Supporting information 'Kinetics and mechanism of the sphere-to-rod transition of tri-block copolymer micelles in aqueous solutions.'

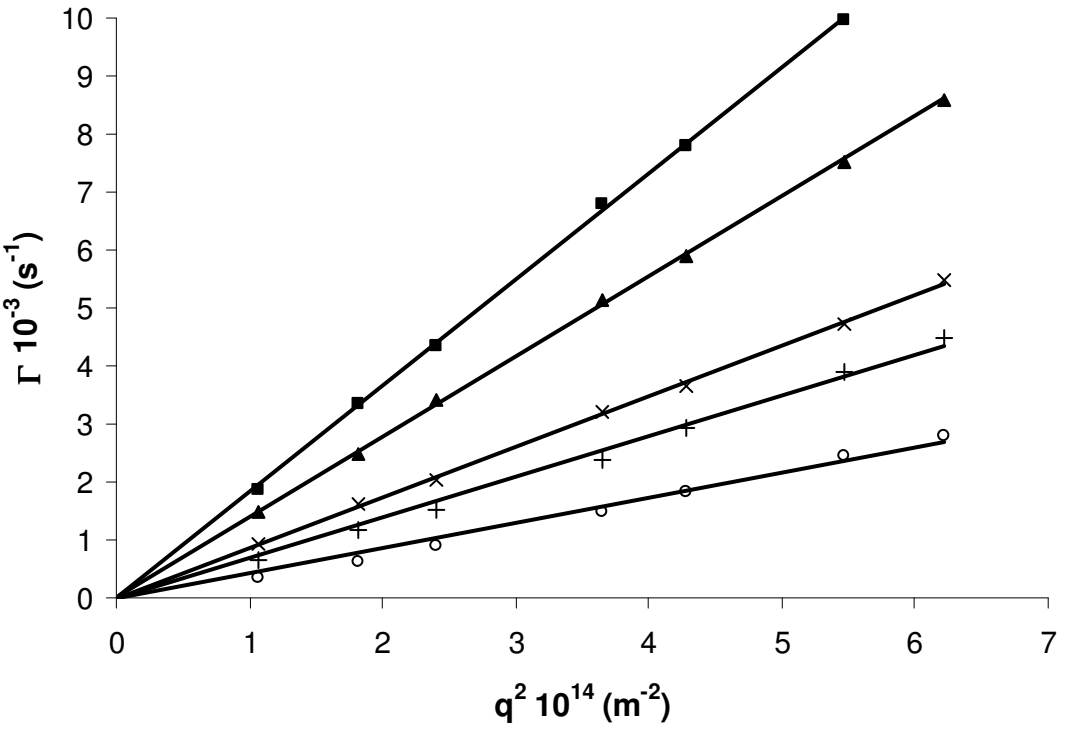


Figure 1 The relaxation rate as a function of q^2 for a sample containing 8 g/L P123, 2 M KCl and 8 vol% EtOH for different growth times: 10 min (■), 1h (▲), 3h (×), 5h (+) and 70h (○). The lines are linear fits of the data.

Calculation of the association and dissociation rate constant

A simple random micelle aggregation model can be used to describe the sphere-to-rod transition of micelles. [1,2] This model can be written as:

$$M_i + M_j \underset{k_{diss}}{\overset{k_{ass}}{\rightleftharpoons}} M_{i+j} \qquad i, j = 1, 2, \ldots \qquad (1)$$

Where M_i and M_j correspond to micellar species containing different numbers of spherical micelles, i and j. In its most simplified form, this model assumes that each step has the same equilibrium constant $K = k_{ass} / k_{diss}$, where k_{ass} is the association and k_{diss} the dissociation rate constant, respectively. In the association and dissociation reactions micellar species and not separate surfactant chains are involved.

This model is very similar to the one discussed by Turner and Cates concerning the length distribution of micellar worm-like species after a perturbation.[3] The relaxation time of the system represents the life-time of the micelles and is related to the breaking rate constant (k_b) as follows:

