Supporting Information of

Fine-Tuning the Nonequilibrium Behavior of Oppositely Charged

**Macromolecule/Surfactant Mixtures via the Addition of Nonionic Amphiphiles**

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*

* Phone: +36-1-372-2500/1906 , e-mail: meszaros@chem.elte.hu

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

Part I: Additional graphs in the absence of added electrolyte
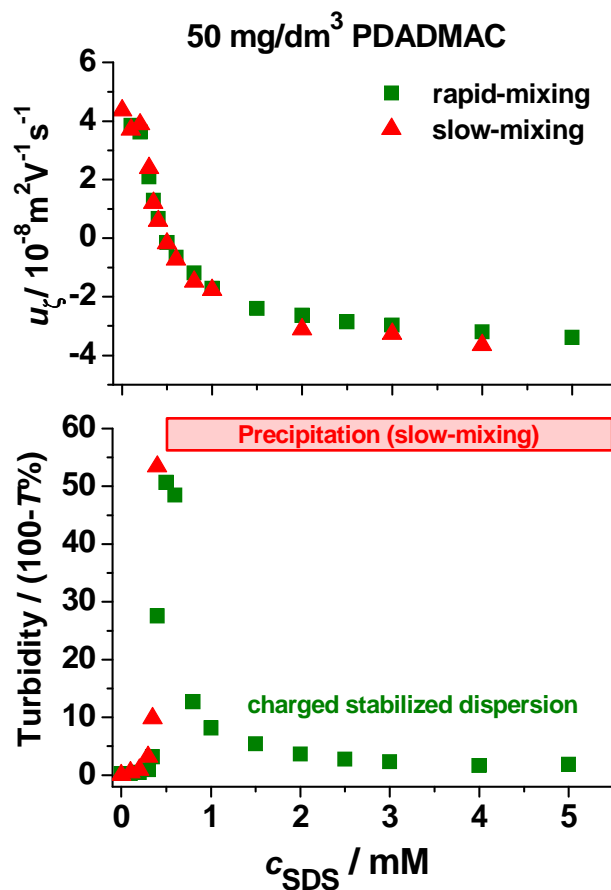
Figure S1. Mean electrophoretic mobility (u_ζ) of the PDADMAC/SDS complexes and the turbidity (100-T%) of the systems as a function of SDS concentration at $c_{PDADMAC}$=50 mg·dm^{-3}, via application of rapid- (■) and slow-mixing (▲). The red box indicates the precipitated composition range for slow-mixing. For the sake of clarity, the very narrow precipitation concentration range, observed for rapid-mixing, is not shown in Figure S1.
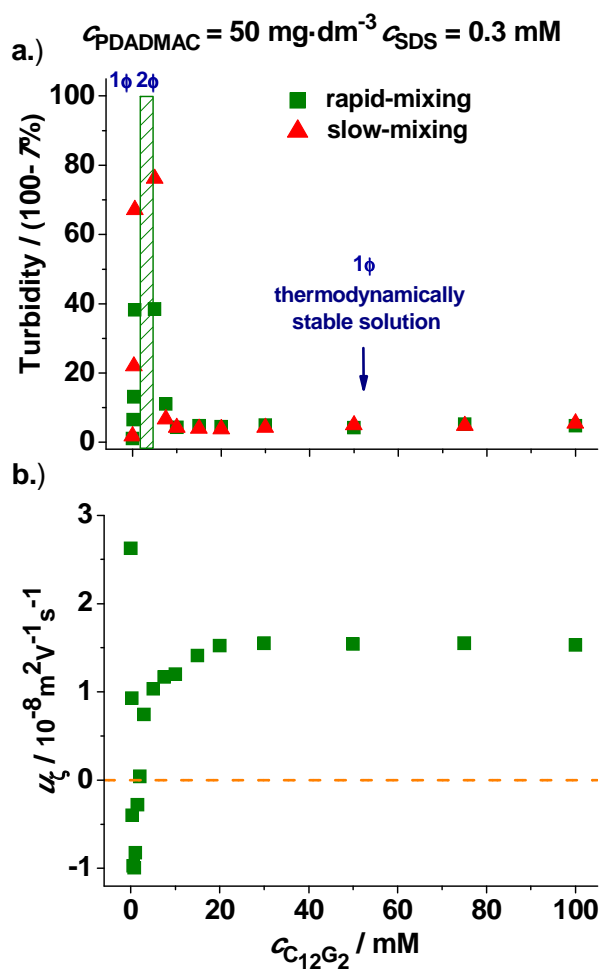
Figure S2. a.) Turbidity (100-T%) of the systems measured immediately after rapid- (■) as well as slow-mixing (▲); b.) mean electrophoretic mobility (u_ζ) (■) of the PDADMAC/mixed surfactant complexes measured immediately after rapid-mixing as a function of the $C_{12}G_2$ concentration. $c_{PDADMAC} = 50$ mg·dm^{-3} and $c_{SDS} = 0.3$ mM. The precipitated concentration range for rapid-mixing is denoted by the green striped area in Figure S2a. For the sake of clarity, the mobility data and the precipitation concentration range measured for slow-mixing are not shown in Figure S2 since they are nearly the same within the experimental error as in the case of rapid-mixing.

