# Application Report

## Studies on the Stability of Foams

Application report: AR267e
Industry: Surfactants, food
Author: Dr. Ch. Bilke-Krause
Dipl.-Phys. T. Schörck
Dr. T. Winkler
Date: May 2010

Dynamic Foam Analyzer – DFA100

Drop Shape Analyzer – DSA100R

Method:

Keywords: Foam Stability, Foamability, Interfacial Rheology, Surfactants

## Foam behavior and foam stability of aqueous surfactant solutions

### Abstract

Industrial production and cleaning processes place high demands on the surfactants used. In addition to temperature and pH stability, a defined foam formation and stability behavior is required which covers a broad range of capacities and times.

In many areas, for example in flotation separation methods or in foam cleaning, foams are deliberately generated. In other areas foams have an interfering effect and must be avoided: They adversely affect mixing processes by the formation of a foam phase, increase the volume to be transported, influence flow properties or result in a poorer end product, for example in painting processes. This is why foamability and foam stability provide important information.

Foamability and stability data used for liquid foams are frequently limited to a particular measuring range. For example, the waiting periods required for Ross-Miles values cannot be observed for unstable foams, because the foam has already broken down completely. In many methods foam generation also cannot be carried out reproducibly, although this is essential for making a user-independent and location-independent comparison of parameters. The Dynamic Foam Analyzer – DFA100 works with foam generation conditions that can be standardized and provides the foam parameters $t_{dev}$ and $t_{tr}$, which describe stable foams and foams with a very short life using a phase model oriented on the decay process. In this way differentiation is possible between a pure drainage phase, followed by a drainage phase with parallel decay, and finally a third phase in which only decay occurs and in which drainage has been completed.

This paper investigates three surfactants with low to good foam formation tendencies. The foaming and stability behavior of the surfactant solutions could be characterized by the maximum foam height $h_{max}$ and the parameter $t_{dev}$, both measured with the DFA100. Comparative interfacial rheology measurements provided a good correlation between the interfacial rheology parameters and the data from the foam measurements.

## Experimental part

### Studied surfactants

Surfactants with low to good foamability include the successfully used so-called cryptoanionic alkyl polyglycol ether carboxylates[1], which can be adapted to suit the particular requirements for hydrophobic or hydrophilic behavior by varying the chain lengths of the hydrophobic alkyl group and the polar polyether chain.

The surfactants used in this study had the following structures:

| | |
|---|---|
| **A** | $H_3C\text{-}(CH_2)_{11\text{-}13}\text{-}O\text{-}(CH_2CH_2\text{-}O)_{4,5}\text{-}CH_2COONa$ |
| **B** | $H_3C\text{-}(CH_2)_{11}\text{-}O\text{-}(CH_2CH_2\text{-}O)_{4,5}\text{-}CH_2COONa$ |
| **C** | $H_3C\text{-}(CH_2)_{7}\text{-}O\text{-}(CH_2CH_2\text{-}O)_{5}\text{-}CH_2COONa$ |

Surfactant A consists to 65-70% of molecules with a $C_{12}$ chain and to a maximum of 25% of molecules with a $C_{14}$ chain. In contrast, Surfactant B consists to at least 98% of molecules with a $C_{12}$ chain and Surfactant C to at least 98% of molecules with a $C_8$ chain. It was expected that foam stability would decrease from A to C (manufacturer's information).

Measurements of the surfactants were made in a 0.01% w/w aqueous concentration – for all samples the concentration was considerably below the CMC. The solutions had a pH = 6 and a viscosity of 0.98 mPas. The measuring temperature was 21°C.

### Foam characterization

The measurements of the foamability and the determination of the parameter $t_{dev}$ were made[2] using the Dynamic Foam Analyzer – DFA100.

### *1. Setup and measuring procedure*

In each case 50 ml of the particular surfactant solution was placed in the sample vessel of the DFA100 (Fig.1a).

