# Effect of Sodium dodecyl sulfate on the Mass Transfer Rate between Styrene and Water

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**Summary:** The effect of sodium dodecyl sulfate (SDS) on the mass transfer rate between styrene and water has been investigated. SDS increases the solubility of styrene in water even below the critical micelle concentration (CMC) and therefore increases the thermodynamic driving force for the mass transfer. The mass transfer coefficient however is not altered by SDS, even if the interface is almost saturated with emulsifier.

**Keywords:** critical micelle concentration; mass transfer; mass transfer coefficient; sodium dodecyl sulfate; styrene; surfactant

## Introduction

Mass transfer rates between immiscible liquids play an important role in heterogeneous reaction systems such as emulsion polymerizations.[1] They could become rate or quality determinant, considering the loss of kinetic control in the context of process intensification.

Emulsifiers influence mass transfer rates in heterogeneous systems in several ways. Due to a decrease of the interfacial tension, the improved dispersion of the liquid causes an increase of the contact area. Additionally the solubility and therefore the driving force of the transferred species can be different in the presence of emulsifiers and the surface active species could cause additional barriers to overcome at the interface.

In this work the effect of sodium dodecyl sulfate on the solubility of styrene in water and on the mass transfer from the monomer reservoir to the water phase has been investigated.

## Experimental Part

To measure the time evolution of the amount of styrene in water to reach equilibrium using UV-spectroscopy, first a calibration was needed. The measurements were performed in a closed 2000 mL glass mill equipped with a septum to inject the styrene, a stirring bar to circulate the volume and a cuvette in a bypass (Figure 1).

After the system reached its equilibrium, the UV-spectra were recorded. The equilibrium absorption was plotted against the injected amount of styrene in Figure 2.

Several different values for the critical micelle concentration (CMC) of sodium dodecyl sulfate have been published,[2,3] so the CMC of the emulsifier used in this work was measured conductively employing two experiments. In the first setup a dilution series for SDS in water was prepared and the conductivity of each sample measured. In the second experiment, a concentrated SDS-solution was titrated to a sample of water while the conductivity was measured. The conductivity of SDS in water is shown in Figure 3.

The equilibrium values for styrene in water were measured using a cuvette and putting a layer of the monomer on top of the slowly stirred water phase. Different

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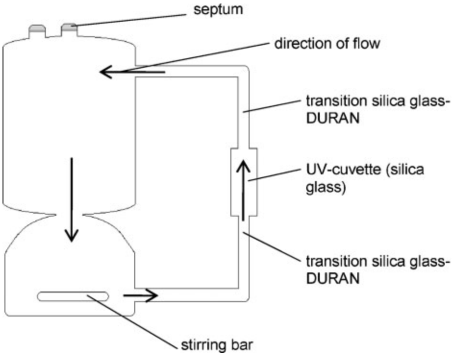