Illustration of the applied mixing procedures of PDADMAC/SDS/$C_{12}G_2$ systems

Rapid- or slow-mixing *Two-step-(rapid)-mixing I.* *Two-step-(rapid)-mixing II.*

Comp.1: **500 mg/dm^3 PDADMAC+ 5 mM $C_{12}G_2$**
Comp.2: **14 mM SDS + 5 mM $C_{12}G_2$**

Comp.1: **1000 mg/dm^3 PDADMAC**
Comp 2: **28 mM SDS**

Comp.1: **1000 mg/dm^3 PDADMAC**
Comp.2: **20 mM $C_{12}G_2$**

step 1.   *Rapid-mixing* of equal volumes of *Comp.1* & *Comp.2*

step 1.   *Rapid-mixing* of equal volumes of *Comp 1* & *Comp.2*

Rapid- or slow-mixing of equal volumes of *Comp.1* & *Comp.2*

500 mg/dm^3 PDADMAC, 14 mM SDS

500 mg/dm^3 PDADMAC, 10 mM $C_{12}G_2$

step 2.   addition of 10 mM $C_{12}G_2$ in equal volume

step 2.   addition of 14 mM SDS in equal volume
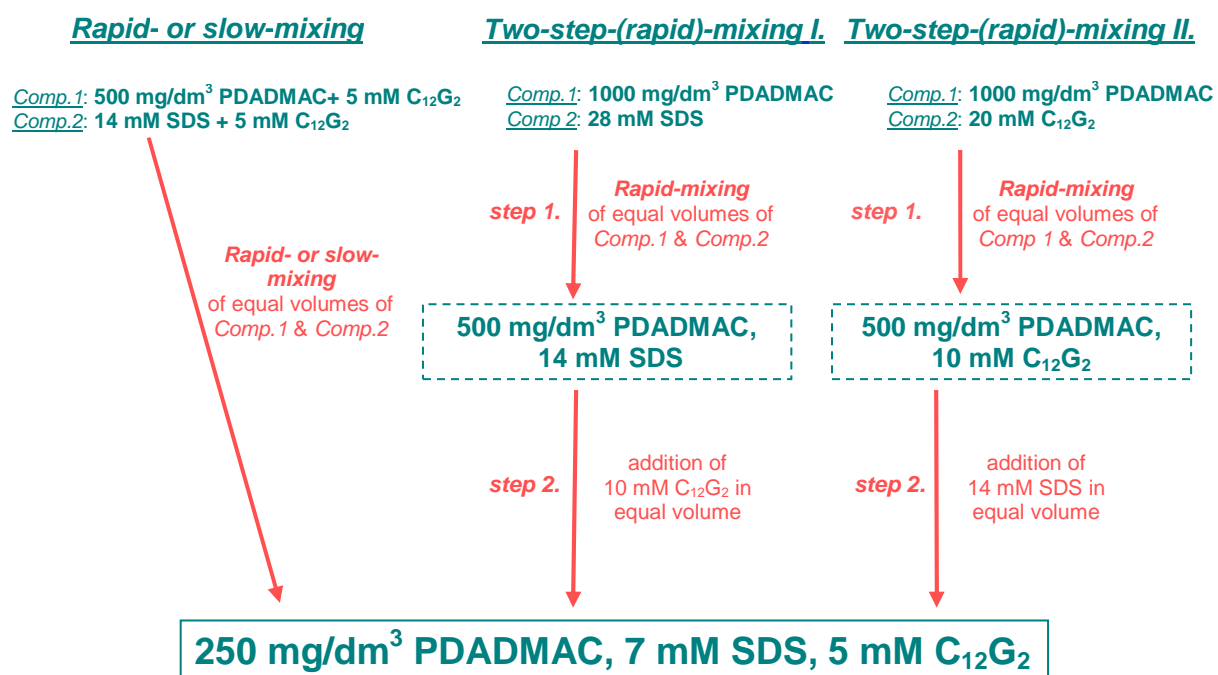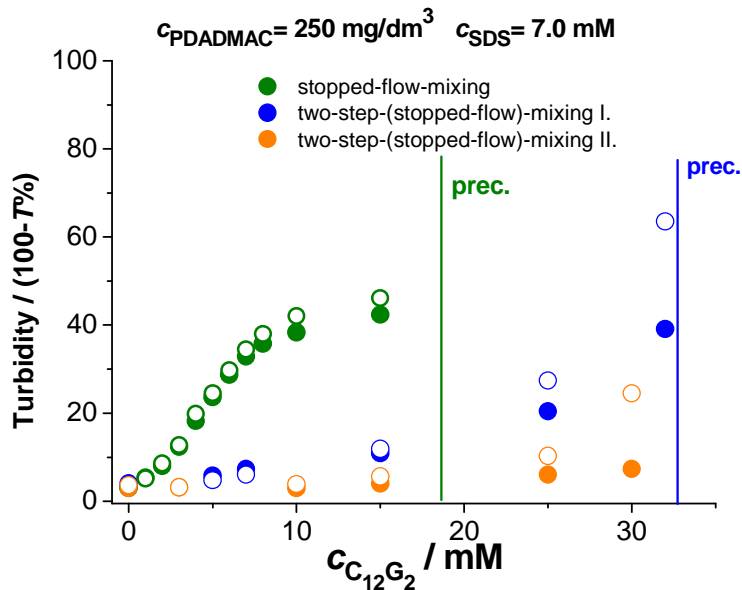
**250 mg/dm^3 PDADMAC, 7 mM SDS, 5 mM $C_{12}G_2$**

