Rheology of colloidal gas aphrons (microfoams) made from different surfactants

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This paper extends our previous study on microfoam rheology made from non-ionic (Tween 20) surfactants to ionic surfactants. Anionic (sodium dodecyl sulfate) and cationic (cetyl trimethylammonium bromide) surfactants were used to generate microfoams by stirring an aqueous surfactant solution at high speed in a baffled beaker. Pipe flow experiments were performed in cylindrical stainless steel pipe 1.5 mm in diameter under adiabatic and fully developed laminar flow conditions. The porosity φ, bubble size distribution, Sauter mean radius r_S, surface tension σ, and pH was reported for each solution. The porosity varied between 0.54 and 0.72 while the Sauter mean radius ranged from 28 to 48 μm. Zero slip velocity was assumed to prevail at the foam–wall interface as previously observed and reported in the literature for stainless steel pipes. Volume equalized method was used to analyze the data obtained from pipe flow viscometer. In all cases, microfoams behave as a shear thinning fluid. The results suggest that the dimensionless wall shear stress τ_w = τ_w r_S/σε is proportional to (Ca*)^m defined as Ca* = μ_e r_S y_w/σε where τ_w is the wall shear stress, y_w is the shear rate, σ is the surface tension, μ_e is the liquid velocity, and ε = 1/(1 – φ) is the specific expansion ratio. The average value of the power–law index m was found to be 0.64 ± 0.04 with 95% confidence interval.

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1. Introduction

This study extends our previous investigation [1] into the rheology of colloidal gas aphrons (CGA), also called microfoams. In Ref. [1], microfoams were formed with aqueous non-ionic surfactant solutions of Tween 20 at different concentrations. The microfoams consisted of closely packed spherical bubbles 10–100 μm in diameter while porosity ranged from 0.63 to 0.73. First, it was established that (i) no slip velocity is present at the stainless steel pipe wall, (ii) CGA can be considered as a shear thinning fluid, (iii) pipe shape and diameter have no effect on the CGA rheology, and (iv) compressibility effects can be accounted for through the volume equalization approach [2]. The present study aims to assess whether similar qualitative and quantitative results prevail for microfoams made with different surfactants and having porosity between 0.54 and 0.72. Our choice focused on anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant cetyl trimethylammonium bromide (CTAB) because both are commonly used in CGA applications [3–7].

2. Background

2.1. Foam rheology

Liquid foams are known to be non-Newtonian fluids. Rheological models have been reviewed in detail previously [1] and need not be repeated. Only the models relevant to the present study will be discussed briefly. First, the pseudo-plastic power–law model is expressed as:

$$\tau_w = K_P \dot{\gamma}_w^n = K_P \dot{\gamma}_a^n = \mu_e \dot{\gamma}_a$$

where τ_w is the wall shear stress, y_w is the true wall shear rate, and y_a is the apparent shear rate. The empirical constants K_P and n are the so-called flow consistency and flow behavior, respectively. The true wall shear rate y_w can be derived from y_a through the Rabinowitsch–Mooney relationship [8].

$$\dot{\gamma}_w = \frac{3n + 1}{4n} \dot{\gamma}_a$$ and $$K_P = K_F \left[ \frac{3n + 1}{4n} \right]^n$$

Alternatively, the Herschel–Bulkley model accounts for the possible existence of yield stress τ_0 and is expressed as

$$\tau_w = \tau_0 + K_{HB} \dot{\gamma}_w^n$$

where K_{HB} is the consistency, and n is the power–law index. It has been used successfully for macrofoams made of aqueous polymer solutions [9,10].
The resulting model predicts that the wall shear stress is expressed caused by a periodic uniaxial strain lower than the elastic limit. in capillary tubes, to 2D-foams with monodispersed hexagonal model [14], predicting the pressure drop along a single bubble microfoams, i.e., ε = μ_L u_b/σ. It accounts for where ε = ω_CGA = 1/(1 − ϕ) where ϕ is the gas volume fraction or porosity. Then, the volume equalized shear stress is given by [2],

$$\tau_w = K_{VE} \left( \frac{\dot{\gamma}_w}{E} \right)^n$$

where $K_{VE}$ and $n^*$ are constants determined empirically.

