



## Short Communication

## Surface dilatational rheology measurements for oil/water systems with viscous oils

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## ABSTRACT

This work presents an application of the capillary pressure tensiometry (CPT) for accurate measurements of the surface dilatational elastic and loss moduli of the interface between water and transparent oil phases with viscosities up to 10,000 mPa s. Surface rheological studies involving viscous oils are not possible with other available methods due to the considerable bulk viscous forces. Theoretical estimations show that successful measurements with such systems are possible by using a suitable frequency range of the oscillating spherical drop method by CPT. Measurements with oils having viscosities between 5 and 10,000 mPa s at a frequency smaller than 1 Hz were performed using the oil as outer phase and the aqueous surfactant solution as inner (drop) phase. As predicted by the theory the measured surface elastic modulus did not depend on the viscosity (within experimental accuracy). Three different approaches to account for the contribution of the bulk shear viscosity to the measured pressure signal were analyzed and applied. The results showed that if exact numerical corrections are used the calculated loss modulus also did not depend on the viscosities of the bulk phases. The two other methods used lead to errors, sometimes significant.

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## 1. Introduction

Surface rheological properties (such as dilatational and shear elasticity and viscosity) are believed to be among the main factors determining the dynamic behavior of foams and emulsions [1–5]. Foam drainage [3] and foam and emulsion rheology [4,5] have been shown to correlate with the surface dilatational modulus. Thus the determination of the surface rheological properties has become an important tool for the characterization of various products.

Surface dilatational elasticity and viscosity are determined experimentally by measurement of the change of the surface tension resulting from defined surface deformation [1,2,6–11]. For the case of sinusoidal oscillations of the area  $A_s(t) = A_m[1 + \alpha_a \exp(i\omega t)]$  around a mean value  $A_m$  with angular frequency,  $\omega$ , and small relative deformation,  $\alpha_a$ , the ensuing oscillating variation of the interfacial tension,  $\sigma$ , can be represented as

$$\sigma(t) - \sigma_m = E^*(\omega, \alpha_a)\alpha_a \exp(i\omega t), \quad (1)$$

where  $i$  is the imaginary unit,  $\sigma_m$  is the mean value of the interfacial tension, and  $E^*(\omega, \alpha_a) = E'(\omega, \alpha_a) + iE''(\omega, \alpha_a)$  is the complex interfacial modulus. For linear systems (viz. at small amplitudes  $\alpha_a$ ), the complex modulus is a function of the frequency  $\omega$  only, and the real and imaginary parts of  $E^*$  are called elastic modulus,  $E'(\omega)$ , and loss modulus,  $E''(\omega)$ , respectively [6].

Measurements of  $E'$  and  $E''$  of aqueous solutions have been realized mostly in the Langmuir trough [1,6] or by means of the oscillating [1,2,10–14] or expanding [8,9,13] drop methods. For the rheological experiments in the Langmuir trough the surface tension is measured by the Wilhelmy plate method or by the du Nouy ring method [1]. The latter methods are usually used for liquid viscosities smaller than 10 mPa s and oscillation frequencies smaller than 0.1 Hz [1]. The oscillating spherical drop and bubble methods have been applied up to 10 Hz (for drops [2]) and to 300 Hz (for bubbles [14]) but for solutions having viscosity of the order of 1 mPa s only. The industrially used and/or produced foams and emulsions contain liquids of various viscosities: water and diluted aqueous solutions (typically 1 mPa s); vegetable hydrocarbons ( $10^1$ – $10^2$  mPa s); synthetic hydrocarbon oils and polymer solutions ( $10^2$ – $10^6$  mPa s); hydrocarbon and silicone resins ( $10^6$ – $10^{10}$  mPa s). Measurement of the surface moduli of interfaces between liquid phases with viscosities, which exceed significantly that of water, has been a challenge for a long time. Applicability of the methods using oscillating drops and bubbles with axisymmetric (nonspherical) shapes has been shown to be limited due to viscosity effects [10–12]. Leser et al. [10] have used the oscillating pendant drop method for liquid/air interfaces and they have shown that for aqueous solutions the method does not give reasonable results for frequencies above 1 Hz. Increase of the viscosity leads to a decrease of the upper limit of the frequency to which the method is applicable [10]. Freer et al. [11] have shown that the viscous forces distort the shape of drops of silicone oil with viscosities 100 and 200 mPa s oscillating with frequencies larger than 0.01 Hz.

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We also tried to measure the surface dilatational moduli,  $E'$  and  $E''$ , by oscillating axisymmetric drops. The obtained dependencies of  $E'$  and  $E''$  with the frequency of oscillations,  $\omega$ , for drops of 0.01 wt.% water solution of BSA (bovine serum albumin) oscillating in silicone oil are shown in Fig. 1. The plot shows that both  $E'$  and  $E''$  values vary significantly and not systematically with the viscosity of the oil. Such behavior could hardly be due to the protein since in all experiments it adsorbs from the aqueous phase to interfaces with oils having the same chemical structures. Furthermore, negative values of  $E'$  and  $E''$  are seen in Fig. 1, which is physically impossible.

