

# Study of Aqueous Solution of Sodiumdodecylsulfate and Polyethyleneoxide 10000 by NMR NOESY

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Z. Naturforsch. **59a**, 291 – 294 (2004); received October 7, 2003

Two-dimensional Nuclear Overhauser Enhancement Spectroscopy NMR has been applied to study sodiumdodecylsulfate (SDS)/polyethyleneoxide (PEO)/D<sub>2</sub>O at 10, 20, 25, and 40 °C. The results indicate that PEO interacts preferentially with the surface of the micelle aggregates at 20 and 25 °C, displacing some water molecules from the hydration sphere. At 40 °C the polymer tends to penetrate the interior of the SDS micelle, since its solubility in hydrophobic media increases with temperature.

**Key words:** Polyethyleneoxide; SDS; NOESY.

## 1. Introduction

The main application of surfactants is the solubilization of compounds in solvents of different polarity, for example hydrocarbons in aqueous micellar solutions. Sodiumdodecylsulfate (SDS) and polyethyleneoxide (PEO) are mixed in many industrial applications, since they behave in a complementary way. The resulting synergism often produces properties that are better than the individual ones [1, 2].

It has often been proposed that these compounds in solution interact significantly above the critical aggregation concentration (CAC). The necklace model is the most commonly accepted structure for these associations, in which the SDS micelles are bound to the polymer like pearls of a collar [3]. Nevertheless, some aspects of these interactions are still not well understood, and information about the specific interactions of the hydrogen atoms could help to explain observations concerning the interactions and stabilisation of the resulting colloid.

This work aims to study the SDS and PEO10000 system in aqueous solution by NOESY, as this NMR technique gives information about the proximity of protons when they are closer than 5 Å to each other by showing how these molecules interact [4, 5]. A previous noesy study [6] has been performed for the SDS and PEO20000 system at 10 and 25 °C and showed fewer interactions than in the present study. The use of PEO10000 should make no difference in relation to

PEO20000, as the association is strong for PEO of a molecular weight beyond 4000 [7].

## 2. Experimental

SDS and PEO of “for gas chromatography” quality with a mean molar mass of 10000 g/mol were obtained from Merck. D<sub>2</sub>O was obtained from Fluka and was of > 99.8% isotopic purity of deuterium.

NMR NOESY experiments were carried out on a Varian Mercury spectrometer at a proton resonance frequency of 300 MHz. All experiments were done with 144 scans, 64 transients, 2 s relaxation delay, 1981 Hz spectral width and 0.4 s mixing time. The spectra were obtained at 10, 20, 25, and 40 °C. The temperature was controlled within  $\pm 0.1$  °C by a Varian temperature controller. In the t<sub>2</sub>- and t<sub>1</sub>-dimension the Free Induction Decays's (FIDs) were apodized with a shifted gaussian window function prior to the Fourier transformation.

## 3. Results and Discussion

The NOESY experiments for the system below the CAC of (SDS/PEO/D<sub>2</sub>O) were set up as standard for the analysis of the spectra above the CAC. A specific interaction of SDS with PEO was not detected by NOESY for the system below the CAC, as expected because these species are not aggregated under these conditions [8]. SDS1/SDS2 coupling was not

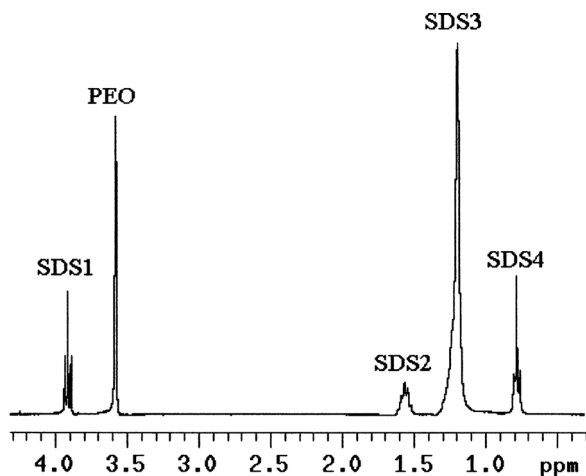


Fig. 1.  $^1\text{H}$  NMR spectrum of the system SDS/PEO/ $\text{D}_2\text{O}$  at 25 °C.

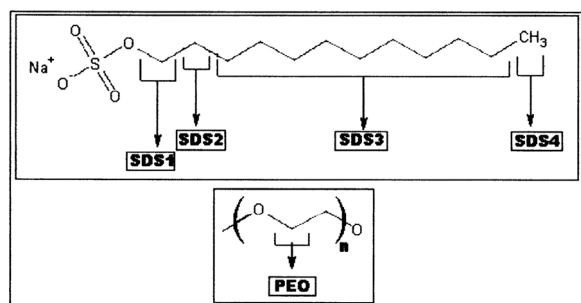


Fig. 2. Formulas and proton numbering of sodiumdodecylsulfate (SDS) and polyethyleneoxide (PEO).

observed, because these weak signals are from only 2 protons. Nevertheless, the strong SDS3 signal (18 protons) brings intramolecular couplings to SDS2 and SDS4.

