APPLICATION NOTE

Stability of cosmetic emulsions quantified with rheology and simultaneous DEA

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Key words
Emulsions, stability, rheology, simultaneous DEA

Introduction
Cosmetic emulsions have to meet consumer demands from many perspectives. They should have the desired effect on the skin, they should have a nice look and feel and they should not change their texture over several months. All these properties are closely related to the long-term stability of an emulsion. Only from a stable emulsion we can expect the active ingredients to stay homogeneously distributed leading to an unchanged look, feel and texture.

The Thermo Scientific™ HAAKE™ MARS™ Rheometer is a versatile universal rheometer that allows combinations with other analytical techniques. For the verification of an emulsion's stability, the integration of a dielectric analysis (DEA) has been selected.

While the HAAKE MARS Rheometer can measure the mechanical properties of an emulsion, the DEA can give information about the microscopic conditions inside the emulsion under precisely defined stresses, deformations and temperatures set by the rheometer.

Regarded in a simplified way, a DEA applies an oscillating voltage to a sample between 2 electrodes and measures the resulting current due to the mobility of charged molecules (ions) in the electrical field. This mobility is influenced by the resistivity of the sample matrix, which is correlated to the viscosity or modulus of the sample. The results of a DEA measurement can be expressed with the so-called ion viscosity, which is the reciprocal ion mobility or reciprocal conductivity of the sample. In other words, the ion viscosity increases when the ion mobility is decreases.

Samples
Two different batches of a skin cream were selected for testing due to their difference in appearance. While one

Fig. 1: A lower measuring plate with Mini IDEX comb sensor.

batch represented the usual quality of the cream with a matt white surface and a rather "solid" appearance, the other had a significantly glossier surface, softer edges and felt softer on the skin.

Test conditions
The tests were performed using a 20 mm plate/plate geometry with a gap of 1 mm. Sample loading was avoiding unnecessary shearing and with reduced lift speed while closing the gap.

A lower measuring plate (TMP) with a DEA comb sensor [1] was used to collect the ion viscosity at different frequencies (Fig. 1). The sensor was connected to a DEA 288 Epsilon (NETZSCH-Gerätebau, Selb, Germany). During the measurements, the NETZSCH Proteus® software was triggered by the Thermo Scientific™ HAAKE™ RheoWin™ Measuring and Evaluation Software at the start of the rheological measurement to guarantee simultaneous data acquisition.

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Because the DEA sensor consists of a pair of interdigitated electrodes, the DEA measurement is independent of the rheometer's measuring gap as long as the gap size is bigger than the distance between the 2 electrodes.

With this setup, an amplitude sweep and a temperature run were done on both samples. The amplitude sweep was performed at 20 °C using the controlled deformation (CD) mode, to have better control of the measurement conditions.

To characterize the temperature dependant behavior, fresh samples were heated up from 0 °C to 40 °C with a heating rate of 1 K/min.

Results and Discussion
The appearance of a cream sold in a container strongly depends on the extent that it flows under its own weight. Another part of consumer perception is related to the cream's handling properties. In other words, how does the cream feel when taking a bit out of the container and rubbing it onto the skin?

Because these properties are related to the force required to make the cream yield, the results of the amplitude sweep have been plotted as a function of the stress applied (Fig. 2), although the measurement has been done with deformation control (CD mode).

The end of the linear viscoelastic range (LVR) has been calculated based on the storage modulus (G') and a 10 % deviation from the plateau value. Between the softer (less stable, open symbols) and the harder (stable, filled symbols) cream lies a factor of about 8 in stress.

Regarding the results from the DEA (Fig. 3), we see an increase of the ion viscosity at higher times which corresponds to higher stresses. The less stable cream shows the earlier increase after 4.8 min when the sample was exposed to a stress of 4.2 Pa, whereas the stable sample shows this increase after 7.2 min or at 40 Pa (stress/time correlation not shown in Fig. 2).