$$\tau_r \approx 1/(2k_b\bar{L}) \qquad (2)$$

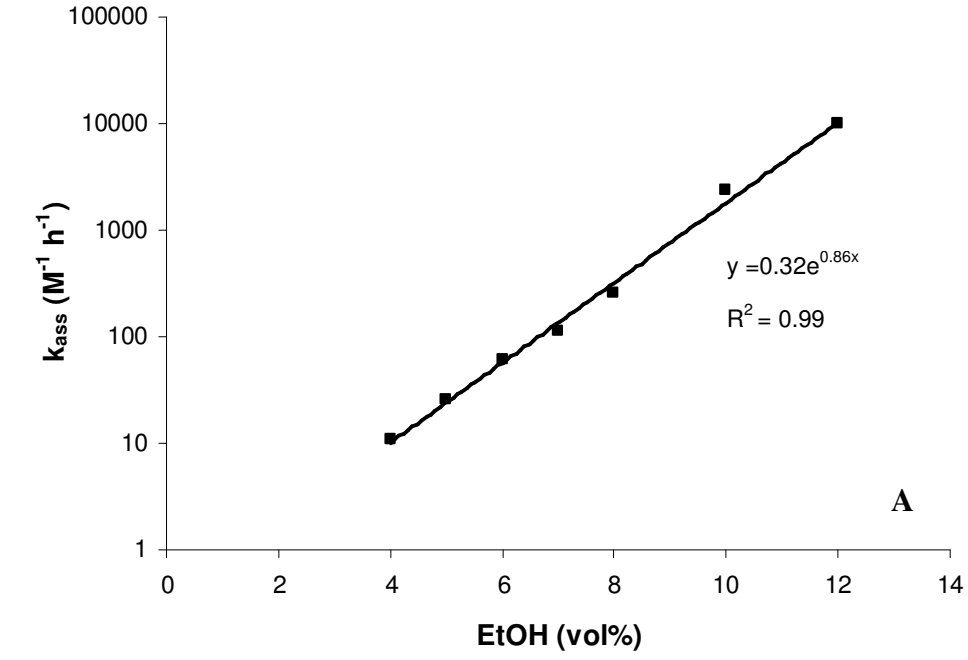
The breaking rate constant is in fact the dissociation rate constant per unit micellar length $k_b = k_{diss} / l_0$, where l_0 is the length of a spherical micelle incorporated in the rod-like micelles and it is assumed to be approximately equal to $2R_{H,0}$.[2]

The relaxation time for the random aggregation model is given by $1/\tau = k_{diss} + k_{ass}\Sigma C_m$, where ΣC_m is the sum of micellar species. For large aggregation numbers the relaxation time becomes:

$$1/\tau_r \approx 2k_{diss}\sqrt{KC_0} \qquad (3)$$

C_0 is the total concentration of micellar units and it is equal to $\Sigma m C_m$, where m is the aggregation number. The complete derivation of this equation can be found in another work.[2] These equations can be used to estimate both the association and dissociation rate constants from the relaxation time of the micelles.

Figure 2 shows the calculated association and dissociation rate constants as a function of the ethanol concentration.



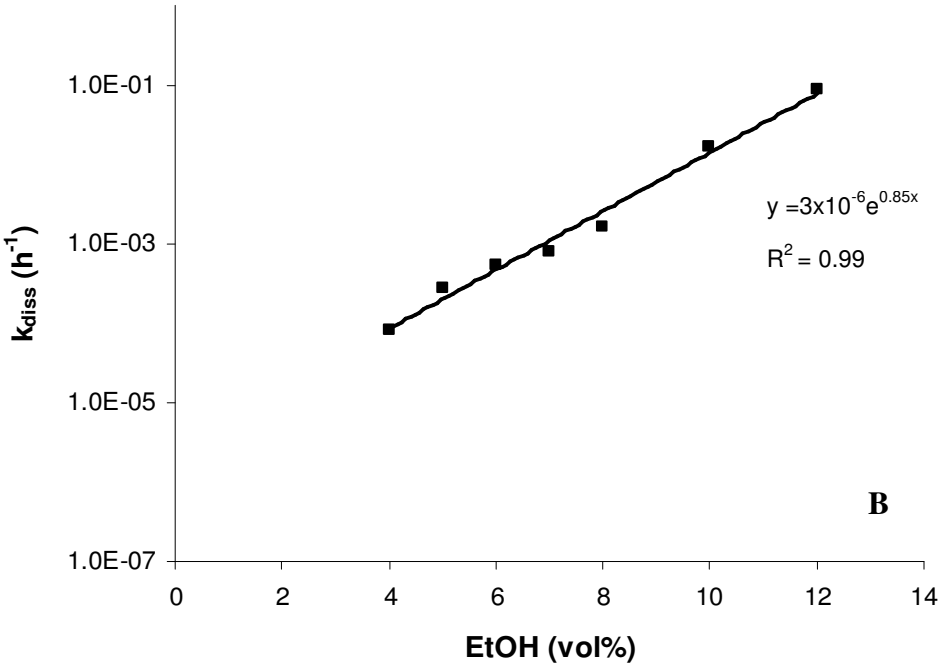


Figure 2 A) The association rate constant and B) the dissociation rate constant as a function of the EtOH concentration for a stirred sample containing $8x10^{-3}$ g/ml and 2 M KCl. The lines are exponential fits to the data.

References:

1. Mukerjee P., In *Physical Chemistry: Enriching topics from Colloid and Surface Science*, van Olphen H., Mysels K., Eds; IUPAC THEOREX: La Jolla, CA, **1975**, Chapter 9.

2. Ilgenfritz G., Schneider R., Crell E., Lewitzki E., Ruf H., *Langmuir*, **2004**, 20, 1620.

3. Turner M.S., Cates M.E. *J. Phys. France* **1990**, 51, 307.