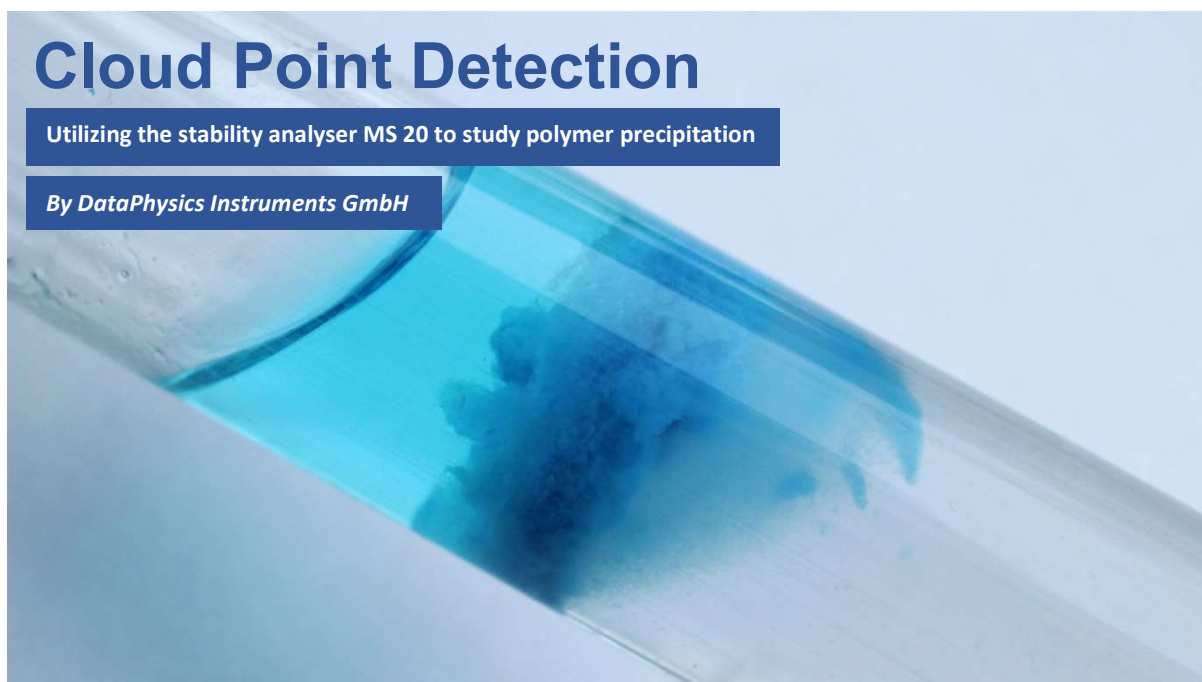**How an optical stability analyser can help find the cloud point of polymer solutions**

Cloud Point Detection

Utilizing the stability analyser MS 20 to study polymer precipitation

By DataPhysics Instruments GmbH

Scientists are looking for cost-effective solutions that can make water-soluble polymer solutions useable under high-temperature-high-salinity (HTHS) condition, which is extremely challenging due to thermal degradation and precipitation of the polymer. Polyethylene oxide (PEO) is commercially applied to enhance the viscosity of aqueous solution. However, PEO solutions will phase-separate at elevated temperature. Hence, researchers proposed a variety of strategies to solve this problem, like adding surfactants, changing pH, adding co-solvents, *etc*. Although the interaction between PEO and surfactant sodium dodecyl sulfate (SDS) was widely investigated there are only a few studies about salt effects on the PEO/SDS interaction. Recently, Chen has shown the correlation between the cloud point behavior and the molecular structures of polymer-surfactant complex at HTHS condition through precisely controlling the temperature and observing changes with an optical stability analysis system.

In this work, the author elucidated the effect of salts on the interaction between PEO and different types of surfactants, such as anionic surfactant SDS and cationic dodecyl tri-methyl ammonium chloride (DTAC). They first tested the solubility of PEO (MW 300-6,000K) in NaCl by cloud point measurements with the stability analysis system MultiScan MS 20 were the cloud points can be easily detected. All cloud points were found at 78 ± 1 °C, showing little effects of the MW.