It is interesting to see, that in both cases the onset of the ion viscosity increase occurs at stresses about 4 times higher than the stresses for the end of the LVR calculated from the rheological results. Similar to the rheological results, the onset of the increase differs by a factor of almost 10.
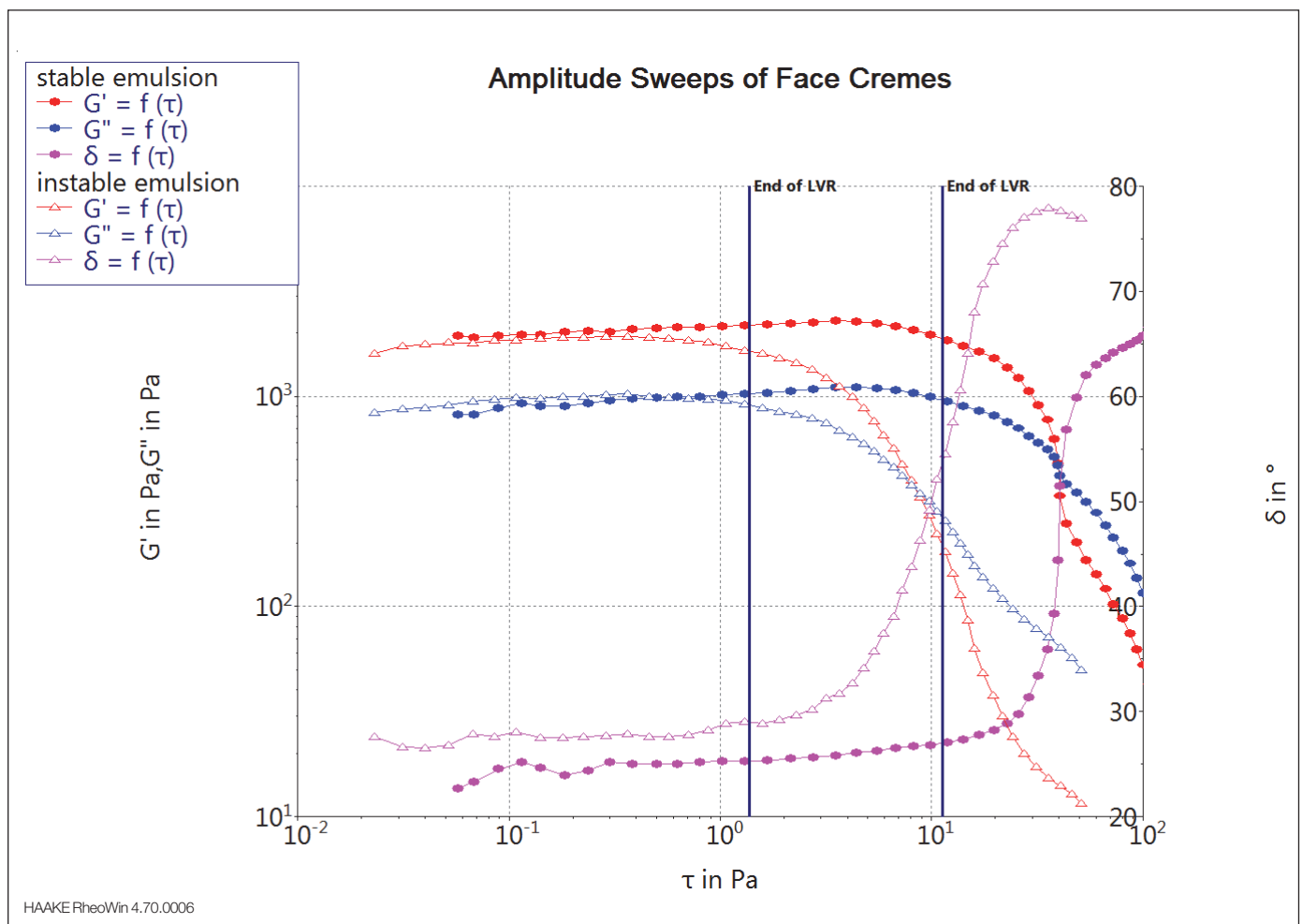

