Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Novel self-assembling system based on resorcinarene and cationic surfactant

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Supporting Information Available: description of the NMR self-diffusion procedure, calculations of binding constants, and plots on self-diffusion coefficients and the ΔE values.

PGSE (Pulsed Gradient Spin-Echo) experiments

All diffusion-ordered (DOSY) experiments were performed by BPP-STE-LED (bipolar pulse pair–stimulated echo– longitudinal eddy current delay) pulse sequence.45 Data were acquired with a 50.0 ms diffusion delay, and gradient pulse duration from 2.4 to 6.2 ms (depending on the system under investigation), 1 ms spoil gradient pulse and a 5.0 ms eddy current delay. The sine-shaped pulse gradients were incremented from 2 to 95% of the maximum gradient strength in a linear ramp (up to 0.32 T/m in 16 or 32 steps).

The diffusion experiments were performed at least three times. All separated peaks were analyzed and the average values were presented. The temperature was set and controlled at 22º C with an air flow of 535 l/h in order to minimize convection effects. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker XWINNMR software package (version 3.5). The error of the determination of self-diffusion coefficients did not exceed 5%.

Details of the coefficient K_S calculation

Two-site "bound-free" model:

$$D_{obs} = X_{free} D_{free} + X_{bound} D_{bound}\,, \qquad \text{(S1)}$$

where X_{free}, D_{free} is the the mole fraction of free molecules (monomers) and corresponding self-diffusion coefficient, respectively; X_{bound}, D_{bound} is the the mole fraction of bound molecules (e.g. associated, aggregated, etc.) and the corresponding self-diffusion coefficient, respectively.

By definition:

$$X_{free} + X_{bound} = 1\,. \qquad \text{(S2)}$$

After combining (S1) and (S2) one can obtain:

$$X_{bound} = \frac{D_{free} - D_{obs}}{D_{free} - D_{bound}}. \quad \text{(S3)}$$

When applied to the molecules of **1** in the binary system (**1**+DABCO-16, see text for details) this model results in the dependence of X_{bound} on concentration of DABCO-16 (Table S1). Thus, the coefficient $K_S = \frac{C_{1(bound)}}{C_{DABCO}}$, where $C_{1(bound)}=X_{bound} \times C_{1(total)}$ is the concentration of the bound molecules of **1**, can be calculated (Table S1). Here $C_{1(total)}$ is the total concentration of **1** (constant and equal 1 mM).

The following constant values were used:

$D_{free}=2.31\cdot10^{-10}$ m^2/s – self-diffusion coefficient of **1** in individual solution at the same concentration as in binary systems (1 mM).

$D_{bound}=0.1\cdot10^{-10}$ m^2/s – self-diffusion coefficient of mixed aggregates '1+DABCO-16' (see text for details). This value was estimated by extrapolation of concentration dependence of the self-diffusion coefficient of **1** to the low concentration region.

Table S1. Dependencies of self-diffusion coefficient, mole fraction, concentration of bound **1** and coefficient K_S on the concentration of DABCO-16 in binary systems

C_{DABCO}, 10^{-3} M	D_1, 10^{-10} m^2/s	$X_{1(bound)}$	$C_{1(bound)}$, 10^{-3} M	K_S
0.05	2.21	0.05	0.05	0.90
0.14	2.05	0.12	0.12	0.84
0.21	1.93	0.17	0.17	0.82
0.43	1.76	0.25	0.25	0.58
0.786	1.69	0.28	0.28	0.36
1.07	1.6	0.32	0.32	0.30
4.29	0.86	0.66	0.66	0.15
5.7	0.74	0.71	0.71	0.12
11.4	0.62	0.76	0.76	0.07

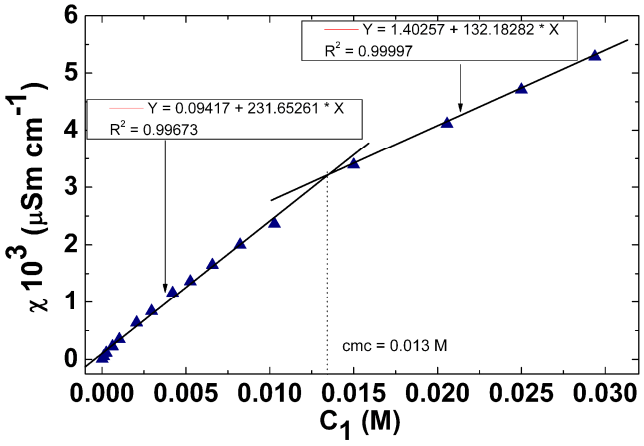

Fig. 1S. Linearization of the conductivity versus calixarene concentration data below and above the cmc value.

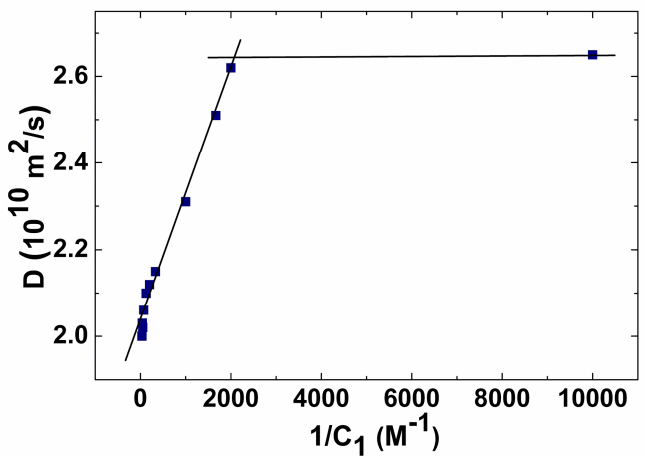

Fig. 2S. Dependence of self-diffusion coefficients of **1** on its inverse concentration; pH 9.0.

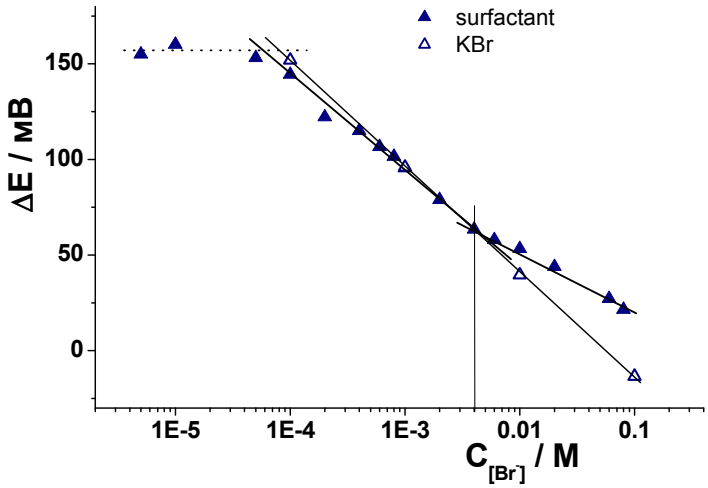

Fig. 3S. The ΔE versus [Br^-] dependence for the mixed **1**-DABCO-16 system and KBr solution; pH 9.0; 25^{0}C.