

# Application Report

## Dynamic properties of surfactants

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Method:



Bubble Pressure Tensiometer – BP100

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## Kinetic investigations into the effectiveness of surfactants

### Abstract

Surfactants reduce the surface tension of solutions in thermodynamic equilibrium to a particular level depending on the concentration which can be measured using *static* tensiometric methods. In dynamic processes such as spraying or printing, the surface tension in equilibrium is not the determining factor – this is often only achieved after several seconds or, in the extreme case, after hours. The decisive factor is the value which is achieved in the time from the formation of the surface to the instant of use – for example, when a drop of ink makes contact with the paper. The time between the formation of the surface and the instant of observation is referred to as the surface age.

The Bubble Pressure Tensiometer – BP100 measures the surface tension as a function of surface age. The diffusion coefficient, which correlates with the diffusion rate for short surface ages (up to a few tenths of a second), can be determined from the measuring curve. The time and value of the highest rate of reduction of surface tension provide further information about the dynamic behavior. Both quantities can be obtained using an evaluation according to Rosen [1].

The measured curve of SFT with respect to time and the above-mentioned parameters provide important information about the kinetic properties of a surfactant which can be used to optimize the technical process. Typical time ranges for some dynamic interfacial processes are listed in Table 1 [2]:

| <b>Application / Process</b>                         | <b>Surface age (ms)</b> |
|--|-------------------------|
| Analytical determination of surfactant concentration | 1 - 10000               |
| Polymer dispersions in coating processes             | 10 – 100                |

|   |          |
|---|----------|
| Agro-spray applications                     | 20 – 300 |
| Foam flotation - separation of minerals     | 10-1000  |
| Printing and painting                       | 200-600  |
| Wetting of textile fibers, "spin finishing" | 10       |

Tab. 1: Overview of application and time ranges for the dynamics of surfactants

## Theoretical principles

In the ideal case, the initial SFT  $\sigma$  of the freshly formed surface of a surfactant solution is the same as that of the solvent. The equilibrium value of the SFT is not achieved until after a certain time. This time can range from milliseconds to hours depending on the surfactant structure, concentration and temperature.

The surface excess concentration  $\Gamma$ , which is the decisive factor for the reduction of SFT, is affected by the dynamics of diffusion, adsorption and desorption of the surfactant molecules at the interface. Different mechanisms for this process are discussed in the literature [3, 4].

### Diffusion coefficient

The Ward and Tordai model [5] does not take into account possible obstacles to adsorption, and describes the diffusion of surfactant molecules from the bulk phase to the surface and the back diffusion to the bulk phase when the surface is completely occupied with surfactant molecules. The surface excess concentration  $\Gamma$  is shown as a time-dependent function:

$$\Gamma = 2c_0 \left( \frac{Dt}{\pi} \right)^{0.5} - 2 \left( \frac{D}{\pi} \right)^{0.5} \int_0^{\sqrt{t}} c_s(t-\tau) d\tau^{0.5} \quad (1)$$

$c_0$  = Bulk (volume) concentration;  $c_s$  = Subsurface concentration (concentration in a thin boundary layer below the surface); D = Diffusion coefficient;  $\tau$  = Integration variable; t = Time

Taking into account the Henry isotherms for determining  $\Gamma$  and  $\sigma_t$  or  $\sigma_0$ , from Equation 1 Joos and Rillaerts [6] have derived a diffusion-controlled model for non-ionic surfactants of low concentration and short times (< 100 ms):

$$\sigma_t = \sigma_0 - 2RTc \left( \frac{D \cdot t}{\pi} \right)^{0.5} \quad (2)$$

$\sigma_t$  = SFT at surface age t;  $\sigma_0$  = SFT of the pure solvent; R = Gas constant; T = Absolute temperature; c = Molar surfactant concentration; D = Diffusion coefficient

In this model, the time for adsorption is ignored, as initially the surface is coated with hardly any surfactant molecules and adsorption proceeds unhindered. In this phase, the diffusion of the molecules to the surface is the rate-determining step ( $r_{ts}$ ), enabling the process to be characterized by means of the diffusion coefficient D.

The Ward and Tordai model can also be used to describe the adsorption process for greater surface ages ( $t \rightarrow \infty$ ) and higher surface excess concentrations. Here, the  $r_{ts}$  is the absorption at the interface. An adsorption coefficient corresponding to this phase can also be determined using the LabDesk software.

### Timing according to Rosen

The definition of a diffusion-dominated and an adsorption-dominated time range describes limiting cases of the time during which diffusion, adsorption and desorption compete with one another. Hua and Rosen [1] have modelled the transition from the initial SFT to the equilibrium value in the following equation:

$$\sigma_t = \sigma_m + (\sigma_0 - \sigma_m) / [1 + (t/t^*)^n] \quad (3)$$

$\sigma_m$  = Interfacial tension in meso-equilibrium;  $t^*$  = Time of the transition to meso-equilibrium

Meso-equilibrium describes the surface age range after the time  $t^*$  in which the rate of surface coating reduces. The greatest rate of reduction of SFT is reached at the time  $t^*$ .