Fig. 2: Results of amplitude sweeps on 2 different cosmetic emulsions with the 2 perpendicular lines indicating the end of the respective linear viscoelastic range based on the storage modulus. For the less stable cream, the LVR ends at 1.4 Pa; for the stable cream it ends at 11.2 Pa.
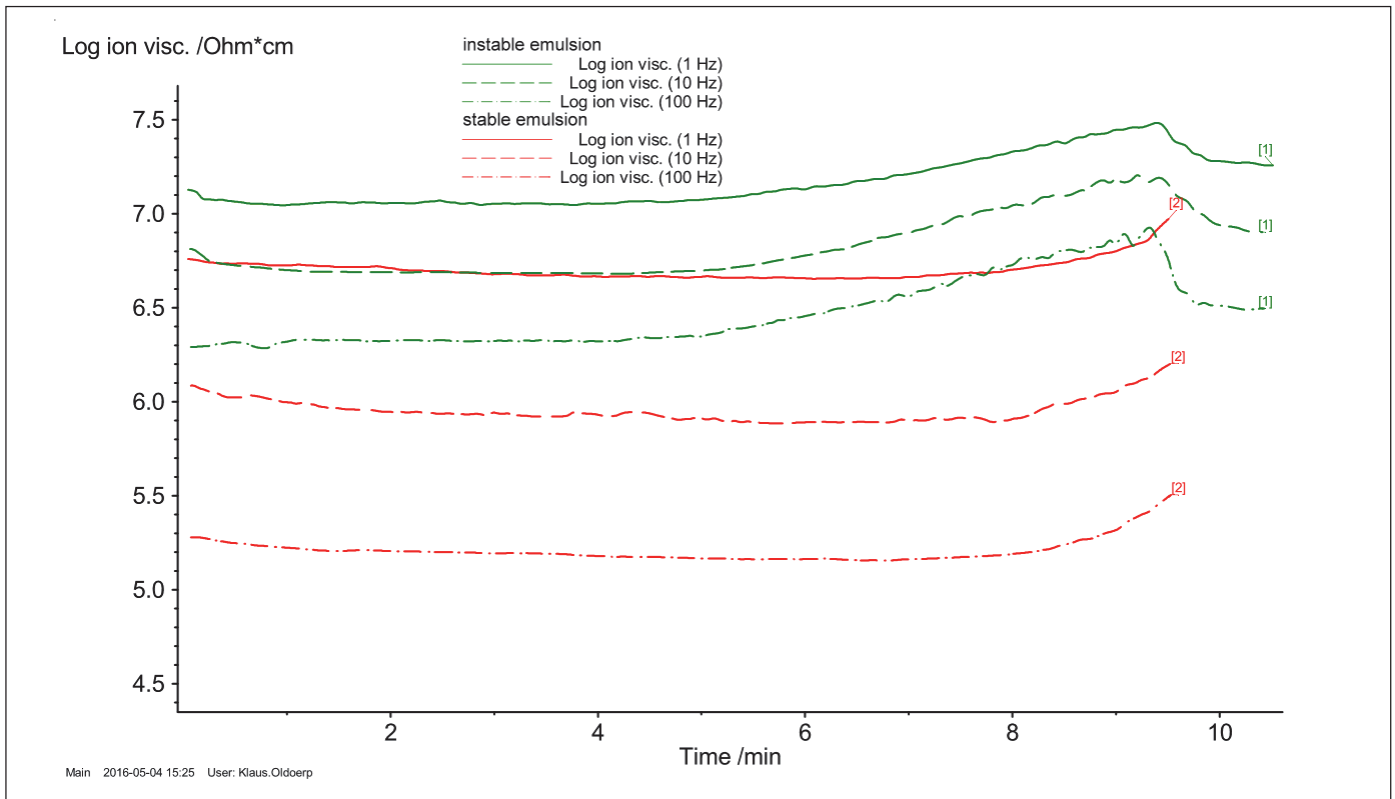
Fig. 3: Results of amplitude sweeps on 2 different cosmetic emulsions. The data is plotted over time since the Proteus software does not read the current rheometer status during the measurement.