We are not acquainted with any detailed theoretical analysis of the applicability of the oscillating axisymmetric drop method for determination of the surface rheological parameters of oil/water interfaces. In the *static case* the Laplace equation of capillarity relates the capillary pressure with the hydrostatic pressure difference between the two sides of the interface. Thus knowing the geometry of the surface one calculates the interfacial tension. For *moving surfaces* the tangential and the normal stress boundary conditions relate the bulk viscous force and the pressure difference on both sides of the interface to the surface stress [7]. Since the fluid flow around the surface is unknown, the precise calculation of the interfacial tension for such systems is an almost unsolvable, for the time being, task.

When the drops or bubbles have a spherical shape the description of the surface stress was calculated quite accurately due to the spherical symmetry [7]. Measurements with systems having spherical symmetry are possible by capillary pressure tensiometry. This method has been analyzed in detail by several authors [14–18]. Wantke et al. [14] and Kovalchuk and co-workers [16–18] investigated the oscillations of spherical bubbles in different cell configurations and Chang and Franses [15] examined precisely the work of the “pulsating bubble surfactometer.” In our recent work [13] we applied pressure tensiometry and oscillations of spherical drops to measure the values of  $E'$  and  $E''$  for various interfaces at frequencies up to 1 Hz. We found that the values of  $E'$  and  $E''$  measured by oscillating spherical drops of water in silicone oils of viscosity 5 and 50 mPa s coincided and were quite reasonable in contrast to the values obtained by the oscillating axisymmetric drop method (see Fig. 8 in Ref. [13]).

The aim of this work is to explore further the range of applicability of the capillary pressure tensiometry with spherical drops for

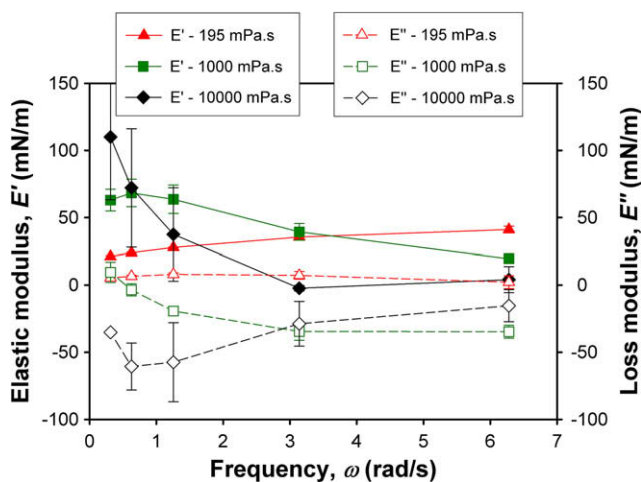


Fig. 1. Elastic,  $E'$  (full symbols, left ordinate), and loss,  $E''$  (empty symbols, right ordinate), moduli as determined by the oscillating pendant drop method versus the frequency. The measurements were performed with drops from 0.01 wt.% BSA (bovine serum albumin) aqueous solutions in silicone oils with different viscosities (as indicated in the legend).

determination of the surface dilatational rheological properties for interfaces between water surfactant solutions and oils of viscosity as high as 10,000 mPa s. Surfactants insoluble in the oil phases are used. Under Theoretical we present briefly the main bulk dynamic contributions to the measured pressure signal when a spherical drop is oscillating in another liquid. Several approaches for description of the outer phase viscous contribution are listed. These are used for the recalculation of the experimental data and the results are compared. Further extension of the method is discussed.

## 2. Theoretical

Below we briefly present the principle of operation of the capillary pressure tensiometry (CPT) method and the main physical contributions to the measured signal and calculated surface rheological parameters. The basic equations are presented, which are afterward used in the experimental part to process the data and to analyze the validity of the method.

With the CPT in the *static case* one calculates the surface tension,  $\sigma$ , of a *spherical surface* by independent determination of the radius of curvature,  $R_s$ , and the capillary pressure,  $P_c$ , using the Laplace equation [2,7,8,13–18]:

$$\sigma = \frac{P_c R_s}{2}. \quad (2)$$

In the *dynamic case* one measures a pressure,  $P_m$ , which contains several contributions (one of which is  $P_c$ ) [13–18]:

$$P_m = P_{\text{hydr}} + P_{\text{dyn}} + P_c. \quad (3)$$

The hydrostatic pressure term,  $P_{\text{hydr}}$ , accounts for the hydrostatic pressure difference from the pressure transducer membrane to the spherical drop apex and from the apex to the surface of the outer phase, see Eq. (6) in Ref. [13]. The dynamic pressure term,  $P_{\text{dyn}}$ , accounts for the contributions due to bulk flows (due to oscillations of the drop area and volume). In the static case,  $P_{\text{dyn}} = 0$ .