Alternatively, Schwartz and Princen [13] expanded Bretherton’s model [14], predicting the pressure drop along a single bubble in capillary tubes, to 2D-foams with monodispersed hexagonal cells and large porosity subjected to small oscillatory deformations caused by a periodic uniaxial strain lower than the elastic limit. The resulting model predicts that the wall shear stress is expressed as [15],

$$\tau_w = t_0 + \frac{C(\phi)}{\gamma_{32}} (\text{Ca})^{2/3}$$

where $\gamma_{32}$ is the Sauter mean bubble radius, and $\sigma$ is the surface tension of the gas/liquid interface. The Capillary number Ca is defined as,

$$\text{Ca} = \frac{\mu L}{\rho V_{CGA}}$$

where $\mu_L$ is the viscosity of the liquid phase. However, as noted by Denkov et al. [16], Eq. (5) is not valid for continuous shear flow. On the other hand, Cantat and co-workers [17,18] showed that the pressure drop along a chain of a few large polyhedral bubbles flowing in a narrow rectangular channel was proportional to $(\text{Ca}^*)^{2/3}$ for $\text{Ca}^* < 1$ and defined as Ca* = μ_L u_b/σ where $u_b$ is the average bubble velocity [17]. Simultaneously, Denkov et al. [16,19] developed a model accounting for the viscous friction over the entire area separating the bubbles from the wall and distinguishing between tangentially mobile and immobile bubble bubble surface. Surface mobility depends on various parameters but most importantly on the surface dilatational modulus $E_S$ whose large value ensures tangentially immobile surface. Their models predict the foam-wall shear stress in 3D-foams with immobile and mobile bubble surfaces, respectively as [16],

$$\tau_w = C_{IM} \left( \frac{\sigma}{\gamma_{32}} \right) (0.511 - 0.731 \phi) \left( 1 - 5.12 \phi + 4.03 \phi^2 \right)^{1/2} (\text{Ca})^{1/2}$$

for $0.73 < \phi < 0.99$ and $E_S \geq 60$ mN/m

$$\tau_w = 3.0 C_M \left( \frac{\sigma}{\gamma_{32}} \right) \sqrt{1 - 3.2 \left( \frac{\phi}{1 - \phi} + 7.7 \right)^{1/2}} (\text{Ca})^{2/3}$$

for $0.71 < \phi < 1$ and $E_S < 60$ mN/m

Where $C_{IM}$ and $C_M$ are empirical constants and $\text{Ca}^*$ is the capillary number defined as $\text{Ca}^* = \mu_L u_b/\sigma$ where $u_b$ is the relative velocity between the foam and the wall [16]. The models and more specifically, the power–law index associated with Ca' and equal to either 1/2 or 2/3, was validated against experimental data obtained with a shear rheometer and aqueous foams made from various surfactant solutions with porosity of 0.90 ± 0.01 and Sauter mean radius between 35 and 200 μm [16,20]. The authors determined experimentally that $C_{IM} \approx 4.6$ and $C_M \approx 3.9$ [16]. Note that the range of porosity for which these models are valid corresponds to relatively dry foams ($\phi > 0.7$) with non-spherical bubbles.

Experimentally, care should be taken to isolate the rheological properties of CGA or foams from transient phenomena such as liquid drainage and bubble coalescence. In particular, the foam porosity and bubble size distribution should remain the same during the course of the measurements. Flow pipe viscometers appear to offer the best compromise between these considerations and accuracy requirements and have been used by various authors for studying rheology of macrofoams [2,11,12] and CGA [1,2].