The maximum rate of reduction  $v_{max}$  of the SFT can be determined according to Equation 4 by differentiating Equation 3 with respect to t and substituting t by  $t^*$ :

$$-\left( \frac{d\sigma_t}{dt} \right)_{max} = v_{max} = \frac{n(\sigma_0 - \sigma_m)}{4t^*} \quad (4)$$

The parameter  $t^*$  provides important information on the time-related behavior of a surfactant, and the parameter  $v_{max}$  on the effectiveness of the surfactant with regard to the SFT-reducing effect.

## Experimental part

### Measuring methods

The CMCs of the surfactants under investigation were determined fully automatically at 20°C with the help of the Wilhelmy plate method using a KRÜSS K100 tensiometer combined with a double dosing unit.

Measurements of the dynamic SFT were carried out with the KRÜSS Bubble Pressure Tensiometer – BP100. This instrument measures the SFT on freshly produced surfaces using the maximum bubble pressure method. With the BP100, the surface age can be specified over a wide measuring range, enabling the SFT to be measured as a function of surface age.

The diffusion coefficient D was determined in accordance with Joos and Rillaerts with the help of the KRÜSS LabDesk tensiometer software. A plateau region for D, in which the calculated value is not yet dependent on the surface age, was determined in the software evaluation module.

### Samples under investigation

The samples were non-ionic surfactants of the Imbentin type (Dr. W. Kolb AG, Hedingen Switzerland):

- Linear and branched alcohol ethoxylates (symbol C<sub>x</sub>E<sub>y</sub>; x and y represent the respective number of atoms or groups)

- Linear and branched alcohol ethoxylate propoxylate/butoxylate adducts (symbol CxEO-PO/BO)

| <b>Surfactant</b> | <b>Symbolic structure</b> |
|-------------------|---------------------------|
| C13EO8            |                           |
| C11EO7            |                           |
| C10EO6            |                           |
| C9-11EO-PO/BO     |                           |
| C8-10EO-PO/BO     |                           |

Tab. 2: Symbolic structure of surfactants used

The concentration of the surfactant solutions was 0.1g/L in each case. The measurements on all surfactant solutions were carried out at 20°C; the temperature dependency of the dynamic SFT in the range between 20 and 60°C was also determined for the surfactant C9-11EO-PO/BO.

## Results and discussion

### CMC measurements

Table 3 contains the CMC values determined for the surfactant group.

| <b>Surfactant</b> | <b>CMC (mg/l)</b> |
|-------------------|-------------------|
| C13EO8            | 75.5              |
| C11EO7            | 406.8             |
| C10EO6            | 351.1             |
| C9-11EO-PO/BO     | 344.4             |
| C8-10EO-PO/BO     | 462.1             |

Tab. 3: CMC values of the surfactants under investigation

With regard to CMC, the surfactant C13EO8 is the most efficient active substance in the group under investigation. Together with the two other ethoxylates, C13EO8 can also be categorized as effective with regard to the maximum reduction of SFT (effectiveness) (Fig. 1).

At first glance, the two propoxylate/butoxylate adducts appear to be less effective, as the maximum reduction in SFT is less and is only achieved at high concentrations.

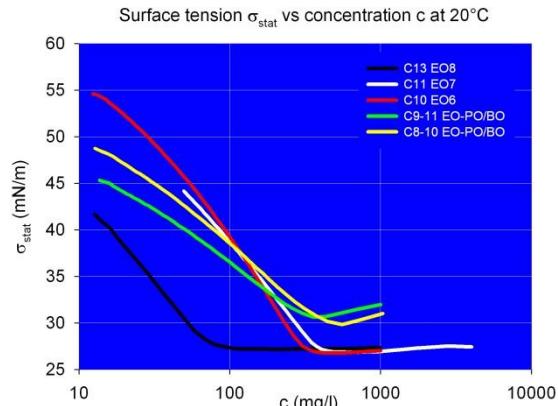


Fig. 1: Static SFT as a function of concentration

### Dynamic surface tension

Consideration of the dynamic SFT gives a different picture. Figure 2 shows the time-dependent reduction in SFT at 20°C for the five surfactants under investigation.