Unlike the case of mechanical equilibrium when the capillary pressure is exactly proportional to the surface tension,  $\sigma$ , during surface deformations the capillary pressure fluctuations are proportional to the total surface stress, which contains also contributions from the surface viscosity [7,8,15,20].

Substituting Eqs. (2) and (3) in (1) and having in mind the spherical geometry we generalize Eq. (8) from Ref. [13] to the following expression for the complex interfacial modulus,  $E^*$ ,

$$E^* = \frac{d\sigma}{d \ln A_s} = \sigma_m \left( 1 - \frac{R_{s,\text{eq}}}{H_{s,\text{eq}}} \right) + \frac{R_{s,\text{eq}}}{2} \frac{d}{d \ln A_s} (P_m - P_{\text{hydr}} - P_{\text{dyn}}), \quad (4)$$

where  $H_s$  is the drop height and the subscript “eq” denotes that the value of the respective quantity is taken at the initial time before oscillations start when the surface tension has reached its equilibrium value. Eq. (4) can be rewritten in the form

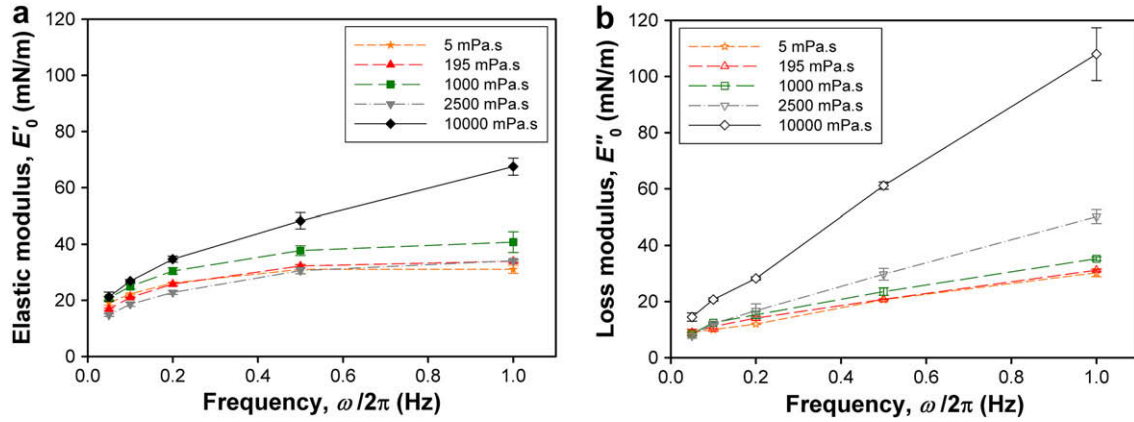
$$E^* = E_0^* - \frac{R_{s,\text{eq}}}{2} \frac{dP_{\text{dyn}}}{d \ln A_s}, \quad (5a)$$

$$E_0^* \equiv \sigma_m \left( 1 - \frac{R_{s,\text{eq}}}{H_{s,\text{eq}}} \right) + \frac{R_{s,\text{eq}}}{2} \frac{d}{d \ln A_s} (P_m - P_{\text{hydr}}), \quad (5b)$$

where  $E_0^* = E_0' + iE_0''$  denotes the *measured complex interfacial modulus*, because  $E_0^*$  is calculated from the measured pressure  $P_m$  (by neglecting  $P_{\text{dyn}}$  in Eq. (4)). Typical measured values of the real,  $E_0'$ , and imaginary,  $E_0''$ , parts of  $E_0^*$  are shown in Fig. 2.

A large contribution of the second right-hand term, i.e.,  $P_{\text{dyn}}$ , in Eq. (5a), the imaginary part  $E_0''$  could be considerably different from  $E_0''$  (see Tables 1 and 2).

$P_{\text{dyn}}$  contains viscous and inertial contributions [2,14–18]. Estimates [15] show that the inertial term in  $P_{\text{dyn}}$  becomes significant



**Fig. 2.** Values of the elastic,  $E'_0$  (a), and loss,  $E''_0$  (b), moduli, corresponding to  $P_{\text{dyn}} = 0$ , as determined by the oscillating spherical drop method as a function of the frequency. Measurements were performed with drops from 0.01 wt.% BSA aqueous solutions in silicone oils with different viscosities, as indicated in the legend.