The present study differs from previous studies and in particular Ca’ those of Denkov and co-workers’ [16,19,20] in that it investigates 3D microfoams having relatively small porosity (0.54 < $\phi < 0.72$) and spherical bubbles. Unlike assumptions made by Denkov and co-workers, it was previously established experimentally that the wall slip velocity is zero for microfoams flowing in stainless steel pipes, i.e., $u_s = 0.0$ [1,22]. Finally, pipe flow viscometer is used as opposed to shear rheometer.
3. Experiment

The reader is referred to Ref. [1] for detailed description of the experimental setup, procedure, and data analysis. In brief, the test section consisted of a stainless steel 304 pipe with diameter \( D_0 \) equal to 1.4859 \( \pm 0.0240 \) mm with a 95% confidence level. The length of the pipe was 0.338 m ensuring accurate measurements of the pressure drop and fully developed laminar flow conditions [1]. The pipe diameter was previously shown to have no effect on the CGA rheology once compressibility effects have been accounted for through the volume equalization method [12,11,12]. Thus, only one pipe diameter was used in this study which focuses on the effect of the surfactant ionicity and concentration. Microfoam was treated as a pseudo-homogeneous time-independent non-Newtonian fluid. The pipe diameter was much larger than the bubble size so that CGA could be treated as a continuous medium [23,24]. Previous studies with stainless steel pipes of various diameter shows that the slip velocity was zero at the wall [1,2]. This was assumed to be also valid in the present study.

Microfoam was generated by stirring continuously an aqueous surfactant solution with a Silverson L4RT mixer at 7000 rpm in a baffled container [1]. The solution made from an arbitrary amount of SDS or CTAB (both from Fisher Scientific) in deionized water was continuously produced and flown through the test section. This solution was made from an SDS or CTAB in deionized water and acted as a thermal reservoir to maintain the CGA at constant temperature. The container was placed in a large tank filled with water and acting as a thermal reservoir to maintain the CGA at constant temperature. The parameters measured experimentally were (i) the pressure drop along the channel \( \Delta P \), (ii) the microfoam temperature, (iii) the volumetric flow rate \( Q \), (iv) the mass flow rate \( \dot{m} \), (v) the porosity \( \phi \), (vi) the bubble size distribution and the Sauter mean bubble radius \( r_{32} \), as well as (vii) the surface tension \( \sigma \) of the surfactant solution/air interface, and (viii) the solution pH.

The wall shear stress \( \tau_w \) and the apparent shear rate \( \dot{\gamma}_a \) were determined experimentally according to [2,11],

\[
\tau_w = \frac{D_0 \Delta P}{4L} \quad \text{and} \quad \dot{\gamma}_a = \frac{32Q}{\pi D_0^2} \tag{9}
\]

where \( D_0 \) is the hydraulic diameter, \( \Delta P \) is the pressure drop measured between the inlet and outlet of the pipe separated by a distance \( L \), and \( Q \) is the volumetric flow rate.

Error analysis was performed as reported in Ref. [1]. The uncertainty in porosity \( \Delta \phi/\phi \) was estimated at about 7%. For CGA made of SDS and CTAB subjected to apparent shear rate \( \dot{\gamma}_a \) less than 2000 s\(^{-1}\), the measured pressure drop oscillated significantly and experimental uncertainties associated with \( \tau_w \) and \( \dot{\gamma}_a \) were large. Thus, we considered only data for shear rate larger than 2000 s\(^{-1}\) with experimental uncertainty \( \Delta \tau_w/\tau_w \) and \( \Delta \dot{\gamma}_a/\dot{\gamma}_a \) less than 15 and 7%, respectively.

Finally, the setup, sensors calibration, and analysis (see Ref. [1]) were successfully validated by measuring the viscosity of deionized water and comparing it with values obtained from the thermophysical properties database DIPPR [25]. It establishes that the measured viscosity of deionized water fell within 7.4% of that reported in the literature and equal to 0.927 mPa s at 23°C [25].