The NOESY for the system SDS/ $\text{D}_2\text{O}$  above the CMC (Fig. 3) presented cross correlations between all neighbouring SDS hydrogen atoms, which could be due to specific intermolecular interactions, but were certainly due to intramolecular dipolar coupling, since the COSY (two-dimensional COrrelated SpectroscopY, spectrum not shown) showed the same cross correlations for this system.

The system SDS/PEO/ $\text{D}_2\text{O}$  above the CAC, at 10, 20, 25, and 40 °C (Figs. 4–7) showed cross correlations from SDS to SDS and from SDS to PEO, indicating that the protons of these species are spatially close, and hence the formation of aggregates. These results agree with models found in the literature [9], for example the collar model, where the complex poly-

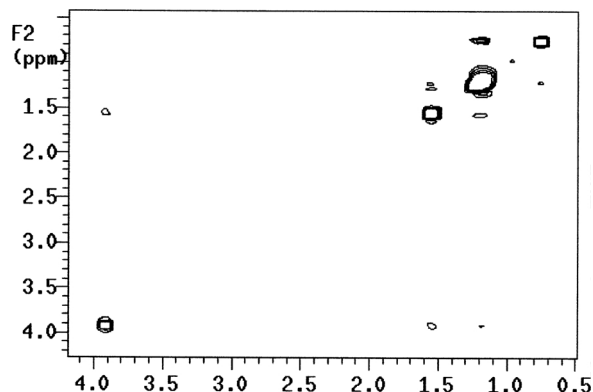


Fig. 3. NOESY NMR of the system SDS/ $\text{D}_2\text{O}$  ( $16.057 \cdot 10^{-3}$  mol/l) above the Critical Micelle Concentration (CMC) at 25 °C.

mer/surfactant would be formed by surfactant aggregates bound to polymeric chains.

It has been reported that an increase in temperature decreases the PEO solubility, sometimes resulting in the formation of an aqueous biphasic system, because of dehydration caused by the increase in temperature [10]. Thus at higher temperatures the probability of polymer interaction with the interior of the micelle is higher, as this environment is hydrophobic. Therefore one should observe an increase in the NOESY correlations of PEO with SDS3 and SDS4. As expected, the PEO/SDS3 correlation was stronger at 40 °C compared to the NOESY at 20 and 25 °C. Although the strongest PEO/SDS3 correlation occurred at 10 °C, this could be explained by slower movements of the molecules, because the NOE interaction is more effective when the motions are slow, and so the correlations are strengthened [11].

At 10, 20, 25, and 40 °C the intensity of the PEO/SDS1 correlation is approximately equal to or bigger than that of the PEO/SDS2 and PEO/SDS3 correlations. In some cases, the PEO and SDS1 correlation show almost the same cross-peak volume as the PEO/SDS3 correlation. Nevertheless, it should be pointed that the SDS3 signal ( $\delta = 1.4$ ) arises from 18 protons, while the SDS1 signal ( $\delta = 3.9$ ) comes from 2 protons. Therefore the PEO/SDS1 correlation is more intense than the PEO/SDS3 correlation. This is a strong indication that PEO interacts with the surface of the micelle aggregate, which is in agreement with the  $^{13}\text{C}$  NMR studies by Cabane *et al.* [9]. However Gjerde *et al.* [6] suggested the penetration of the polymer into the interior of the SDS micelles to explain PEO/SDS3 interaction.

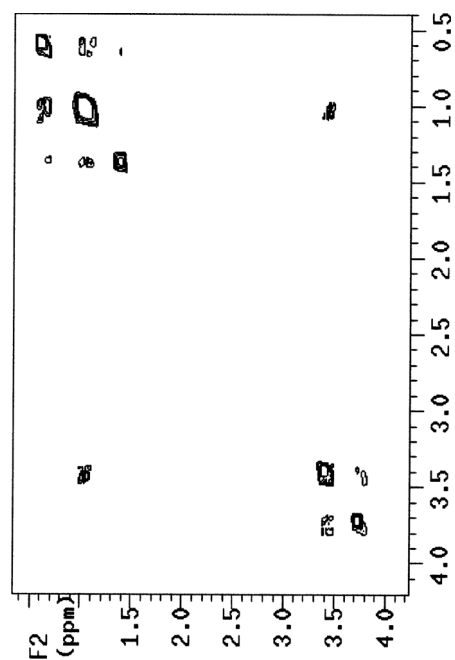


Fig. 4. NOESY NMR of the system SDS ( $52.24 \cdot 10^{-3}$  mol/l), PEO ( $57.35 \cdot 10^{-3}$  mol/l),  $D_2O$  above the (CAC) at  $10^\circ C$ .