**Table 1**

Values of the loss moduli:  $E''_0$  calculated after Eq. (5b), and  $E'' = E''_0 - E''_{\text{Pois}} - E''_c$  determined for drops from 0.01 wt.% BSA aqueous solution oscillating in 10,000 mPa s silicone oil. Values of the different dynamic corrections are also shown:  $E''_{\text{Pois}}$  from Eq. (9), and  $E''_{\text{visc}}$  as follows:  $E''_c$  from Eq. (10a),  $E''_b$  from Eq. (10b) for the case of  $\chi = 1$ , and for  $\chi = H_{s,\text{eq}}/r_c$ ,  $E''_c$  from Eq. (10c).

$\omega/2\pi$ (Hz)	Period, $T$ (s)	$E'_0$ (mN/m)	$E''_{\text{Pois}}$ (mN/m)	$E''_{\text{visc}}$ (mN/m)				$E''$ (mN/m)
				$E''_a$	$E''_b$ ( $\chi = 1$ )	$E''_b$ ( $\chi = H_{s,\text{eq}}/r_c$ )	$E''_c$	
1	1	114.6	4.90	48.8	41.8	74.2	85.3	24.4
0.5	2	62.0	2.41	24.2	20.7	36.8	42.4	17.19
0.2	5	27.9	0.87	8.99	7.94	13.3	14.6	12.43
0.1	10	20.3	0.46	4.79	4.11	7.26	8.54	11.3
0.05	20	13.4	0.20	2.18	1.94	3.20	3.60	9.6

**Table 2**

Values of the loss moduli  $E''_0$  calculated after Eq. (5b), and  $E'' = E''_0 - E''_{\text{Pois}} - E''_c$  determined for drops from 0.01 wt.% BSA aqueous solution oscillating with a frequency of 1 Hz. Values of the different dynamic corrections are also shown:  $E''_{\text{Pois}}$  from Eq. (9), and  $E''_{\text{visc}}$  as follows:  $E''_b$  from Eq. (10b) for the case of  $\chi = H_{s,\text{eq}}/r_c$ ,  $E''_c$  from Eq. (10c). For comparison values for a drop from 0.1 mM SDS solutions in 1000 mPa s oil are also shown. The volume of the drops with SDS was 3  $\mu\text{L}$  and that with BSA was 5  $\mu\text{L}$  but the deformation,  $\alpha_a$ , was the same.

Viscosity (mPa s)	5	195	1000	1000 <sup>a</sup>	2500	10,000
$E''_0$ (mN/m)	29.3	31.4	34.8	16.2	48.5	114.6
$E''_{\text{Pois}}$ (mN/m)	5.90	5.31	4.57	2.24	5.39	4.90
$E''_{\text{visc}} = E''_c$ (mN/m)	0.06	1.68	6.14	6.96	18.6	85.3
$E''_{\text{visc}} = E''_b$ ( $\chi = H_{s,\text{eq}}/r_c$ ) (mN/m)	0.05	1.63	6.82	4.76	19.2	74.2
$E''$ (mN/m)	23.34	24.41	24.09	7.0	24.51	24.4

<sup>a</sup> The values in the column are for a 3  $\mu\text{L}$  drop from 0.1 mM SDS and 150 mM NaCl aqueous solution.

for frequencies larger than 10 Hz. That is why we do not include it in our considerations. Detailed considerations on the inertial term can be found in Refs. [15] (Eq. (9) therein) and [17] (Eq. (37) therein).

The viscous contribution to  $P_{\text{dyn}}$  consists of two parts [7,14–19]:

- (1) Pressure due to the flow in the capillary, which for a Newtonian fluid is given by the Poiseuille law [2,6–8,14–18]

$$P_{\text{Pois}} = \frac{8\eta_{\text{inn}}L}{\pi r_{\text{inn}}^4} \frac{dV_s}{dt} = 8\eta_{\text{inn}} \frac{R_{s,\text{eq}}^2 H_{s,\text{eq}} L}{r_{\text{inn}}^4} \frac{d \ln A_s}{dt}, \quad (6)$$

where  $\eta_{\text{inn}}$  is the dynamic viscosity of the inner (solution) phase moving in the capillary with length  $L$  and inner radius  $r_{\text{inn}}$ , and  $dV_s/dt$  is the change of the drop volume,  $V_s$ , with the time,  $t$ , i.e., the flow rate.