The Stability Analysis System MS 20

The MultiScan MS 20 is a measuring device for the automatic optical stability and aging analysis of a variety of multi-phase dispersions, in particular suspensions and emulsions, and the comprehensive characterization of **time- and temperature-dependent destabilization mechanisms**.

The **transmission** and **backscattering intensity** is scanned and recorded position dependently this allows to detect processes such as **agglomeration, coalescence, sedimentation, creaming and the clouding** which is reported in the current article.
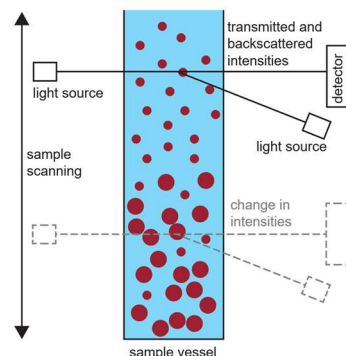
Due to its modular design the MS 20 can be operated with up to six scan towers. The scan towers are independently controllable, which allows to perform **several measurements simultaneously under individual conditions**.


The addition of SDS or DTAC strongly influenced the solubility of PEO at higher temperature leading to different behaviors (**Picture 1**). C_{90} denotes the surfactant concentration when the cloud point increased to 90 °C. For DTAC, the cloud point increased slightly with increasing DTAC concentration and C_{90} of PEO (MW 1000K, 1 g/L) was 12.6 mM. However, when the SDS concentration was increased, the cloud point demonstrated three stages: decreasing, keeping constant (due to precipitation), and increasing.
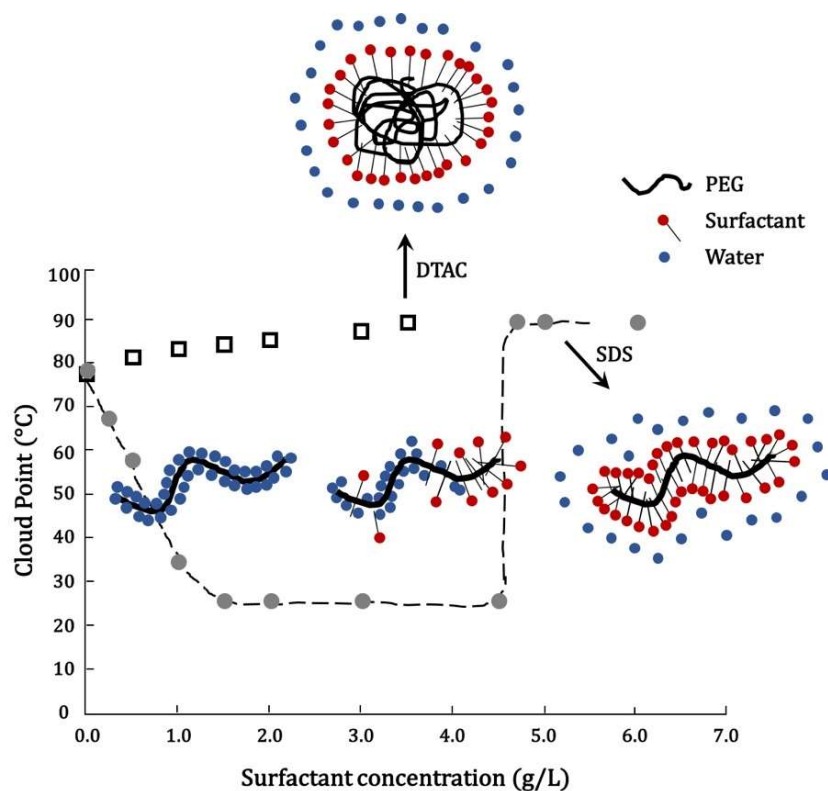
Picture 1: *Cloud point Scheme of PEO/SDS and PEO/DTAC interactions in 1 M NaCl solutions*

