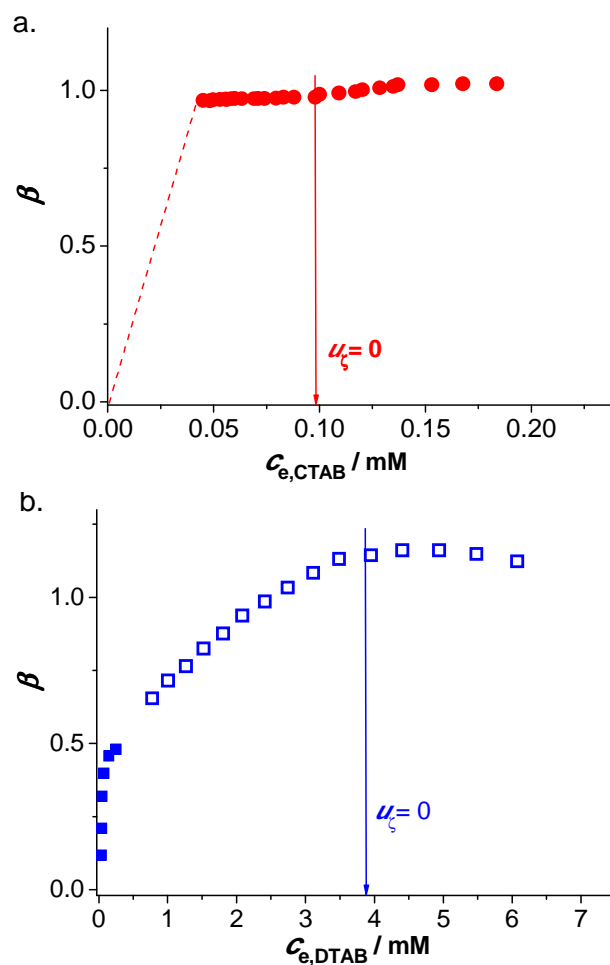
The binding isotherms of DTAB and CTAB on PSS were determined by means of a novel method using electrophoretic mobility measurements. The method is based on the simple assumption that if the electrophoretic mobility is measured at two different polyelectrolyte concentrations ( $c_{p,1}$  and  $c_{p,2}$ ), then the mobility values ( $u_{\zeta}$ ) will be equal at the same amount of bound surfactant but at two different total surfactant concentration values ( $c_{s,1}$  and  $c_{s,2}$ ):

$$\left(u_{\zeta}\right)_{c_{p,1}}^{c_{s,1}} = \left(u_{\zeta}\right)_{c_{p,2}}^{c_{s,2}} \quad (1)$$