- (2) Pressure jump,  $P_{\text{visc}}$ , due to the bulk viscous stresses acting from both contiguous phases on the drop surface. Three different ways for calculation of  $P_{\text{visc}}$  can be found in the literature:

- (a) Representing the deformation of the hanging drop as a radial expansion/contraction of a spherical drop in an outer fluid leads to the following exact expression for  $P_{\text{visc}}$  [7,15,19]:

$$P_{\text{visc}} = \frac{4}{R_{s,\text{eq}}} (\eta_{\text{out}} - \eta_{\text{inn}}) \frac{dR_s}{dt} = 4(\eta_{\text{out}} - \eta_{\text{inn}}) \left(1 - \frac{R_{s,\text{eq}}}{H_{s,\text{eq}}}\right) \frac{d \ln A_s}{dt}. \quad (7a)$$

- (b) Using the method of similarity and dimensional analyzes in Refs. [16,17] the following relationship for  $P_{\text{visc}}$  is obtained,

$$P_{\text{visc}} = \chi \frac{\eta_{\text{out}}}{r_c} \frac{dH_s}{dt} = \chi \frac{\eta_{\text{out}} R_{s,\text{eq}}}{r_c} \frac{d \ln A_s}{dt}, \quad (7b)$$

where  $r_c$  is the radius of the drop contact line, while the dimensionless parameter  $\chi$  accounts for the drop geometry ( $\chi$  should be a function of the ratio  $H_s/r_c$ ). Later on these authors [18] have assumed  $\chi = 1$  and have noted that the exact value of  $\chi$  must be calculated from

the solution of the complex hydrodynamic problem of the drop motion.

- (c) By solving the hydrodynamic problem of an expanding/contracting spherical drop attached to a capillary in an outer fluid phase, in Refs. [21,22] the hydrodynamic drag force,  $F_{\text{visc}}$ , has been calculated. This force creates a pressure [21,22]

$$P_{\text{visc}} = \frac{F_{\text{visc}}}{\pi r_c^2} \frac{\pi r_{\text{inn}}^2}{\pi r_c^2} = \frac{R_{s,\text{eq}}^2 H_{s,\text{eq}} r_{\text{inn}}^2}{\pi r_c^5} [\eta_{\text{inn}} f_{a,0} + \eta_{\text{out}} (f_{ab} + f_b)] \frac{d \ln A_s}{dt}, \quad (7c)$$

where  $f_{a,0}$ ,  $f_{ab}$ , and  $f_b$  are dimensionless coefficients (dependent on the ratio  $H_s/r_c$ ) which can be calculated numerically as shown in Refs. [21,22].

As seen from Eqs. (6) and (7) the viscous forces contributions to  $P_{\text{dyn}}$  are dependent on the rate of surface deformation,  $d \ln A_s/dt$ ; i.e., they contribute to the imaginary part of the complex interfacial modulus only. Thus the expression for the real part of the complex modulus  $E^*$  (see Eq. (5)) reads

$$E' = E'_0, \quad (8a)$$

while the imaginary part of  $E^*$  can be presented as

$$E'' = E''_0 - E''_{\text{Pois}} - E''_{\text{visc}}, \quad (8b)$$

where  $E''_{\text{Pois}}$  and  $E''_{\text{visc}}$  are dynamic corrections to the loss modulus due to the flow in the capillary and to the drop expansion/contraction, respectively. Below we give expressions for calculation of  $E''_{\text{Pois}}$  and  $E''_{\text{visc}}$ .

Using Eqs. (5), (6) and (8b) the correction  $E''_{\text{Pois}}$  due to the Poiseuille flow can be expressed as

$$E''_{\text{Pois}} = 4\omega \eta_{\text{inn}} \frac{R_{s,\text{eq}}^3 H_{s,\text{eq}} L}{r_{\text{inn}}^4}. \quad (9)$$

From Eqs. (5), (8b), and (7a), (7b), or (7c) we obtain for  $E''_{\text{visc}}$  the following relationships:

$$E''_{\text{visc}} = E''_a = 2\omega (\eta_{\text{out}} - \eta_{\text{inn}}) R_{s,\text{eq}} \left( 1 - \frac{R_{s,\text{eq}}}{H_{s,\text{eq}}} \right) \quad (\text{for radial drop expansion}), \quad (10a)$$

$$E''_{\text{visc}} = E''_b = \chi \omega \frac{\eta_{\text{out}} R_{s,\text{eq}}^2}{2r_c} \quad (\text{from Refs. [16, 17]}), \quad (10b)$$

$$E''_{\text{visc}} = E''_c = \omega \frac{R_{s,\text{eq}}^3 H_{s,\text{eq}} r_{\text{inn}}^2}{2\pi r_c^5} [\eta_{\text{inn}} f_{a,0} + \eta_{\text{out}} (f_{ab} + f_b)] \quad (\text{for an attached drop expansion}). \quad (10c)$$

All theoretical considerations described above have been known in the literature but their applicability for describing accurately  $E^*$  has not been checked so far, most probably due to the absence of a suitable experimental setup. That is why we performed a series of measurements with oscillating aqueous drops in outer oil phases with the same chemical structure but different viscosities. The experimental configuration was chosen to ensure a relatively small contribution of the inner phase viscosity (Eq. (9)) in order to analyze more precisely the viscosity contribution from the outer phase (e.g., Eq. (10)). The results were processed using Eq. (8), the effect of the viscous contribution was calculated by different approaches, Eq. (10), and the obtained results were analyzed (see Section 4).