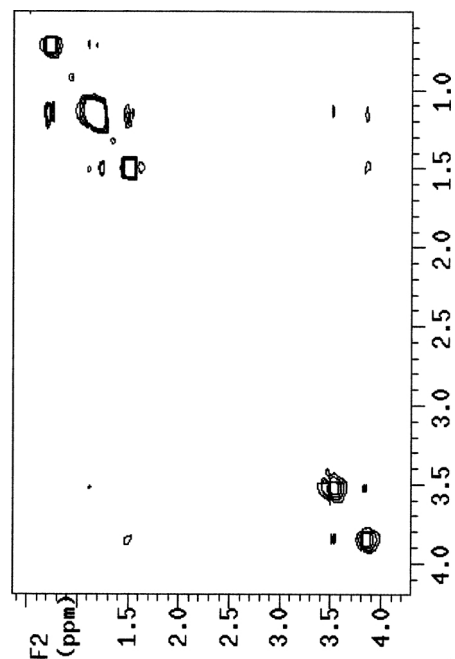


Fig. 5. NOESY NMR of the system SDS ( $52.24 \cdot 10^{-3}$  mol/l), PEO ( $57.35 \cdot 10^{-3}$  mol/l),  $D_2O$  above the CAC at  $20^\circ C$ .

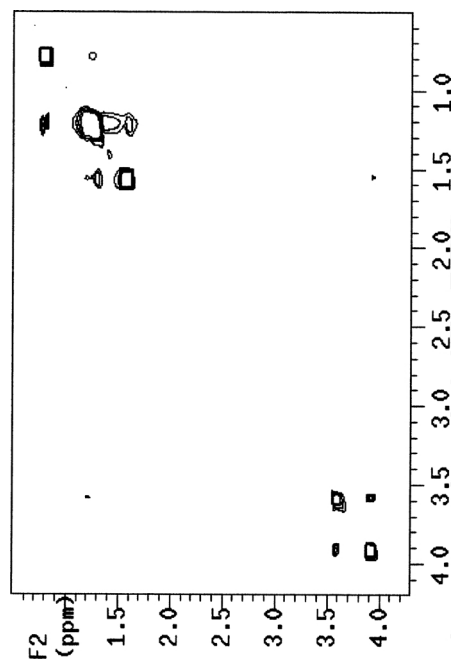


Fig. 6. NOESY NMR of the system SDS ( $52.24 \cdot 10^{-3}$  mol/l), PEO ( $57.35 \cdot 10^{-3}$  mol/l),  $D_2O$  above the CAC at  $25^\circ C$ .

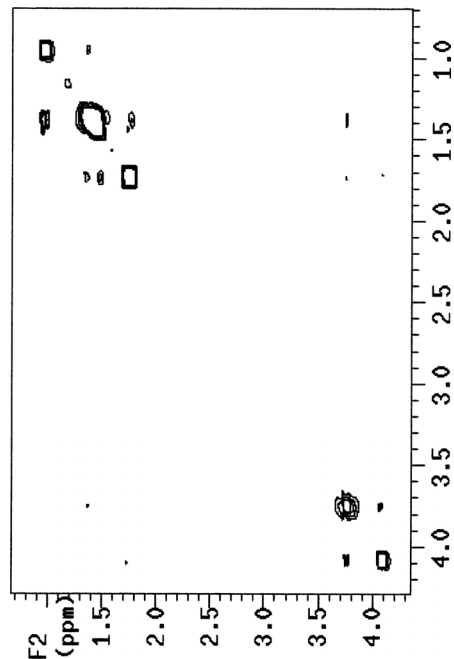


Fig. 7. NOESY NMR of the system SDS ( $52.24 \cdot 10^{-3}$  mol/l), PEO ( $57.35 \cdot 10^{-3}$  mol/l),  $D_2O$  above the CAC at  $40^\circ C$ .

The interior of the micelle aggregates has many physico-chemical properties similar to liquid hydrocarbons. Because PEO is insoluble in hydrocarbons [12], this suggests that PEO does not penetrate the SDS micelles at temperatures below  $40^\circ C$ .

One should also take into consideration that surfactant aggregates are not rigid and stay in solution in a dynamic equilibrium involving the constant exchange of monomers with the bulk aqueous phase [13]. PEO in aqueous environment is not a rigid

molecule [14], therefore, due to the complex dynamics of the molecular movement, it is to be expected that segments of PEO molecules, sometimes penetrate the interior of the micelle aggregate, as demonstrated by the PEO/SDS3 correlation in the NOESY spectrum.

These results show that the complex movement of the molecules occasionally induces polymer segments to collide with the interior of the SDS micelles, or the surfactant tail bends into the PEO micellar interface, affording PEO/SDS3 interaction. The NOESY experiments show that PEO interacts preferentially with the

surface of the micelle aggregates at 20 and 25 °C, displacing some water molecules from the hydration sphere. The explanation for this phenomenon may be that the cations attract both surfactant anionic groups, and the non-bonding electron pairs of the polymer oxygen atoms so as to bring these together. Nevertheless, at 40 °C the polymer tends to penetrate the interior of the SDS micelle, since its solubility in water decreases with increase in temperature.

#### Acknowledgements

We would like to thank CNPq/PADCT for the NMR.

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