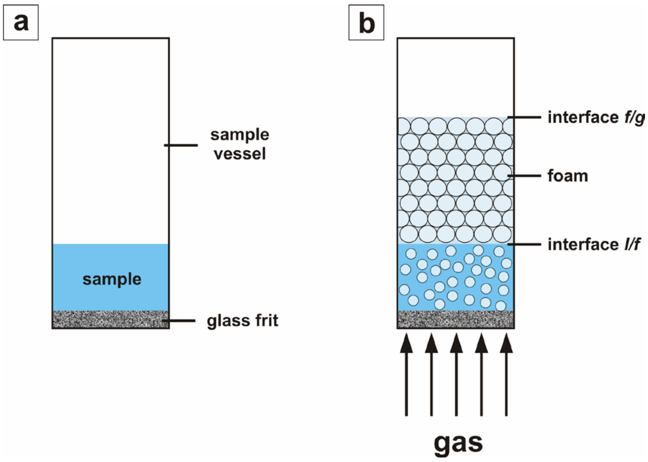

Fig. 1: Working principle of the Dynamic Foam Analyzer – DFA100.

Air was passed through the porous sample vessel base (G2; pore size 40 - 100 µm) for 12 s (volume flow Q = 5 ml/s) which resulted in reproducible foam generation (Fig. 1b). During foam generation and afterwards the height of the liquid column $h_l$ ("l" for "liquid") and the foam column $h_f$ ("f" for "foam") were followed *in situ* by measuring the light transmission as a function of time (Fig. 2).

In the DFA100 the measurement is made by using an LED panel and a photo detector between which the column is located. The liquid and gas phases are light-permeable; the phase boundaries liquid / foam (l/f) and foam / gas (f/g), i.e. the upper and lower limits of the foam column, are detected by the changes in Intensity (Fig. 2).

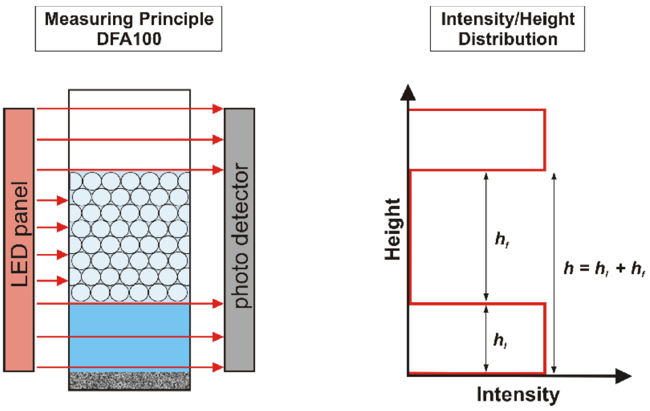

Fig. 2: Working principle of the DFA100.

During foam generation the foam height $h_f$ increases continuously while the liquid height $h_l$ decreases (Fig. 3).

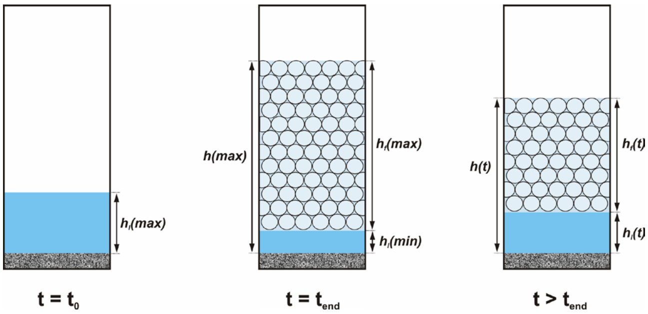

Fig. 3: Variation of the quantities $h_l$, $h_f$ and $h$ with time.

The reason for this is that during foam generation liquid is bound in the foam phase, which reduces the volume of the liquid initially present. At the same time the total height $h$ ($h = h_l + h_f$) also increases as a result of the volume of gas bound in the foam.

At the end of the foam generation time ($t = t_{End}$), $h$ and $h_f$ have a maximum value and $h_l$ has a minimum value. As time continues ($t > t_{End}$), a decay of the foam column occurs; $h$ and $h_f$ decrease and liquid height $h_l$ again increases.

### *2. Determining the parameters $t_{dev}$ and $t_{tr}$*

Foam decay occurs in three time-related phases. At first liquid flows out of the foam column b (= drainage) without destroying the column. In this phase the total height *h* remains constant, as the reduction in the foam column $h_f$ is exactly compensated by the increase in the liquid level $h_l$. The end of the first phase of drainage alone is known as $t_{dev}$ (deviation time; corresponds to the start of decay).[3] In the second phase the foam starts to collapse, while the drainage process is continuing. During this phase the total height *h* decreases. The end of this phase is known as $t_{tr}$ (transition time; corresponds to the end of drainage). In the third phase drainage has been completed to a large extent, and the foam height is reduced primarily because of the bursting of the lamellas. The total height in this phase decreases at a slower rate than in phase 2.