### 3. Materials and methods

As oil phase we used a series of silicone oils (polydimethylsiloxane) with viscosities: 5, 50, 195, 1000, 2500, and 10,000 mPa s (products of Rhodia, France). As aqueous phase we used either 0.1 mM solution of the anionic surfactant sodium dodecyl sulfate

(SDS,  $M_w = 288.4$  g/mol Acros, USA) or 0.01 wt.% solution of bovine serum albumin (BSA,  $M_w = 65,000$  g/mol, Sigma). Sodium chloride (NaCl, Merck) was added to the solutions of SDS in a concentration of 150 mM. Deionized water from a Milli-Q purification system (Millipore, USA) was used for the solutions preparation. The water was additionally degassed by applying 1 h of heating under a decreased pressure. In all experiments the working temperature was  $25 \pm 0.5$  °C.

The used glassware and all parts of the instrument contacting with the studied oils and solutions were cleaned with an alcoholic base solution and rinsed abundantly with deionized water.

The measurements were performed on the recently described module for oscillating and expanding drops measurements [13] on the Krüss DSA 100 M system (Krüss GmbH, Hamburg, Germany) allowing experimental determination of the surface dilatational parameters by several complementary methods, e.g., oscillating pendant drops, oscillating spherical drops by pressure tensiometry, and expanding drops by pressure tensiometry. We applied only the oscillating pendant drop and the oscillating spherical drop methods to obtain the surface dilatational parameters. The commercial version of the instrument calculates automatically  $E'_0$  and  $E''_0$  measured by CPT.

The aqueous phase was used as inner phase and the drops were formed using a metal needle with inner diameter  $2r_{\text{inn}} = 1.54$  mm, outer diameter  $2r_c = 1.84$  mm, and length  $L = 30$  mm. The contact line of the formed drops was fixed at the outer capillary diameter. Oscillations with frequencies 1, 0.5, 0.2, 0.1, and 0.05 Hz were applied (corresponding to periods of oscillations 1, 2, 5, 10, and 20 s, respectively).

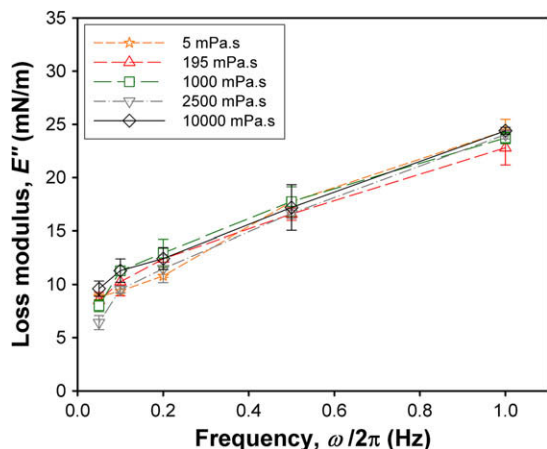
### 4. Results and discussion

We performed a series of measurements by the method of the oscillating spherical drop with 0.01 wt.% BSA solutions in various silicone oils. Fig. 2 presents the measured values of the dilatational surface elastic,  $E'_0$ , and loss,  $E''_0$ , moduli as a function of the frequency,  $\omega$ . As one sees from Fig. 2a  $E'_0$  followed the same trend and had almost the same value ( $\pm 5$  mN/m) for the same frequencies for all oils, except for 10,000 mPa s. With 10,000 mPa s (the highest viscosity used) the measured  $E'_0$  deviated significantly from the common trend only for  $\omega/2\pi > 0.2$  Hz. In contrast to  $E'_0(\omega)$ , the measured  $E''_0$  (Fig. 2b) increased noticeably with oil viscosity at a given frequency. This behavior of  $E'_0$  and  $E''_0$  had to be expected since only  $E''$  is supposed to depend on the dynamic contributions; see Eq. (8).

To compare the different approaches for the calculations of  $E''_{\text{visc}}$  we used Eqs. (10a), (10b) and (10c) for the data obtained with drops from 0.01 wt.% BSA solution in 10,000 mPa s oil. The results are given in Table 1 together with the values of  $E'_0$  and  $E''_{\text{Pois}}$ . To illustrate the effect of oil viscosity in Table 2 we compare results obtained with oils of different viscosity at the same frequency (1 Hz).

The last column of Table 1 and the last row of Table 2 represent the values of  $E''$  calculated by Eq. (8b) using the exact Eq. (10c); i.e.;  $E''_{\text{visc}} = E''_c$ . Remarkably the calculated values of  $E''$  (including those for 10,000 mPa s) for 0.01 wt.% BSA aqueous solution using the exact expression for the viscous contribution (10c) laid on a master curve as a function of the frequency; see Fig. 3.