4. Results and discussion

4.1. Solution characteristics and CGA morphology

Table 1 summarizes the characteristics of the Tween 20 [1], SDS, and CTAB solutions and the corresponding microfoams investigated in this study. It includes the surfactant mass fraction \( x \) (in wt.%), molar concentration \( c \) (in mM/L), the surface tension \( \sigma \), the pH, the Sauter mean bubble radius \( r_{32} \), and the average porosity \( \phi \). All variables were measured before each experimental run and averaged. The porosity ranged from 0.54 to 0.70 for SDS and CTAB solutions. In all cases, it was verified that no appreciable changes could be observed in both the porosity and the bubble size distribution between the inlet and outlet of the test section. The CGA temperature was 25 ± 2°C. The absolute operating pressure was about 1 atm for all runs.

![Fig. 1](image)

**Fig. 1** shows \( \tau_w \) versus \( \dot{\gamma}_a \) for the different single phase surfactant solutions used in this study. It indicates that all surfactant solutions had approximately the same viscosity as deionized water. In addition, **Fig. 2** illustrates representative photographs of microfoams made from SDS and CTAB solutions with the lowest and largest concentrations considered. It shows closely packed spherical bubbles and justifies why the term “microfoams” is used despite the fact that the porosity varies between 0.65 and 0.72. **Fig. 3** shows the associated bubble size distribution measured from 130 to 240 individual bubbles using the image analysis software Image J. Micrographs of CGA were taken under a Leica DM IL microscope within 1 min of being sampled from the baffled container. From both **Figs. 2 and 3**, it is evident that the bubble size distribution narrows as the surfactant concentration increases. This was also observed with Tween 20 [1]. The Sauter mean bubble radius \( r_{32} \) obtained with SDS decreases from 42.8 to 40.8 μm as the concentration increased from 0.081 to 1.194 wt.%. Simultaneously, the porosity increased from 0.65 to 0.70 and the microfoam was more and more stable. This can be attributed to the decrease in surface tension and to the increased availability of surfactant molecules to adsorb at the bubble surface and stabilize it. Similar trend was observed with CTAB. However.
Fig. 1. Shear stress versus shear rate measured for deionized water and aqueous solutions of SDS and CTAB at various concentrations.

the Sauter mean bubble radius for CTAB microfoams was smaller than that of SDS or Tween 20 and varied between 28.3 and 26.4 μm.

4.2. Rheology

The effect of SDS and CTAB concentration on CGA rheology was assessed with aqueous solutions of SDS at mass fractions 0.081, 0.398, 0.780, 1.194 wt.% and of CTAB at mass fractions 0.027, 0.037, and 0.182 wt.%. Figs. 4 and 5 show the volume equalized shear stress \( \tau_w/\varepsilon \) as a function of the volume equalized apparent shear rate \( \dot{\gamma}_a/\varepsilon \) for the above SDS and CTAB solutions, respectively. As observed with Tween 20 [1], experimental data points become less scattered and more consistent as the surfactant concentration increases thanks to more stable CGA. Both Figs. 4 and 5 indicate that the CGA can be considered as a shear thinning fluid in terms of volume equalized apparent shear rate and shear stress with empirical constants depending on the type of surfactant and its concentration. Figs. 4 and 5 also establish that, for a given value of \( \dot{\gamma}_a/\varepsilon \), the volume equalized shear stress \( \tau_w/\varepsilon \) increases with surfactant concentration up to a maximum value beyond which it is independent of concentration. This was also reported in the literature [1,26]. This cannot be attributed to changes in the solution viscosity (Fig. 1) or in surface tension since neither varies significantly over the range of surfactant mass fractions considered (Table 1). The increase in \( \tau_w/\varepsilon \) with surfactant concentration is likely due to the reduction in the maximum packing of spherical bubbles as their size distribution narrows [1,27] and possibly to the hypothetical shell structure of CGA bubbles becoming thicker with increasing surfactant concentration [28].

