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Electronic Supplementary Information

A systematic study of the influence of mesoscale structuring on the kinetics of a chemical reaction

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SANS measurements

Tab. 1 Molar volumes and scattering length densities (SLD) of all components in the binary mixture P (D_2O/TBA 0.86/0.14), the ternary mixture Q (D_2O/TBA/BA 0.87/0.11/0.02) and the ternary mixture Q in the presence of the catalyst (D_2O/TBA/BA 0.87/0.11/0.02 and 2mM $H_5PMo_{10}V_2O_{40}$). The correlation length ξ obtained from Ornstein-Zernike (OZ) fits of the scattering cureves for ξ(P)=0.8nm, ξ(Q)=2.1nm and ξ(Q+2mM $H_5PMo_{10}V_2O_{40}$)=1.9nm.

	Molar volume cm^3mol^{-1}	**Scattering length density (SLD)** Å^{-2}
D_2O	18.1	$6.34*10^{-6}$
tert-butanol	93.8	$-3.15*10^{-7}$
benzyl alcohol	104.0	$1.30*10^{-6}$
$H_5PMo_{10}V_2O_{40}$	566.0	$3.36*10^{-6}$

Adsorption of $H_5PMo_{10}V_2O_{40}$ on the surface of BrijL23 micelles

SAXS experiments were performed on the system Brij L23 (tricosaethylene glycol dodecyl ether) - $H_5PMo_{10}V_2O_{40}$ in order to confirm the affinity of $H_5PMo_{10}V_2O_{40}$ to adsorb on surfaces covered with polar functional groups.

The concentration of $C_{12}E_{23}$ (c = 50 mM) is above the critical micellar concentration (CMC = 0.09 mM). Therefore, micelles of $C_{12}E_{23}$ are present in aqueous solution indicated by the black curve in Fig S1. 10mM $PMo_{10}V_2O_{40}^{5-}$ provide a scattering pattern typical for spherical objects in pure water. The mixture of $C_{12}E_{23}$ and $PMo_{10}V_2O_{40}^{5-}$, respectively, at 50 and 10 mM revealed a completely different scattering pattern, showing large and intense oscillations typical for a core–shell system with an increased electron density in the shell. Consequently, these SAXS pattern indicate an adsorption of $PMo_{10}V_2O_{40}^{5-}$ to the surface of $C_{12}E_{23}$ micelles.[1] Hence, this measurement also confirms the conclusions drawn from SANS measurements that $PMo_{10}V_2O_{40}^{5-}$ has the tendency to adsorb on neutral soft interfaces covered with functional groups.

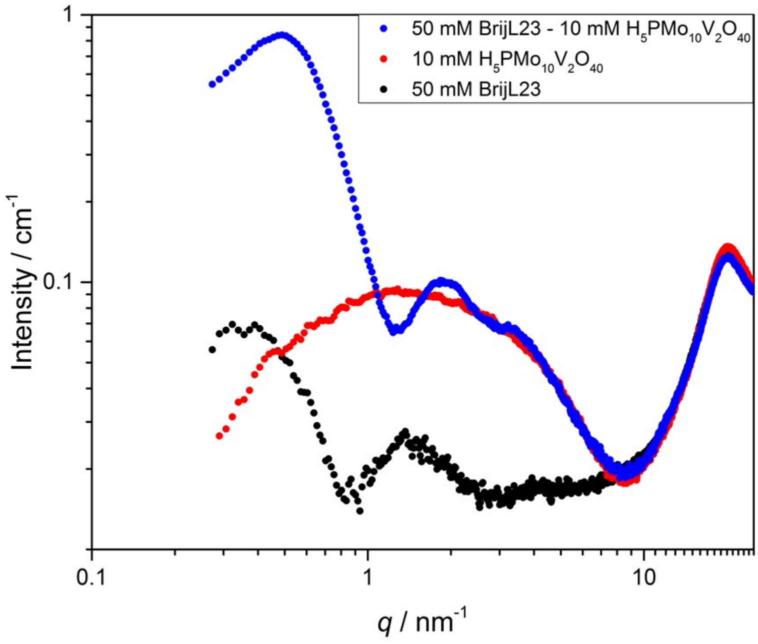

Fig. S1 SAXS spectra of (black) $C_{12}EO_{23}$, (red) $PMo_{10}V_2O_{40}^{5-}$, and their mixture in aqueous medium. The Y-axis is the absolute scattered X-ray intensity. All experiments were performed at 23 °C.