***Figure 1.***
Experimental setup for the UV-calibration (glass mill).

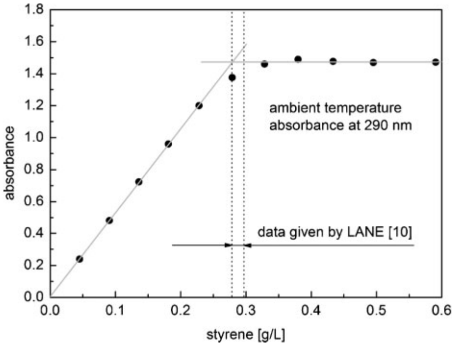

***Figure 2.***
Calibration curve for styrene in water.

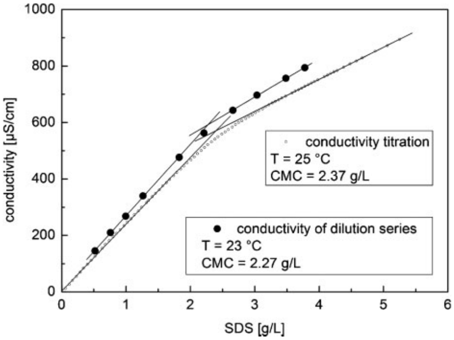

***Figure 3.***
Measurement of the critical micelle concentration.

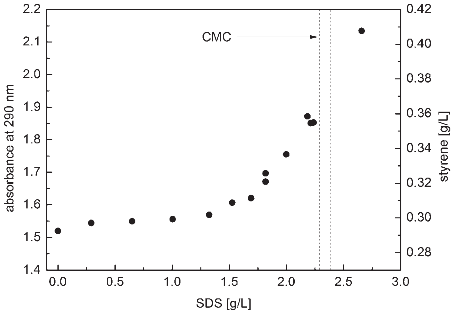

***Figure 4.***
Equilibrium values for styrene in water depending on the concentration of SDS.

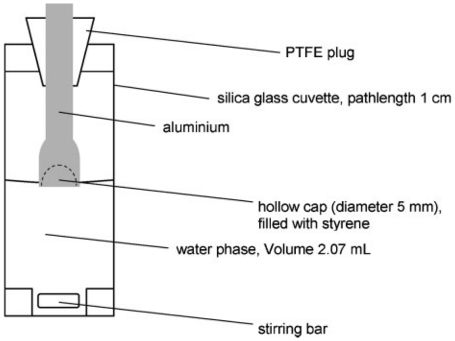

***Figure 5.***
Stirred UV-cuvette with defined contact area between styrene and water.

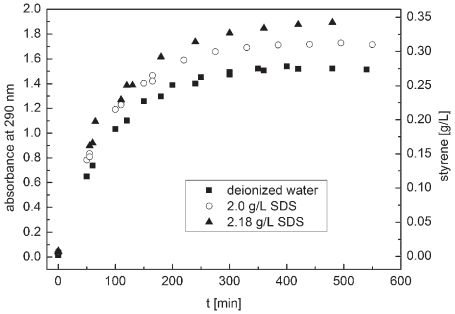

***Figure 6.***
Time evolutions of the concentration of styrene in water.

equilibrium values were obtained as shown in Figure 4.

The measurements for the time resolved concentration of styrene in water were performed in a cuvette equipped with a stirring bar. The styrene was put in a cap (5.0 mm in diameter) and positioned close to the surface of the aqueous phase (Figure 5).

All experiments were carried out at ambient temperature and the stirring speed was constantly kept at ~250 $\text{min}^{-1}$. The volume of the aqueous solution was always 2.07 mL. Each experiment was executed at least two times in order to ensure reproducibility. The results are shown in Figure 6.

## Results and Discussion

The absorbance of styrene in water at 290 nm is linear up to the vicinity of saturation (Figure 2). This relation was extrapolated to connect the absorbance with the styrene concentration even when the solubility was enhanced by SDS. The solubility of styrene in water at ambient temperature fits well with the literature values given by LANE.[4] The obtained values of the CMC for SDS of 2.27–2.37 g/L for ambient temperature (23–25 °C) are in good agreement with values recently published in.[5]

Figure 4 shows that the solubility of styrene in water is increased significantly by SDS even below the CMC. Similar results are published for pyrene.[6] FUANGSWASDI et al. reported that the solubility of styrene in water remains constant until the concentration of SDS reaches the CMC,[7] contradictory to our experimental results. Furthermore crossing the CMC had no apparent influence on the solubility. A possible explanation for this discrepancy could be, that the presence of styrene is altering the CMC, although there is no experimental evidence, yet. An explanation for the observed results could be, that the styrene solubilized in water includes heterogeneous structures whose states are stabilized by any surfactant present even below the CMC. There is evidence, that styrene among other hydrophobic substances forms small aggregates or droplets and that styrene in water is not only molecularly disperse, if at all.[8]

The mass transfer rate between two phases in general can be written as

$$\frac{d[M_w]}{dt} = \beta \cdot \frac{a}{V} \cdot ([M_{w,sat}] - [M_w]), \tag{1}$$

where $[M_w]$ is the concentration of the solute, β the mass transfer coefficient, a the interfacial area, V the volume of the solvent and $[M_{w,sat}]$ the equilibrium value for the concentration of the solute in the solvent, respectively.

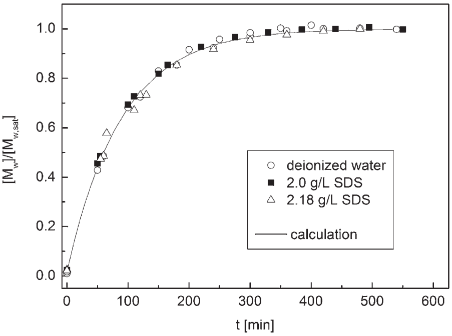

***Figure 7.***
Standardized time evolution of experiments and calculation (ambient temperature).

Dividing (1) by $[M_{w,sat}]$ gives the standardized form

$$\frac{d([M_w]/[M_{w,sat}])}{dt} = \beta \cdot \frac{a}{V} \cdot \left(1 - \frac{[M_w]}{[M_{w,sat}]}\right). \tag{2}$$

Dividing the time evolution from Figure 6 by the equilibrium values shows, that a constant mass transfer coefficient is able to explain the experimental data. In Figure 7 the experimental data of the standardized curves are plotted with Equation (2) using $\beta = 19.8\ \mu\text{m/s}$, $a = \pi r^2$ with $r = 2.5$ mm and $V = 2.07$ mL.

## Conclusion

The influence of sodium dodecyl sulfate on the time evolution of the styrene content in water was investigated. The results show, that SDS increases the solubility of styrene in water even below the critical micelle concentration, but is not altering the mass transfer coefficients. The influence is therefore thermodynamic and not kinetic by nature.

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