4.3. Dimensional analysis

In order to generalize the results, the volume equalized apparent shear rate and shear stress are made dimensionless through the use of volume equalized Capillary number \( \text{Ca}^* \) and dimensionless shear stress \( \tau_w^* \) expressed respectively as,

\[
\text{Ca}^* = \frac{\mu \dot{\gamma}_a}{\varepsilon} = \text{Ca}/\varepsilon \quad \text{and} \quad \tau_w^* = \frac{\tau_w \dot{\gamma}_a}{\sigma \varepsilon}
\]

First, a power–law relationship was assumed between \( \text{Ca}^* \) and \( \tau_w^* \) for its capability to fit a wide range of data and as suggested by theoretical models [16,19], i.e.,

\[
\tau_w^* = B(x)(\text{Ca}^*)^m
\]

Fig. 6 shows the evolution of the power–law index \( m \) as a function of surfactant mass fraction \( x \) for SDS, CTAB, and Tween 20 [1]. It establishes that \( m \) was nearly constant for all concentrations and surfactants considered. The average value of the power–law index \( m \) was found to be 0.64 ± 0.04 with 95% confidence interval. Note also that the surface dilatational modulus of aqueous SDS [16] and CTAB

![Fig. 2. Typical micrograph of CGA formed with different aqueous solutions of SDS (top) and CTAB (bottom) at 25 ± 2 °C.](image-url)
Fig. 3. Bubble size distribution of CGA formed with different SDS and CTAB aqueous solutions at 25 ± 2 °C corresponding to micrographs shown in Fig. 2.

Fig. 4. Volume equalized shear stress versus shear rate for CGA made from SDS aqueous solution with different concentrations obtained in the 1.5 mm diameter pipe at 25 ± 2 °C.

Fig. 5. Volume equalized shear stress versus shear rate for CGA made from CTAB aqueous solution with different concentrations obtained in the 1.5 mm diameter pipe at 25 ± 2 °C.
Fig. 6. Empirical power–law index $m$ as a function of surfactant mass fraction $x$ obtained in the 1.5 mm diameter pipe at $25 \pm 2$ °C for microfoams made of SDS, CTAB, and Tween 20. Solid line corresponds to $m = 2/3$.

Both show a linear relationship between $\tau_w^* = C(x)(Ca^*)^{2/3}$ and $(Ca^*)^{2/3}$ as observed with Tween 20 [1]. In other words, $\tau_w^* = C(x)(Ca^*)^{2/3}$ where the coefficient of proportionality $C(x)$ increases with concentration until it reaches a maximum value. This also agrees well with results obtained with Tween 20 [1]. The values of the parameter $C(x)$ are summarized in Table 1. It is of the order of unity and increases with surfactant mass fraction $x$. However, quantitative relationship between $C(x)$ accounting for the effect of concentration and the type of surfactants is not obvious and will not be sought. The same conclusions can be reached when $C(\phi)$ is plotted as function of porosity (not shown).

5. Conclusion

This study focused on the rheology of microfoams made with aqueous solutions of Tween 20, SDS, and CTAB at various concentrations featuring (i) closely packed spherical bubbles, (ii) porosity ranging from 0.54 to 0.72, and (iii) Sauter mean radius between 26.4 and 47.6 μm. The following conclusions can be drawn:

1. CGA can be treated as a shear thinning fluid for all the surfactant solutions considered.
2. The dimensionless volume equalized shear stress $\tau_w^*$ is proportional to the volume equalized Capillary number $Ca^*$ raised to a power–law index $m$ between 0.6 and 0.66 which is closed to 2/3.
3. The results are consistent with different theoretical and experimental studies for foams with larger porosity, non-spherical bubbles, and non-zero wall slip velocity [16,17,19].
4. Increasing the surfactant concentration causes the shear stress to increase for a given apparent shear rate. This is likely due to the associated reduction in polydispersity of the bubbles.

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