Oxygen solubility measurements in binary mixtures H_2O/TBA and H_2O/EtOH

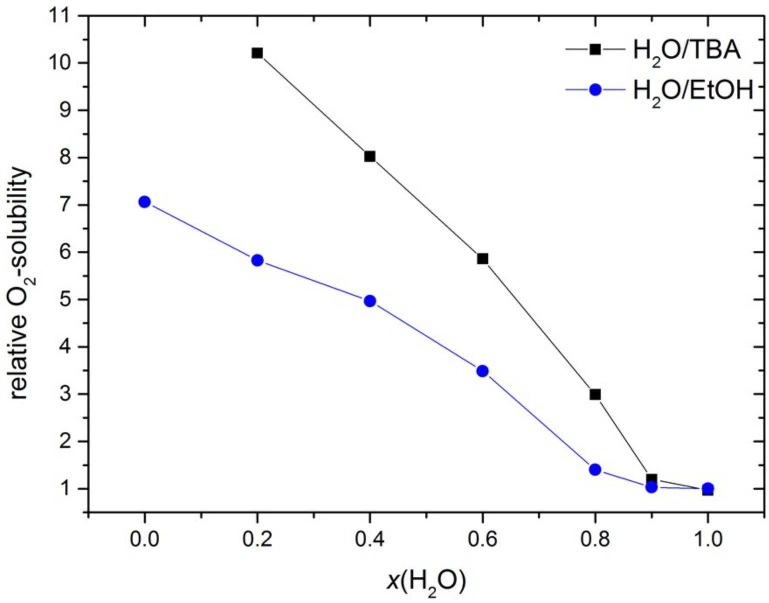

Fig. S2 Oxygen solubility for binary mixtures H_2O/TBA and H_2O/EtOH at room temperature (T = 23 ± 0.2 °C) relative to water for binary mixtures H_2O/TBA and H_2O/EtOH. The amount of water of the binary H_2O/alcohol mixture is given in mole fractions $x(H_2O)$.

Measurements of the dissolved oxygen in binary mixtures of H_2O/EtOH and H_2O/TBA were carried out at 23 ± 0.2 °C using a TPS Aqua-D oxygen-meter connected with a TPS ED1 electrode (Brisbane, Australia). A two-point-calibration was performed against air and against a solution of 2 g sodium sulfite in 100 mL water. No corrections were made for the ambient air pressure. Samples (each 10 g) were stirred overnight in closed vials for ideal mixing and equilibration. By doing so, it was ensured that conditions for sample preparation are close to those of the reactivity measurements. Measurements themselves were performed without stirring and values were taken after an equilibration time of 30 min to ensure constant and reproducible results. Note that solutions are not necessarily saturated with oxygen, since conditions of sample preparation were adjusted to those of the reactivity experiments. All values are given relative to water. To be more precise, the relative oxygen solubility is given as the molar fraction of oxygen dissolved in the water/alcohol mixtures $x_{\text{mix}}(O_2)$ divided by the molar fraction of oxygen dissolved in pure water $x_{\text{water}}(O_2)$.