Comparing the results from the temperature runs on the rheometer, the 2 creams behave in a similar way, with the less stable cream being less elastic throughout the whole measurement (Fig. 4). After having almost constant elasticity as indicated by the almost constant phase angle (δ), both samples start to lose elasticity above 12 °C. The only significant difference lies in the maximum of δ above 30 °C. At 33 °C the phase angle of the less stable cream reaches a maximum and starts decreasing until the end of the measurement. For the stable cream, the maximum occurs at 35 °C and afterwards the decreasing part of the curve runs almost identical with the curve of the less stable cream.
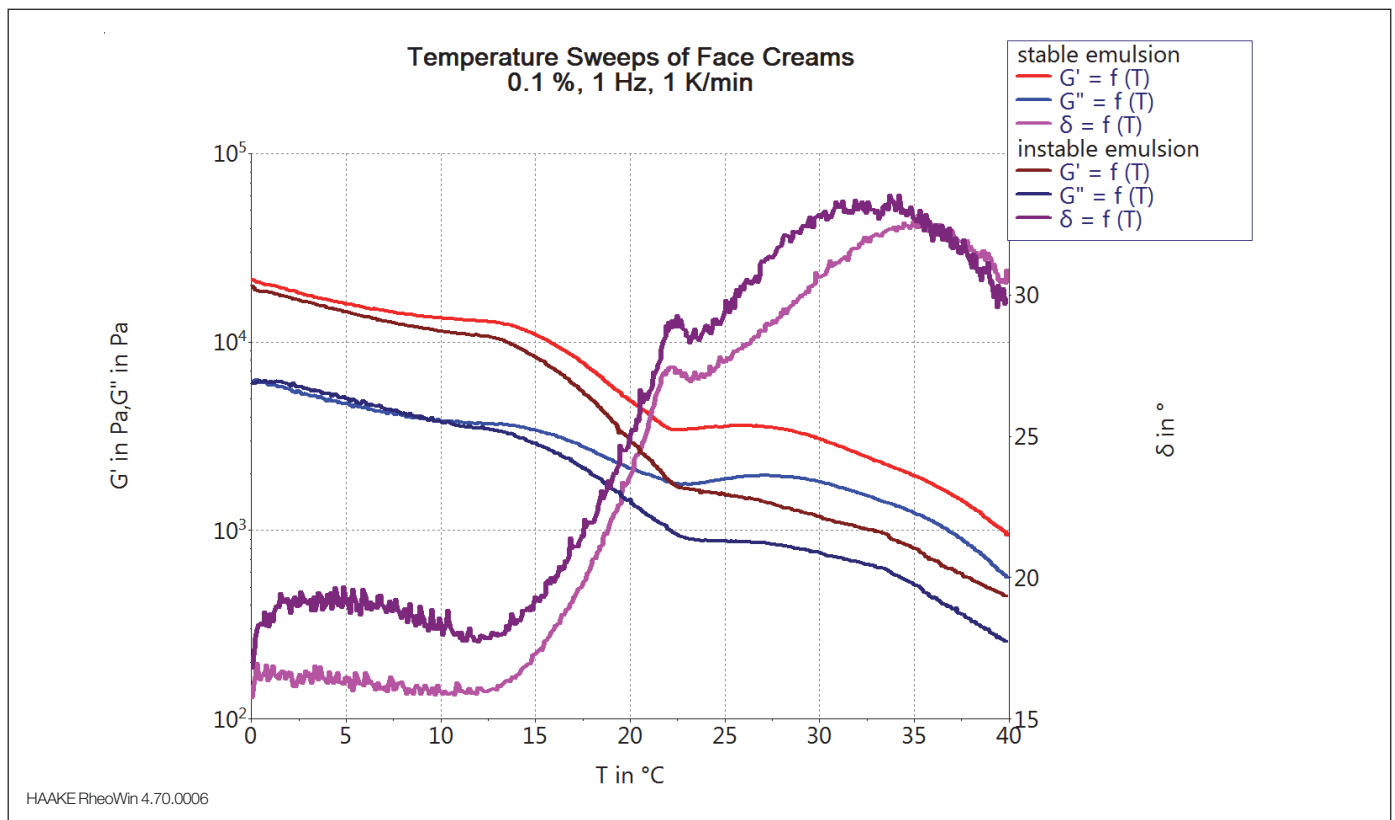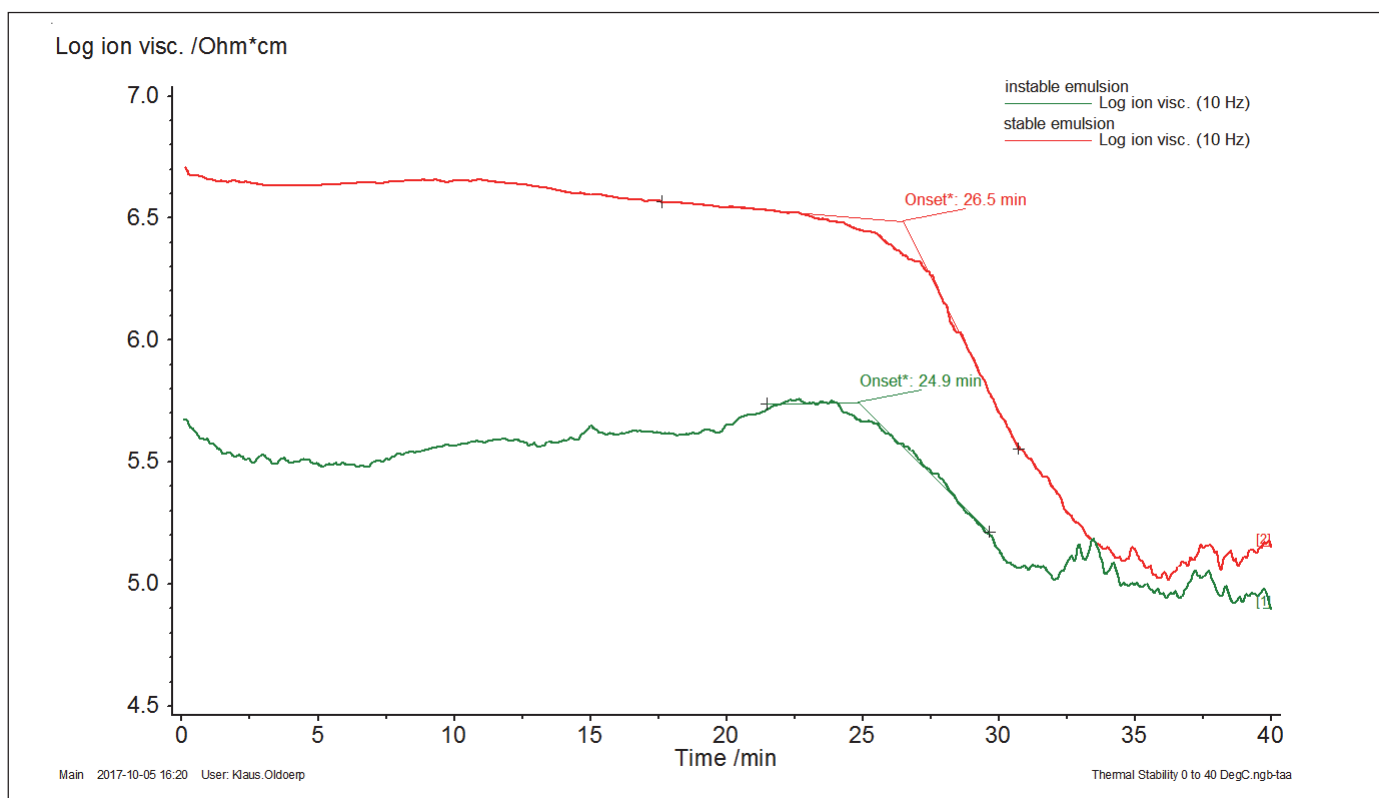