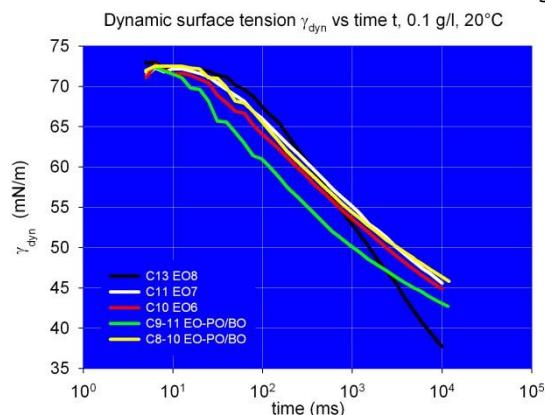


Fig. 2: Dynamic SFT as a function of surface age

The surfactants hardly differ in the surface age range up to 0.01 seconds. After this, the curves diverge, wherein the ethoxylates with larger chain length tend to deviate later from the plateau value and start to have an effect correspondingly later. The most effective surfactant in the group is initially the linear propoxylate/butoxylate adduct C9-11 EO-PO/BO. Only at surface ages above about two seconds does the long-chain ethoxylate C13EO8 become the most effective surfactant.

## Temperature dependency

An increase of effectiveness which is similar to that as a function of surface age can be seen with temperature-dependent measurements (Fig. 3).

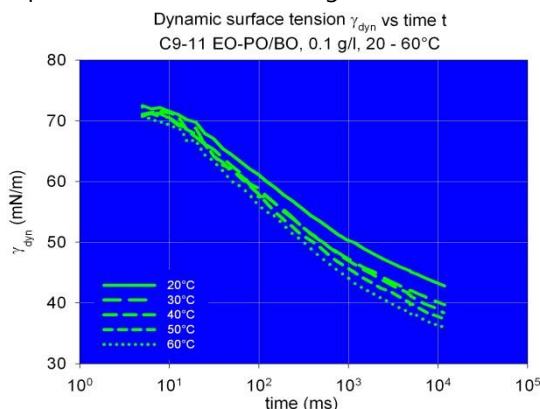


Fig. 3: Dynamic SFT at different temperatures

Heating has hardly any effect on the initial SFT. Temperature clearly starts to affect the SFT from approx. 50 ms and becomes increasingly significant at greater surface ages. The process time should therefore be taken into account when assessing the efficiency of a surfactant at a given process temperature.

## Diffusion coefficients

From Table 4, it can be seen that the diffusion coefficient of the alcohol EO-PO/BO adducts is greater than that of the alcohol ethoxylates.

| Surfactant    | D ( $m^2 s^{-1}$ ) |
|---------------|--------------------|
| C13EO8        | 2.0E-09            |
| C11EO7        | 1.9E-09            |
| C10EO6        | 1.6E-09            |
| C9-11EO-PO/BO | 1.0E-08            |
| C8-10EO-PO/BO | 4.7E-09            |

Tab. 4: Diffusion coefficients of the samples under investigation

The branched adduct C9-11EO-PO/BO has the highest diffusion coefficient. It is the most quickly diffused surfactant in the group.

## Fit according to Hua and Rosen

Table 5 shows the parameters for establishing meso-equilibrium determined from the fit according to Hua and Rosen.

| Surfactant    | $\sigma_m$ (mN/m) | t* (s) | $v_{max}$ (mN/m $s^{-1}$ ) |
|---------------|-------------------|--------|----------------------------|
| C13EO8        | 38.43             | 0.93   | 6.71                       |
| C11EO7        | 28.71             | 0.52   | 4.47                       |
| C10EO6        | 29.23             | 0.39   | 3.15                       |
| C9-11EO-PO/BO | 28.75             | 0.21   | 3.33                       |
| C8-10EO-PO/BO | 26.56             | 0.36   | 3.63                       |

Tab. 5: Dynamic SFT parameters according to Hua and Rosen at T = 20°C

The lower t\* value for the two ethoxylate adducts with simultaneously low meso-equilibrium value  $\sigma_m$  indicates a greater effectiveness in the reduction of dynamic SFT. The greater effectiveness of the surfactant C13EO8 at longer times shown in Fig. 2 is corroborated by the results in Tab. 5: The value of the highest rate of SFT reduction  $v_{max}$  is the greatest, but this maximum rate is achieved later than with all other samples.

## Summary

As well as static tensiometry, dynamic investigation of the time-related behavior is important when assessing the effectiveness of surfactants which are to be used in dynamic processes.

A comparison of CMC measurements with bubble pressure measurements on a group of linear and branched alcohol ethoxylates and alcohol ethoxylate-propoxylate/butoxylate adducts has illustrated that the assessment of the effectiveness of surfactants is highly dependent on the surface age. CMC measurements using the static Wilhelmy method showed that the branched ethoxylate C13EO8 has the highest efficiency and effectiveness with regard to the reduction of SFT in the long term range. At the same time, the alcohol ethoxylate-propoxylate/butoxylate adducts exhibit the lowest reduction in SFT.

The picture is reversed when it comes to the short term range: Dynamic measurements of 0.1% solutions of the surfactants and the corresponding parameters D, t\* and  $v_{max}$  showed the best performance for the adduct C9-11EO-PO/BO at surface ages up to 2 s.

## **Source / Acknowledgement**

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*Möhle, H. L.: Dynamic interfacial properties of non-ionic surfactants. SÖFW-Journal, 130, 3(2004).*

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