Yields of benzyl aldehyde in H_2O/TBA mixtures after 72 h

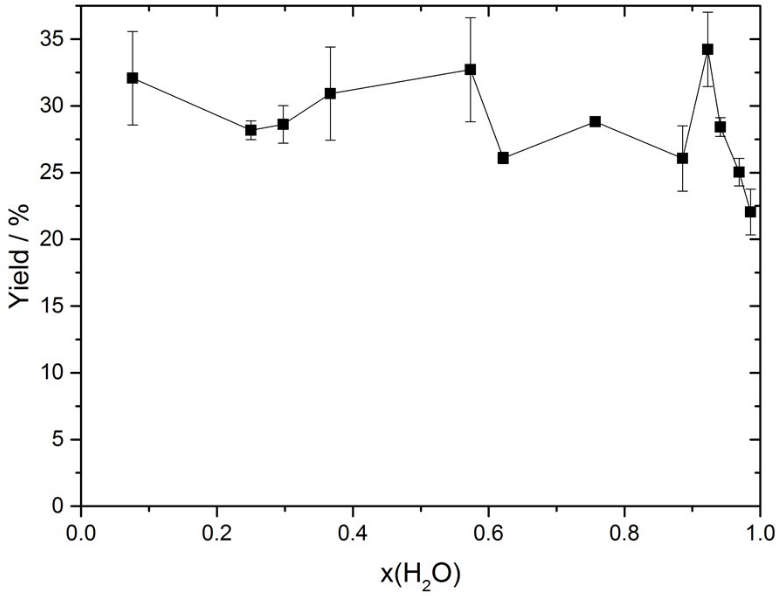

Fig. S3 Yields of the reaction product, benzyl aldehyde, with the corresponding standard deviations for the binary system H_2O/TBA at 25 °C after 72 h determined with GC-FID.

Dynamic light scattering experiments

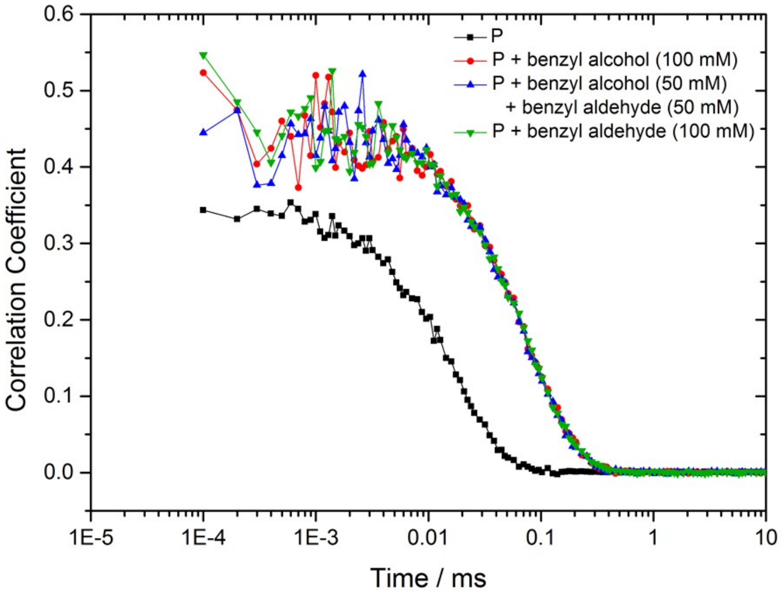

Fig. S4 Self-correlation functions obtained by DLS measurements at 25 °C.

Dynamic light scattering (DLS) experiments were performed using a temperature controlled CGS-3 goniometer system from ALV (Langen, Germany) equipped with an ALV-7004/FAST Multiple Tau digital correlator and a vertically polarized 22 mW HeNe laser (wavelength λ = 632.8 nm). Before starting the measurements, all samples were filtered into dust-free cylindrical light scattering cells (10 mm outer diameter) using a 0.2 mm PTFE membrane filter. The sealed measurement cells could be directly placed into the measurement apparatus. Measurements were performed at a scattering angle of 90° after thermostatting to 25 ± 0.1 °C. Data points were collected for 300 s.

Light scattering experiments were performed in order to investigate the influence of benzyl aldehyde (produced during benzyl alcohol oxidation) on the solvent structure (see Fig. S5). Point P (H_2O/TBA, molar fractions 0.86/0.14) was chosen, since SANS experiments were also carried out for this composition (see main article Fig. 2). Light scattering experiments show that correlation functions get more pronounced with a shift to higher lag times when adding benzyl alcohol (100 mM), benzyl aldehyde (100 mM) or a mixture of both (each 50 mM). These concentrations are equivalent to 0, 50 and 100% conversion regarding the reactivity measurements. The results indicate a strengthening of the structuring and swelling of the aliphatic (or TBA/BA) rich pseudo-phase, as already concluded from SANS measurements. Furthermore, no distinct differences of the correlation functions are visible when adding benzyl alcohol, benzyl aldehyde or a mixture of both. Thus, we conclude that there is no significant effect on the mesoscopic structuring during the reaction. Accordingly, a successive breakdown of the structuring of the reaction mixture with increasing reaction time can be excluded.

