Application Report

Interfacial rheology with high-viscosity oils

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Method:

DSA100R
(Interfacial Rheology)

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Interfacial rheology measurements on an oil/water system with high-viscosity oils

Abstract

Interfacial rheology describes the change of the surface and interfacial tension, and surfactant adsorption, upon surface area variations, like those encountered in sheared foams and emulsions. There are several methods allowing a controllable deformation and simultaneous measurement of the surface tension; however, all of them are not directly applicable to high-viscosity systems. This article describes successful surface rheology measurements at the interface between aqueous surfactant solutions and silicone oils with differing viscosities (5 to 10,000 mPa s) using a pressure detection tensiometry and oscillating spherical drops.

Interfacial rheology applications

The rheological behavior of interfaces has a great influence on the dynamic properties of foams and emulsions – for example, on their resistance and stability during flow. This is why the relatively young branch of interfacial rheology is meeting with increasing interest that extends beyond basic scientific research.

Measuring methods

The KRÜSS DSA100R module for interfacial rheology provides two basic methods for surface deformation: the Expanding Drop Method (EDM) and the Oscillating Drop Method (ODM). In addition, two measuring methods can be used: Drop Shape Analysis (DSA) and Spherical Drop Analysis (SDA, i.e. pressure tensiometry).

EDM

In the EDM measurement the interface of a spherical drop (in a gaseous or liquid surrounding phase) is enlarged or reduced in a step-wise manner. At the same time the interfacial tension value is followed as a function of deformation and time. The interfacial tension (IFT) is obtained by measuring the capillary pressure, i.e. by SDA. The relation between the change of the IFT and the area could be afterwards described with a rheological relation in order to obtain the surface elasticity E and viscosity η [1].

ODM

In the ODM measurement the interface of a drop (immersed in gaseous or liquid surrounding phase) is altered at a defined frequency and amplitude in the form of a sine-wave. When a surfactant is present on the oscillating interface, the interfacial tension also changes sinusoidally, with a phase shift to the area oscillation. The result of the measurement is the complex modulus E^*, which consists of two components: the modulus of elasticity (storage modulus) E' and the modulus of viscosity (loss modulus) E''. The first describes the dependency of the IFT on the extent of interface alteration, the second the dependency on the speed of interface alteration.

DSA

The DSA method is based on the fact that, from a particular size onward, the shape of a pendant drop varies significantly from a sphere because of the effect of gravity. The interfacial tension is calculated from an optical evaluation of the drop shape by the Young-Laplace method.

SDA

The SDA method works with smaller, virtually spherical drops; the interfacial tension is measured via the capillary pressure.

The DSA method has been in use for a long time, but has its limitations:

a) when the viscosity of the surrounding phase is high, or the difference in density between the phases is small;

b) when the surrounding phase is opaque or the difference in the refractive indices of the phases is very similar, so that an optical analysis is impossible;

c) when the necessary frequency is so high that it cannot be used with a pendant drop.

Such difficulties can be mastered by the SDA method – as this article demonstrates, even with high-viscosity silicone oils.

Experimental section

Investigated systems

A series of silicone oils produced by Rhodia was used as (surrounding) oil phase; these had the following viscosities: 5, 50, 195, 1000, 2500 and 10000 mPa s. Because the oils were chemically homologous we were able to exclude chemically caused alterations to the interfacial tension to a great extent.

In each case the drop phase consisted of a 0.1 millimolar solution of the anionic surfactant sodium dodecyl sulfate (SDS, Acros) with 150 mmol sodium chloride, or a 0.01% w/w solution of bovine serum albumin (BSA; Sigma). These surfactants were selected in order to determine whether the measuring method can be used for structurally completely different surfactants with very different molar masses and different areas of application (e.g. SDS in personal care products, and BSA in food and medical applications).

Selected measuring parameters

Theoretical considerations [2-6] state that high-viscosity oils can be measured by determining the pressure by the SDA method in a suitable frequency range, using a suitable measuring setup. In our measurements we used frequencies of 1 Hz and below (1; 0.5; 0.2; 0.1 and 0.05 Hz). The high-viscosity liquid was used as the surrounding phase in order to minimize dynamic effects during oscillation [2].