Figure S3.

Figure S4. Turbidity (100-T%) of the PDADMAC/mixed surfactant systems against the $C_{12}G_2$ concentration at $c_{PDADMAC} = 250$ mg·dm^{-3} and $c_{SDS} = 7.0$ mM. The systems were prepared by three different mixing methods: stopped-flow-mixing (●,○), two-step-(stopped-flow)-mixing I. (step1. PDADMAC/SDS mixture via stopped-flow-mixing, step2. + $C_{12}G_2$ stopped-flow-mixing) (●,○) and two-step-(stopped-flow)-mixing II. (step1. PDADMAC/$C_{12}G_2$ mixture via stopped-flow-mixing, step2. + SDS stopped-flow mixing) (●,○). The solid and open symbols designate the turbidity data measured immediately as well as 24 hours after the solution preparation is completed, respectively. The green and blue vertical lines indicate the appearance of precipitation during the timescale of the experiments for the stopped-flow-mixing and two-step-mixing-I. protocols, respectively. In the case of the two-step-mixing II. protocol the onset of phase separation is very close to that of the two-step-mixing I. procedure.

In the case of Figure S4 the PDADMAC/SDS/$C_{12}G_2$ mixtures were prepared by the stopped-flow mixing procedure in which equal volumes of SDS/$C_{12}G_2$ and PDADMAC/$C_{12}G_2$ solutions, with the same dodecyl maltoside concentration but at double the intended final concentrations of the polyelectrolyte and that of SDS, were mixed by means of the stopped-flow mixing apparatus of Applied Photophysics (Model RX 1000, see refs 24, 35, 38-39, 44 of the manuscript). In addition, the systems were also made by the two-step-(stopped-flow)-mixing I. and II. protocols which are analogous to the two-step-(rapid)-mixing I. and II. protocols, presented in Figure 5 of the manuscript, with the only exception that instead of rapid-mixing the ultrafast stopped-flow mixing procedure was applied throughout the experimental paths.