Yields of benzyl aldehyde in H_2O/EtOH mixtures after 16 h

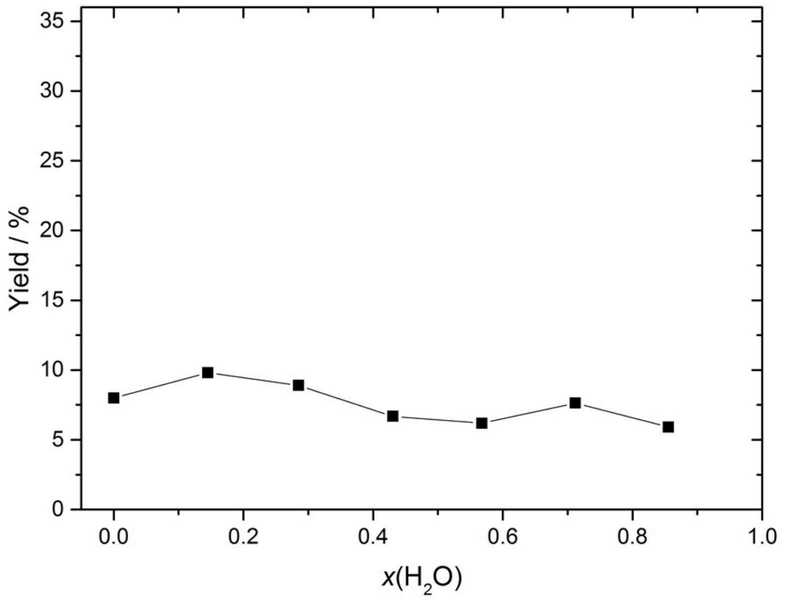

Fig. S5 Yields of the reaction product, benzyl aldehyde, for the binary system H_2O/EtOH at 25 °C after 16 h determined with GC-FID.

In case of the unstructured binary solvent H_2O/EtOH 6-10% of benzyl aldehyde are obtained, see Fig. S4. The yields can be regarded as almost constant over the investigated H_2O/EtOH compositions. As no (or at least very weak) mesoscopic structuring is present in H_2O/EtOH mixtures, structure induced reactivity changes can be neglected in this case and no steep changes in the yields of benzyl aldehyde are observed by changing the solvent composition.

Viscosities of binary mixtures H_2O/TBA and H_2O/EtOH

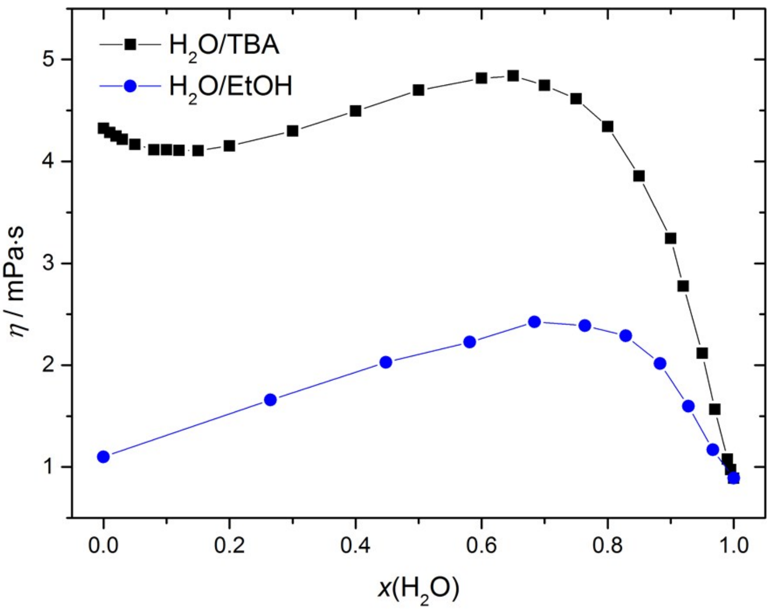

Fig. S6 Dynamic viscosities η for binary mixtures H_2O/TBA and H_2O/EtOH at 25 °C. Data were taken from literature.[2,3] The amount of water of the binary H2O/alcohol mixture is given in mole fractions $x(H_2O)$.

References

1 B. Naskar, O. Diat, V. Nardello-Rataj and P. Bauduin, *J. Phys. Chem. C*, 2015, **119**, 20985–20992.

2 I. S. Khattab, F. Bandarkar, M. A. A. Fakhree and A. Jouyban, *Korean J. Chem. Eng.*, 2012, **29**, 812–817.

3 P. K. Kipkemboi and A. J. Easteal, *Can. J. Chem.*, 1994, **72**, 1937–1945.