Eq. (10b) was used in two ways: (i) with  $\chi = 1$  (as suggested in Ref. [18]); and (ii) with  $\chi = H_{s,\text{eq}}/r_c$  as a first approximation. The values of  $E''_{\text{visc}} = E''_b$  when  $\chi = H_{s,\text{eq}}/r_c$  (see Table 1) were close to the ones obtained with the exact numerical solution ( $E''_c$ ) and almost two times larger than those obtained with  $\chi = 1$ . The values calculated with Eq. (10a), i.e.  $E''_{\text{visc}} = E''_a$ , were also significantly smaller than the ones calculated with the exact numerical solution



**Fig. 3.** Loss modulus,  $E'' = E''_0 - E''_{\text{Pois}} - E''_{\text{visc}}$ , for 0.01 wt.% BSA aqueous solution as a function of the frequency of oscillations. The measured values,  $E''_0$ , were determined by the oscillating spherical drop method assuming  $P_{\text{dyn}} = 0$  (see Eq. (5b) and Fig. 2b). The dynamic contributions  $E''_{\text{Pois}}$  and  $E''_{\text{visc}}$  were calculated according Eqs. (9) and (10c).

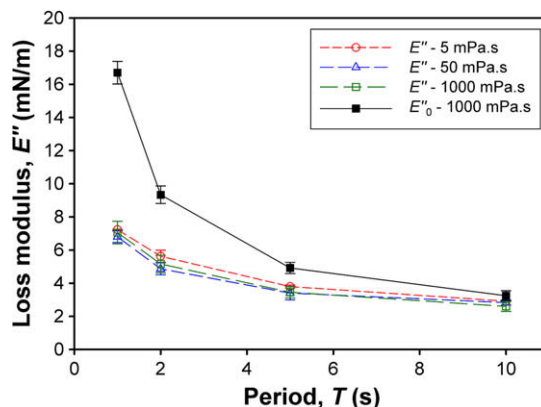
( $E''_c$ ). As a result, the use of  $E''_a$  or  $E''_b$  ( $\chi = 1$ ) would not lead to a universal dependence of the modulus vs  $\omega$  for all oils, while using  $E''_b$  ( $\chi = H_{s,\text{eq}}/r_c$ ) would give acceptable results, especially at lower frequencies (cf. the values in Table 1).

The values of  $E''_{\text{visc}}$ , given in Tables 1 and 2, and the data plotted in Fig. 2b show that the dynamic contribution of the viscous stress from the outer phase ( $P_{\text{visc}}$ , described by Eq. (7) and used in Eq. (10)) becomes significant when the oil viscosity is greater than 200 mPa s.

The magnitude of  $E''_{\text{Pois}}$  becomes significant for periods of oscillations  $< 5$  s ( $\omega/2\pi > 0.2$  Hz) (see Tables 1 and 2), i.e., at higher flow rates. As seen from Eq. (9)  $E''_{\text{Pois}}$  does not depend on the viscosity of the outer phase (since it is due to the water flow) but on the geometrical parameters of the used drop and on the oscillating frequency,  $\omega$ , i.e., on the flow rate. To illustrate the role of the flow rate on  $E''_{\text{Pois}}$  in Table 2 we compare values at the same deformation for a 5  $\mu\text{L}$  drop (with BSA) to those for a 3  $\mu\text{L}$  drop (with SDS) in 1000 mPa s oil. A smaller value of  $E''_{\text{Pois}}$  is calculated for the 3  $\mu\text{L}$  drop than for the larger 5  $\mu\text{L}$  drop. This is due to the proportionality between  $E''_{\text{Pois}}$  and the drop dimensions  $R_{s,\text{eq}}$  and  $H_{s,\text{eq}}$  (cf. Eq. (9)). Note that the values of  $E''_{\text{Pois}}$  shown in Tables 1 and 2 are relatively low ( $< 6$  mN/m) because the low viscosity aqueous solution is the inner phase and the used capillary is relatively wide ( $2r_{\text{inn}} = 1.54$  mm). If 1000 mPa s oil were used as the inner phase the values of  $E''_{\text{Pois}}$  would increase 1000 times, i.e., to  $\sim 5000$  mN/m at 1 Hz oscillations at all other parameters the same as those used in the series shown in Table 1. One should pay also special attention to the inner capillary radius (see Eq. (9) showing that two times smaller radius would increase the values of  $E''_{\text{Pois}}$  16 times).