Part II: Additional graphs in 0.3 M NaCl
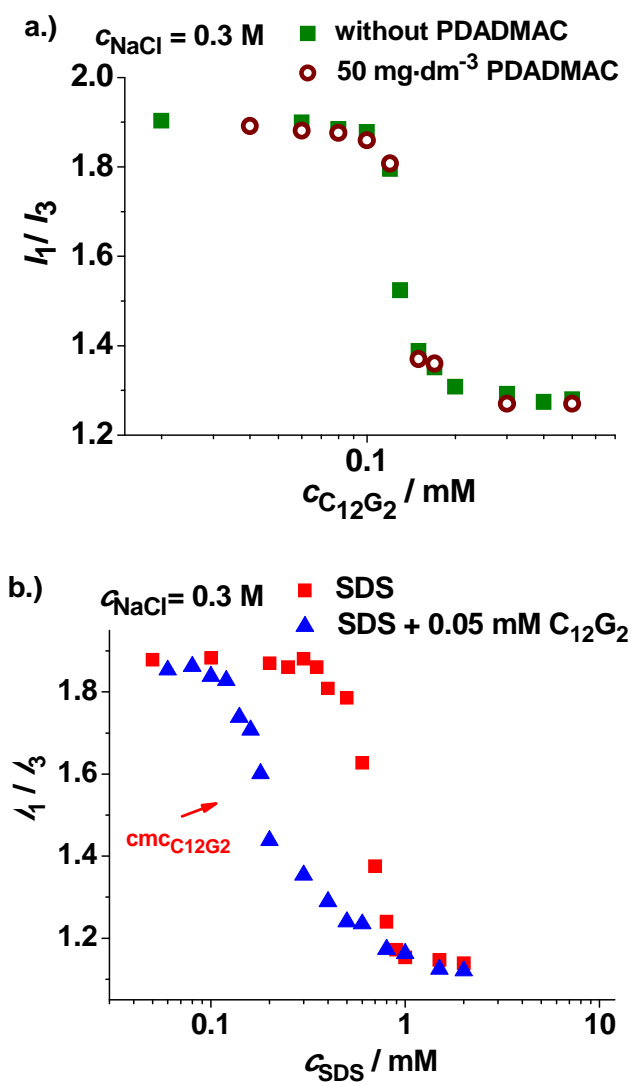
Figure S5. Fluorescence I_1/I_3 intensity ratio a.) as a function of nonionic surfactant concentration (for pure $C_{12}G_2$ (■) and for PDADMAC/$C_{12}G_2$ solutions ($c_{PDADMAC}$ = 50 mg·dm^{-3}) (O) b.) as a function of SDS concentration for pure SDS solutions (■) as well as in the case of SDS/$C_{12}G_2$ mixtures (▲) at constant 0.05 mM concentration of the sugar surfactant. All solutions were prepared in the presence of 0.3 M NaCl.
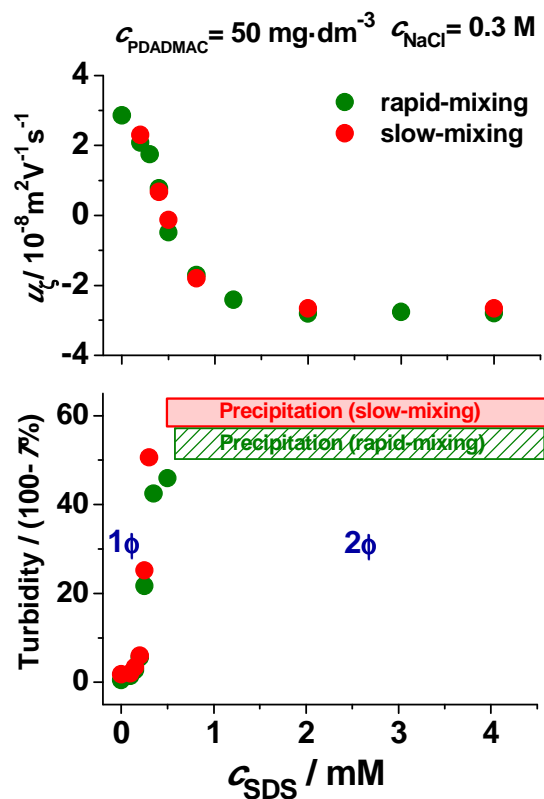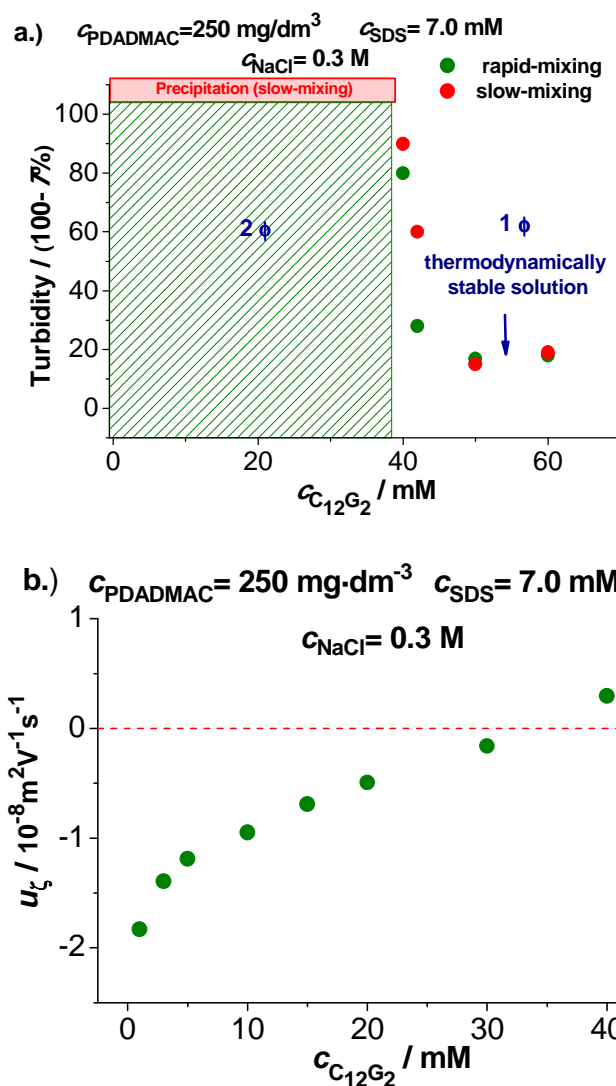
Figure S6. Mean electrophoretic mobility (u_ζ) of the PDADMAC/SDS complexes and the turbidity (100-T%) of the systems as a function of SDS concentration at $c_{PDADMAC}$= 50 mg·dm^{-3}, via application of rapid- (●) and slow-mixing (●), respectively, in 0.3 M NaCl. The red and the green striped boxes indicate the precipitated composition range for slow- and rapid-mixing, respectively.