A mathematical model was adapted to the curve of the decay process. In the characteristic curve of the total height *h* (Fig. 4), $t_{dev}$ can be read off from the start of the reduction of the total height and $t_{tr}$ from the point of inflection.

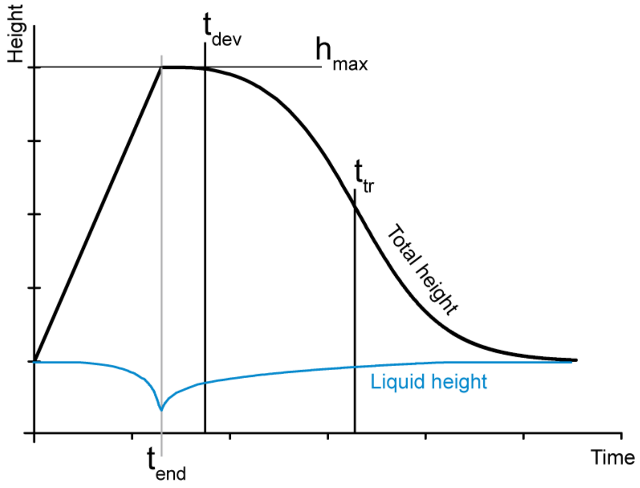

Fig. 4: Determining the foam generation and decay processes using the heights *h* and $h_l$.

Both $t_{dev}$ and $t_{tr}$ are a measure of the stability of a foam: The higher the numerical value, the more stable the foam.[2]

The foamability of a surfactant solution can be correlated directly with the maximum value of the total height $h_{max}$.

## Interfacial rheological measurements

A KRÜSS DSA100R instrument was used for the interfacial rheological measurements.

The interfacial rheological properties of the surfactants used were studied by the "*Oscillating Spherical Drop Method*" (OSDM).[4] In this method the pressure of the curved surface resulting from the surface tension (Laplace pressure) is measured in a spherical drop that is oscillating sinusoidally. In solutions of surface-active substances the surface tension calculated from the pressure is a function of time and surface area. From the surface tension curve the complex interfacial dilatation modulus E*, the modulus of elasticity (storage modulus) E′ as well as the modulus of viscosity (loss modulus) E′′ are determined. The relationship between these quantities is: $E^* = E' + iE''$. A relationship between E* and the foam stability could be demonstrated for the selected surfactant systems.[5-10]

The measurements presented here were made at an oscillation frequency of 0.2 Hz.

## Results

Measurements on surfactant solutions A, B and C could show that the foam stability behavior known to the manufacturer can be represented by using the new parameter $t_{dev}$, which correlates with the foam stability. This result could be confirmed by interfacial rheological investigations of the three surfactants.

## Foamability

The foamability can be read off directly from the maximum foam height at the end of the foam generation time (Fig. 5).

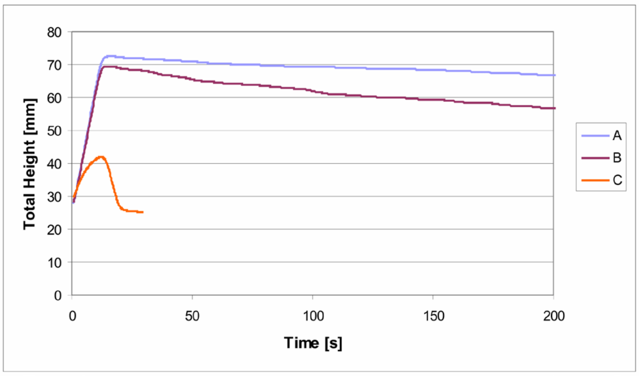

Fig. 5: Time-dependent curve of the total height h for aqueous solutions of surfactants A, B and C (c = 0.01% w/w).