Fig. 4: The change in temperature dependent behavior of both creams is almost the same with the less stable cream being less elastic.

Fig. 5: Results of amplitude sweeps on 2 different cosmetic emulsions. Due to the temperature range from 0 °C to 40 °C, the time axis can accidentally be used as a temperature axis as well.

Comparing the DEA results collected during the temperature increase, the stable cream shows a higher ion viscosity before the values start to drop at 26 °C (Fig. 5). The corresponding curves of the less stable cream already go down from 24 °C on. These changes occur at a temperature, where the rheological curves do not show any similar change. Whether it is a coincidence to find the same temperature difference here, like between the maxima of the phase angle in Fig. 4, cannot be answered based on the data available here.

The DEA results confirm the finding that the behaviour of both creams becomes the same above 34 °C. A possible interpretation of the combined information could be that the stable cream has a better homogeneity with smaller droplets of the aqueous phase, which would explain the higher initial ion viscosity. The less stable cream seems to have a more coherent water phase from the beginning on and therefore the lower initial ion viscosity. Above 34 °C the temperature-induced coalescence leads to the same conditions in both creams and hence the same properties.

Summary

With the HAAKE MARS Rheometer, the two different creams were successfully characterized. The visual difference between both products was confirmed with significant differences in their mechanical response to different forces (stresses) and temperatures. The results from the DEA delivered additional information which helped to explain why the differences exist. Understanding why differences exist can be used as a starting point to analyze why the differences appeared based on the formulation, temperature history, homogenization technique used or other process parameters.

Reference

[1] Thermo Fisher Scientific product information P060 "Standard measuring geometries with integrated DEA-sensor for the HAAKE MARS rheometer plaform" Cornelia Küchenmeister-Lehrheuer, Klaus Oldörp

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