We performed measurements with oscillating drops from aqueous solution of 0.1 mM low-molecular-weight surfactant sodium dodecyl sulfate (in the presence of 150 mM NaCl) in silicone oils with viscosities 5, 50, and 1000 mPa s. The values of the measured elastic moduli  $E'_0(\omega)$  did not depend on the oil viscosity (similar to the observations with BSA; see Fig. 2a). That is why in Fig. 4 we show only the results for the measured loss moduli dependencies on the period,  $T = 2\pi/\omega$ . The values of  $E''_0(T)$  coincided ( $\pm 2$  mN/m) for oils with viscosities 5 and 50 mPa s, but the values for 1000 mPa s oil deviated. After the correction for the viscosity contributions (using Eq. (8b) with  $E''_{\text{Pois}}$  from Eq. (9) and  $E''_{\text{visc}}$  from Eq. (10c)) the calculated dilatational loss moduli,  $E''$ , for 1000 mPa s oil coincided with those for the lower viscosities (see Fig. 4).

In conclusion the performed measurements with two different water soluble surfactants confirmed the theoretical predictions that the dynamic contributions of viscous origin affected only the loss



**Fig. 4.** Dilatational loss modulus as a function of the period of oscillations,  $T = 2\pi/\omega$ , for aqueous droplets with 0.1 mM SDS and 150 mM NaCl in silicone oils with different viscosities. The values of  $E''_0$  for 1000 mPa s oil deviate from the common curve obtained with 5 and 50 mPa s oils. Values for 1000 mPa s oil overlaid the common trend after accounting for the dynamic contributions using Eq. (8b) with  $E''_{\text{Pois}}$  from Eq. (9) and  $E''_{\text{visc}}$  from Eq. (10c).

modulus determined with oscillating spherical drop experiments by CPT. The exact and several different approximate expressions for the dynamic viscous contribution were tested and the results showed that modeling a hanging drop as an ideal spherical drop underestimated the effect (values of  $E''_a$  are much smaller than those of  $E''_c$ ). One of the approximate equations (Eq. (10b) with  $\chi = H_{s,\text{eq}}/r_c$ ) predicts the contribution with acceptable accuracy.

Note that all these measurements were possible due to the restricted frequency range ( $< 1$  Hz) and the suitable setup configuration: The inner low viscosity phase ensured a small contribution of the Poiseuille pressure. Furthermore there was no contribution from the elastic properties of the used cell. We suppose that the large volume of the outer phase and the free interface prevents the appearance of strong stresses during drop deformation. A possible explanation for the observed deviations of the measured elastic moduli,  $E'_0$ , at the higher frequencies with the oil 10,000 mPa s (see Fig. 2a) might be due to the cell elasticity, which was negligible for lower viscosity oils and especially at low frequencies.

The obtained dependencies  $E'(\omega)$  and  $E''(\omega)$  were not affected by the viscosity of the used silicone oil (for the range of the used viscosity). Indeed, it is known that the adsorption of a given surfactant depends in principle on the chemical properties and the molecular conformation of the oil phase. On the other hand it was shown that the surface tension depends only on the adsorption no matter how it was reached [20]. Finally, Ivanov et al. [23] showed that the adsorption of surfactants does not depend on the shape and the length of the oil molecules. Therefore, one can make the conclusion that the interfacial properties with all oils were the same, which explains the identity of the results. This statement was proven by experiments with surfactants with different chemical natures, namely BSA and SDS. It will remain valid if the viscous phase is diluted by less viscous compounds but with the same chemical composition. This additionally extends the applicability of our method—if the oil is too viscous it can be diluted by similar less viscous oil. Besides, the fact that the surface rheology is not affected by the bulk properties means that it will be the same for drops in oil-in-water and water-in-oil emulsions.

However, when the surfactant is soluble in the viscous phase, changes in the measured moduli are to be expected upon phase dilution since the viscosity influences the diffusion coefficient and the rate of adsorption consequently [1,7,20]. This might be the reason why Aske et al. [12] found that the dilution of the viscous phase had affected the results obtained by the oscillating pendant drop method.

## 5. Summary

A procedure for measurement of the dilatational surface rheological parameters for the interface between low and high viscosity liquids has been developed based on the oscillating spherical drop method by pressure detection and existing theoretical predictions.

Measurements with oils having viscosities between 5 and 10,000 mPa s at frequencies smaller than 1 Hz were performed using the oil as outer phase and the aqueous surfactant solution as inner (drop) phase. At this experimental configuration the measured surface elastic modulus,  $E'$ , did not depend on the viscosity (within an experimental accuracy of  $\pm 5$  mN/m) except for the 10,000 mPa s oil (highest viscosity used) at frequencies  $>0.2$  Hz. The calculated surface loss modulus depended on the way the dynamic viscosity contribution was accounted for. Different approaches for the contribution of the bulk shear viscosity to the measured pressure signal were analyzed and applied. The results showed that when using exact numerical corrections the loss modulus,  $E''$ , also did not depend on the viscosities of bulk phases (within  $\pm 2$  mN/m).

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