The foamability associated with the $h_{max}$ value decreased in the following sequence:

**A** ≥ **B** >> **C**

## Foam stability

The evaluation of the stability of the foams using the parameter $t_{dev}$ determined from the curves (Fig. 6) produced a similar correlation

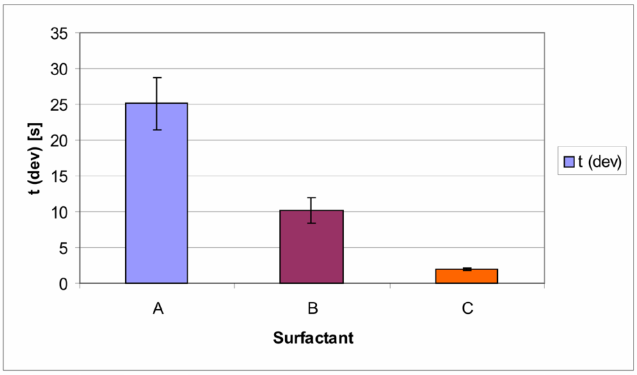

Fig. 6: Deviation Time $t_{dev}$ for aqueous solutions of surfactants A, B and C (c = 0.01% w/w).

From Fig. 6 it can be clearly seen that $t_{dev}$ and therefore the foam stability decreases in the sequence:

**A** > **B** > **C**

At the same time it could be seen that surfactants A and B, with comparable foam formation behavior (see Fig. 5), showed clear differences in their stability behavior. It is possible that the differing chemical composition of surfactants A and B has a greater influence on the stability than on the foamability.

## Interfacial dilatation modulus

In order to compare the results of the foam measurement with those of a second independent method, the three surfactant solutions were characterized by OSDM measurements. Fig. 7 shows the parameters E*, E′ and E′′ obtained.

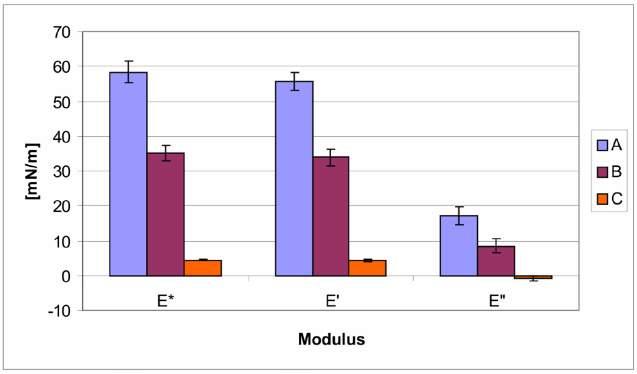

Fig. 7: Interfacial dilatation modulus E*, modulus of elasticity E′ and loss modulus E′′ for aqueous solutions of surfactants A, B and C (c = 0.01% w/w).

The parameter E* describes the stability of the foams. The following applies: The higher the numerical value of E*, the more stable the foam. E′ is the so-called modulus of elasticity, for which a relationship with liquid drainage has been determined in many papers.[5-10] E′ should therefore have a close relationship with parameter $t_{dev}$.

The physical phenomenon of foam behavior that is described by the loss modulus E′′ is currently being studied. That a high value of E′′ is associated with a high value for the foam stability has been shown, for example, by studies on fatty acid solutions.

Two important facts can be obtained from Fig. 7: In the first place the values of E* confirm the stability sequence **A** > **B** > **C**, which was determined by foam measurements. In the second place the data shows that for all three surfactants the quantity E* was strongly dominated by parameter E′, which indicates that drainage has a great influence on foam stability. In the case of the surfactants studied here the drainage parameter $t_{dev}$ is therefore well-suited for describing the foam stability.

A relative comparison between the drainage parameters $t_{dev}$ and E′ shows an excellent to good agreement for all three surfactants (Fig. 8).

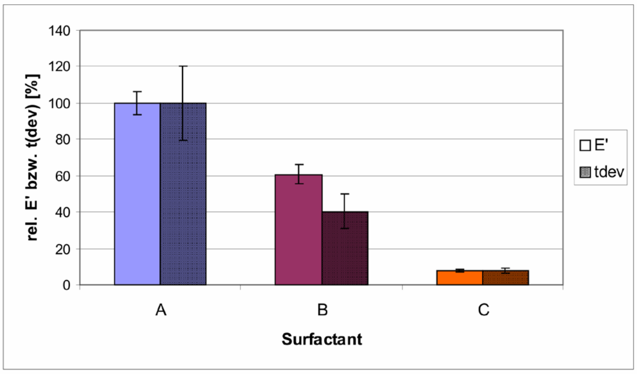

Fig. 8: Relative comparison of drainage parameters $t_{dev}$ and E′.