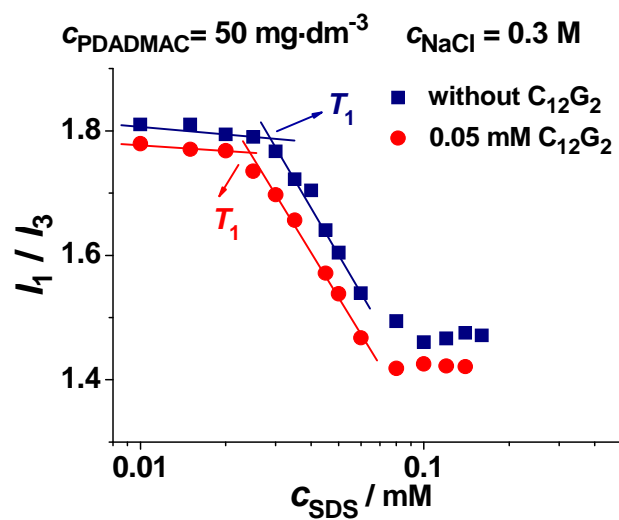
Figure S7. Fluorescence I_1/I_3 ratio as a function of SDS concentration in the absence (■) and presence (●) of 0.05 mM $C_{12}G_2$, at constant PDADMAC (50 mg·dm^{-3}) and NaCl (0.3 M) concentrations.

Figure S8. a.) Turbidity (100-T%) of the systems prepared by rapid- (●) and slow-mixing (●), respectively, in the function of dodecyl maltoside concentration b.) the mean electrophoretic mobility of the polyelectrolyte/mixed surfactant nanoassemblies, prepared by rapid-mixing, against the $C_{12}G_2$ concentration at $c_{PDADMAC} = 250$ mg·dm^{-3} and $c_{SDS} = 7.0$ mM. All the mixtures were prepared in the presence of 0.3 M NaCl. The precipitated concentration range for rapid-mixing is denoted by the green striped area in Figure S8a. For the sake of clarity, the mobility data observed for slow-mixing are not shown in Figure S8b since they are nearly the same within the experimental error as in the case of rapid-mixing.