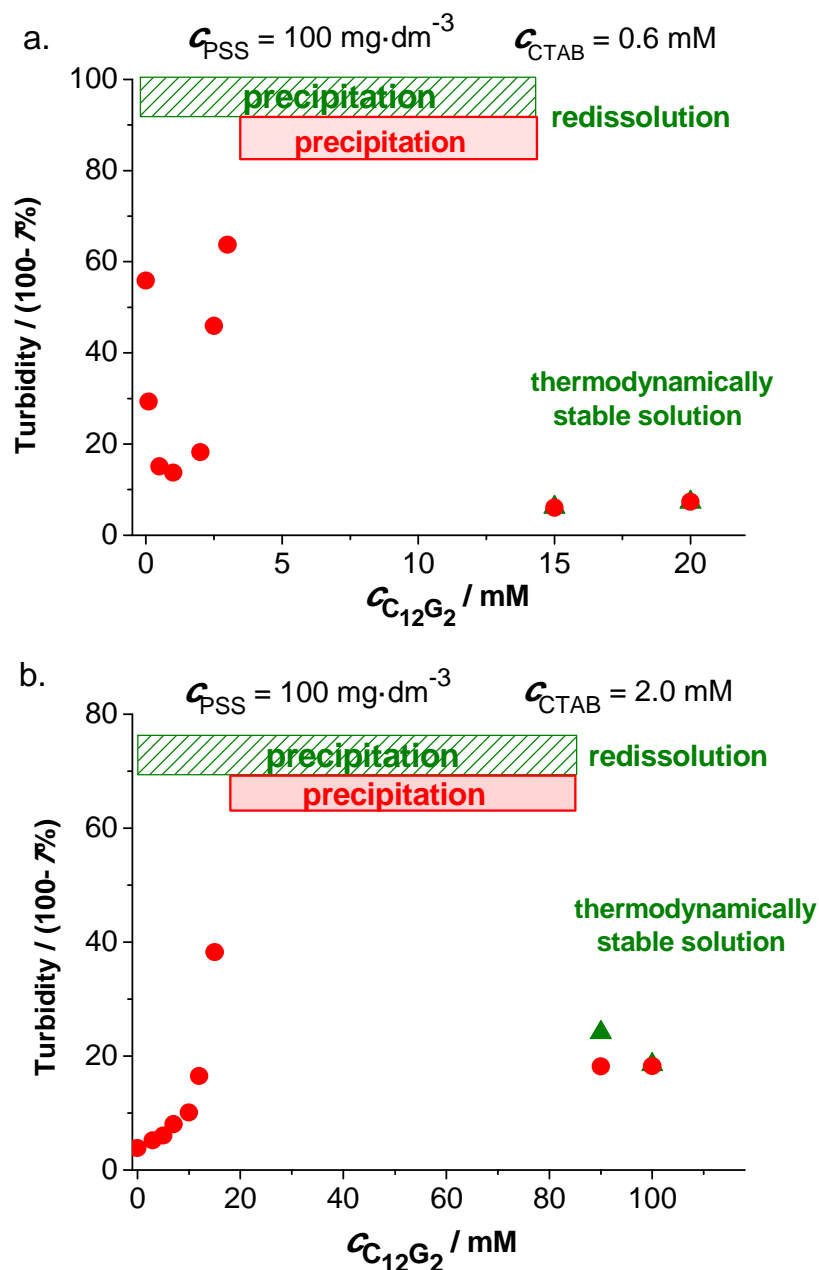
Therefore, the bound amount of surfactant ( $B$ ) can be determined from the following equations:

$$B = \frac{c_{s,1} - c_{e,s}}{c_{p,1}} = \frac{c_{s,2} - c_{e,s}}{c_{p,2}} \quad (2)$$

where  $c_{e,s}$  is the equilibrium concentration of the free surfactant molecules in a polymer-free reference system. Practically  $c_{p,1} = 0.01$  wt% and  $c_{p,2} = 0.05$  wt% PSS concentrations were used. (Further details about the theoretical assumptions and the limitations of this method can be found in ref. 42 of the manuscript.)



**Figure S5.** a) The bound amount of CTAB (normalized to the amount of PSS monomers,  $\beta$ ) as a function of the equilibrium concentration of the free surfactant molecules ( $c_{e,CTAB}$ ) determined by the electrophoretic method (ref. 42 of the MS) (red ●). b) The bound amount of DTAB (normalized to the amount of PSS monomers,  $\beta$ ) as a function of the equilibrium concentration of the free surfactant molecules ( $c_{e,DTAB}$ ) determined by the electrophoretic method (ref. 42 of the MS) (blue □). The data at low DTAB concentrations were taken from ref. 19 of the manuscript (the potentiometric method by Almgren et al., blue ■).



**Figure S6.** Turbidity (100- $T\%$ ) of the systems made by slow-mixing (green ▲) against the concentration of dodecyl maltoside at  $c_{PSS} = 100 \text{ mg}\cdot\text{dm}^{-3}$  and at a) 0.6 mM and b) 2.0 mM CTAB. The turbidity data of the stopped-flow mixed systems (red ●) are replotted from Fig. 7 of the manuscript. The red and green striped boxes indicate the concentration range of precipitated systems for stopped-flow mixing and slow-mixing, respectively.