To understand these completely different behaviors, two-dimensional Nuclear Overhauser enhancement (NOESY) and pseudo two-dimensional diffusion ordered spectroscopy (DOSY) NMR measurements were taken shedding light on the interaction between PEO and the two surfactants. The NMR data illustrated a slight interaction between PEO and the end of SDS´s hydrophobic tail (the methyl group), suggesting PEO interacted with the rear of the hydrophobic chain of SDS. In comparison, no interaction was seen between PEO and DTAC, which was consistent with above cloud point results. To explain the interaction, previous researches on PEO/SDS system proposed a model where SDS micelles are surrounded by PEO. However, in this work the author explained it in a different way showing PEO was covered by SDS. **Picture 1** shows that water molecules distribute along PEO backbone due to hydrogen bridge binding. With increasing temperature, the PEO aqueous solution phase-separated and dehydrate because of the more unfavorable entropy contribution to the free energy. SDS could lower the dehydration speed. When the SDS concentration is increased, more SDS covers the PEO chain to prevent the polymer from collapsing. For DTAC, the behavior was different. After phase-separating, dehydration and collapsing, DTAC served as co-solvent and could not interact with the PEO chain. Since DTAC only solubilized PEO without interacting with PEO, less DTAC was needed comparing with SDS.

As shown in **Picture 2**, the C_{90} of PEO (MW 1000K, 1 g/L) and PEO (MW 1000K, 2 g/L) were 16.6 ± 0.4 mM, 33.4 ± 0.9 mM, respectively. Interestingly, C_{90} doubled when PEO concentration doubled. In order to understand the mechanism behind it, they also studied PEO (MW 20K, 5 g/L) in NaCl and obtained a similar behavior. Hence, the author could underline the finding that an interaction took place between PEO and SDS.
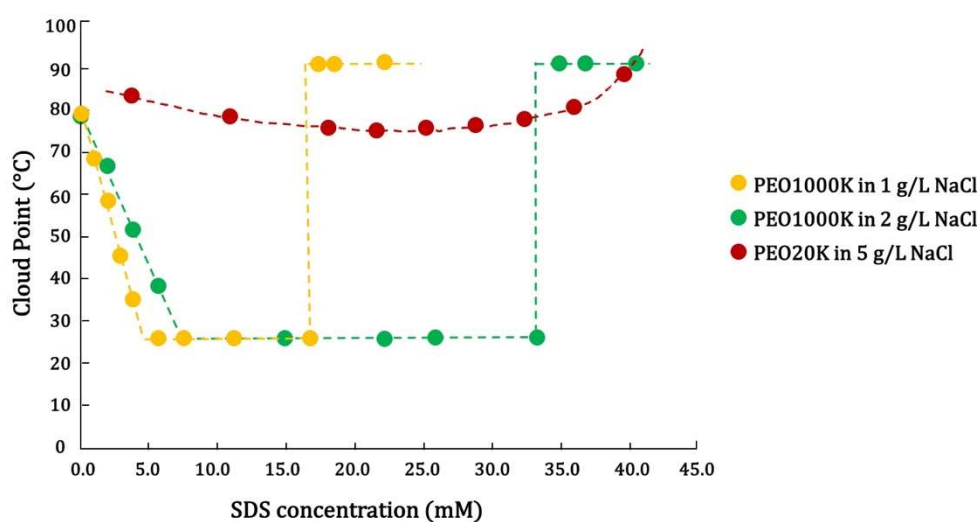
Picture 2: *The cloud point of PEO 1000 K in NaCl solution at 1 g/L (yellow symbols) and 2 g/L (green symbols), PEO 20K in NaCl solution at 5 g/L (red symbols) as a function of SDS concentration*

Overall, the author proposed a different molecular model for the PEO/SDS and PEO/DTAC interaction and explained that the solubility behaviors result from different polymer-surfactant conformations. Understanding the molecular interaction between a polymer and a surfactant may provide the guideline for formulation developement of relevant products applied at high-temperature-high-salinity conditions.

The optical stability analyzer MultiScan MS 20 (DataPhysics Instruments GmbH, Germany) was used in this research to analyze the cloud point under precisely controlled temperature conditions.

For more information, please refer to the following article:

Conformation and solubility of poly(ethylene oxide) in polymer-surfactant complex at high-temperature and high-salinity conditions; Shaohua Chen; *Colloids and Surfaces A* **2019**, 581, 123811; DOI: 10.1016/j.colsurfa.2019.123811