Under the assumption that the contributions of all dynamic pressure components (e.g. the shear viscosity of the drop, the Poiseuille flow, etc.; [s. 2-6]) are negligible, measurements were carried out using the SDA method on both aqueous solutions with the oils in the viscosity series. After data analysis as per the quasi-static measured values [1] for the modulus of elasticity E'_M (index "M" for "measured") and the modulus of viscosity E''_M were obtained.

Viscosity correction

The influence of the dynamic pressure contribution of the shear viscosity of the surrounding phase on the modulus of viscosity E'' was taken into account by further processing of the raw data in order to obtain viscosity-corrected moduli. An analysis using several approaches [2] showed that this target could be achieved by using the following simple equation:

$$E'' = E''_M - \chi\omega\left(\eta_{out} - \eta_{inn}\right)\frac{R_{s,0}^2}{2r_c}$$

where ω is the angular frequency of oscillation, η_{inn} and η_{out} are the viscosities of the inner and outer phase and R_s is the drop radius. Index “0” indicates that the value of the corresponding quantity at the starting point is used. χ is a parameter that depends on the drop shape and, in particular, on the relationship between the drop height H_S and the capillary radius r_c; i.e. $\chi = \chi\left(H_s/r_c\right)$ [2,5,6].

Results

The modulus of elasticity E'_M and the modulus of viscosity E''_M are shown in Figs. 1 and 2 for the measuring series with 0.01% w/w BSA solution, in each case as a function of the oscillation period.

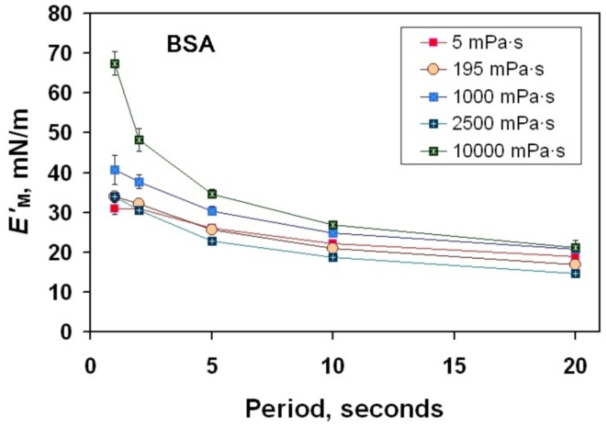

Fig. 1: Modulus of elasticity E'_M for BSA at different oscillation periods

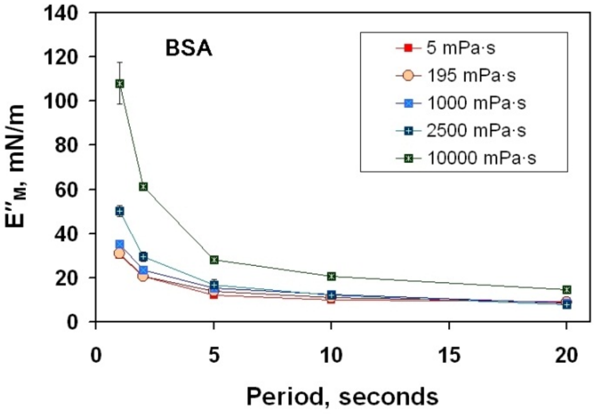

Fig. 2: Modulus of viscosity E''_M for BSA at different oscillation periods

As can be seen from Fig. 1, the data for E' hardly depend on the viscosity of the surrounding phase; the values show the same type of curve and similar values (± 5 mN/m) for one and the same period. Only for the oil with the highest viscosity (10.000 mPa s) did the values clearly vary for oscillation periods < 10 s.

In contrast to these findings, the values for E''_M (Fig. 2) clearly depend on the viscosity of the surrounding phase. The corrected values for the modulus of viscosity are shown in Fig. 3. Remarkably, all the corrected values lie on a common curve, which is direct evidence that the correction was properly conducted.