As a result there is a direct relationship between the parameter $t_{dev}$ and the modulus of elasticity E′ for the surfactants studied here.

## Summary

The foam parameters measured with the DFA100 describe the start of foam decay following a drainage-dominated phase ($t_{dev}$) and the transition to a decay-dominated phase with negligible drainage ($t_{tr}$).

The parameter $t_{dev}$ was determined for three alkyl polyglycol ether carboxylate solutions; these had a slight to good foam formation tendency. The expected differences in foamability and foam stability could be demonstrated by using the maximum foam height $h_{max}$ and the parameter $t_{dev}$, which is associated with the foam stability. For surfactants A and B clear differences in foam stability were found, although their foamability was comparable.

The stability sequence **A** > **B** > **C** obtained from the results for $t_{dev}$ showed a good correlation with the parameters E* (interfacial dilatation modulus) and E` (modulus of elasticity) obtained from OSDM measurements.

This means that the parameter $t_{dev}$ has proved to be suitable for the characterization of surfactant solutions.

## Preview

With the surfactants studied here the parameter E*, which can be correlated with foam stability, was dominated by the modulus E', which is associated with drainage. In this case the correlation with parameter $t_{dev}$, which also describes drainage behavior, could be demonstrated.

In future work a check should be made as to whether the parameter $t_{dev}$ shows the same clear relationship with the stability criterion E* when E* is dominated by the loss modulus E''.

*The authors would like to thank Dr. Horst Denzer from Kao Chemicals GmbH for providing the samples, the lively exchange of ideas and for permission to publish the data.*

## Literature

[1] H. Denzer, „Cryptoanionische Alkylpolyglycolethercarboxylate“, SEPAWA Kongressheft zum 56. SEPAWA Kongress in Würzburg, **2009**.

[2] K. Lunkenheimer, K. Malysa, G. Wienskol, B. Baranska. European Patent Bulletin of 16.01.2008 (Art. 97(3) EPC), European Patent No. 1 416 261

(03 024 885.0) (Application EPA 02024377, 31.10.02).

[3] K. Lunkenheimer, K. Malysa, K. Winsel, K. Geggel, S. Siegel, „Novel Method and Parameters for Testing and Characterization of Foam Stability“, Langmuir, **2010**, 26, 3883-3888.

[4] S.C. Russev, N. Alexandrov, K.G. Marinova, K.D. Danov, N. D. Denkov, L. Lyutov, V. Vulchev, C. Bilke-Krause, “Instrument and methods for surface dilatational rheology measurements”, Rev. Sci. Instr. **2008**, 79, 104102.

[5] K. Malysa, R. Miller, K. Lunkenheimer, “Relationship between foam stability and surface elasticity forces: Fatty acid solutions“, *Colloids Surf.*, **1991**, 53, 47-62.

[6] D. Langevin, „Influence of interfacial rheology on foam and emulsion properties“, *Adv. Colloid Interface Sci.*, **2000**, 88, 209-222.

[7] C. Stubenrauch, V. B. Fainerman, E. V. Aksenenko, R. Miller, “Adsorption Behavior and Dilational Rheology of the Cationic Alkyl Trimethylammonium Bromides at the Water/Air Interface“, *J. Phys. Chem. B*, **2005**, 109, 1505-1509.

[8] C. Stubenrauch, Kh. Khristov, Foams and foam films stabilized by $C_nTAB$: „Influence of the chain length and of impurities“, *J. Colloid Interface Sci.*, **2005**, 286, 710-718.

[9] E. Santini, F. Ravera, M. Ferrari, C. Stubenrauch, A. Makievski, J. Kragel, “A surface rheological study of non-ionic surfactants at the water–air interface and the stability of the corresponding thin foam films“, *Colloids and Surf. A: Physicochem. Eng. Aspects*, **2007**, 298, 12–21.

[10] E. Carey, C. Stubenrauch, “Properties of aqueous foams stabilized by dodecyltrimethylammonium bromide”, *J. Colloid Interface Sci.*, **2009**, 333, 619–627.

You can find many more interesting Application Reports on our website under https://www.kruss.de/services/education-theory/literature/application-reports/