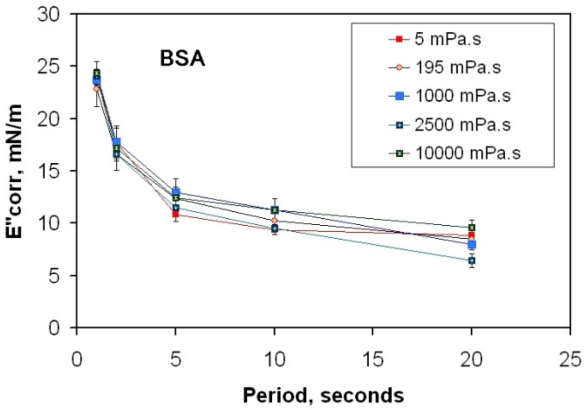

Fig. 3: Dependency of the corrected E'' moduli for BSA on the oscillation period

We studied the 0.1 millimolar solution of the low-molecular surfactant SDS (in a 150 millimolar NaCl solution) in silicone oils with viscosities from 5 to 1000 mPa s. Just as for BSA (Fig. 1), the values for the modulus of elasticity $E'_M(T)$ did not depend on the viscosity. For this reason only the results for the modulus of viscosity $E''_M(T)$ are shown (Fig. 4). The uncorrected values for oils with 5 and 50 mPa s coincide, only the values for the oil with 1000 mPa s are clearly higher. After the shear viscosity correction, the values for the oil with 1000 mPa s lie together with those of the lower viscosity oils on a common curve.

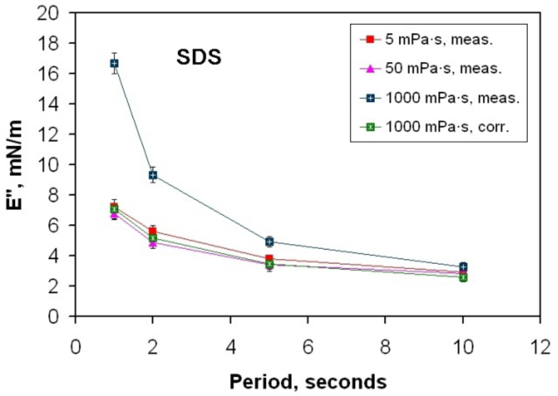

Fig. 4: Dependency of the modulus of viscosity E'' for SDS on the oscillation period, with and without correction

Summary

A method is presented for measuring the interfacial rheological parameters of the phase boundary between a low and a high viscosity liquid. It is based on measuring the capillary pressure at oscillating spherical drops of the low-viscosity phase in the surrounding high-viscosity phase.

At frequencies up to 1 Hz and using the selected geometrical parameters and outer phase oils up to 200 mPa s the pressure contribution of the viscosity does not need to be taken into consideration when calculating the interfacial rheological quantities. However, even for high-viscosity oils up to 10000 mPa s it is possible to calculate correct values for the modulus of viscosity *E*″ if the pressure contribution of the shear viscosity is taken into account. The storage modulus *E*′ is measured properly without correction up to 2500 mPa s viscosity in the entire frequency range and up to 10000 mPa s below 0.1 Hz.

The method presented here could also be used to study interfacial properties of surfactants that are adsorbed from the oil phase – or from both phases. Both cases frequently occur in practice: asphaltenes (tertiary oil recovery), vitamins and amino-acids (food manufacture) or perfumes are examples of oil-soluble surfactants which in emulsions interact with water-soluble surfactants.

Literature

[1] 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. 79 (2008).

[2] N. Alexandrov, K.G. Marinova, K.D. Danov, I.B.Ivanov, “Surface dilatational rheology measurements for oil/water systems with viscous oils”, J. Colloid Interface Sci. (submitted)

[3] K.D. Wantke, K. Lunkenheimer, C. Hempt, “Calculation of the elasticity of fluid boundary phases with the oscillating bubble method” J. Colloid Interface Sci. 159, 28 (1993).

[4] C.-H. Chang, E.I. Franses, “An analysis of the factors affecting dynamic tension measurements with the pulsating bubble surfactometer”, J. Colloid Interface Sci. 164 (1994) 107.

[5] E.K. Zholkovskij, V.I. Kovalchuk, V.B. Fainerman, G. Loglio, J. Krägel, R. Miller, A. Zholob, S.S. Dukhin, “Resonance behavior of oscillating bubbles”, J. Colloid Interface Sci. 224 (2000) 47.

[6] V.I. Kovalchuk, E.K. Zholkovskij, J. Krägel, R. Miller, V.B. Fainerman, R. Wüstneck, G. Loglio, S.S. Dukhin, “Bubble Oscillations in a Closed Cell”, J. Colloid Interface Sci. 224 (2000) 245.´

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