Annex 2

Comparison of the mean drop size in emulsions, prepared in the cylindrical and planar narrow-gap homogenizers

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1. Aim of the study.

The major aim of this study is to obtain experimental information about the mean drop size in emulsions prepared in cylindrical and in planar narrow-gap homogenizers at comparable conditions (equal Reynolds numbers).

2. Studied factors:

The effect of the following factors on the mean drop size were experimentally studied:

(1) Geometry of the processing element with one slit (cylindrical versus planar)

(2) Flow rate (0.095 vs. 0.145 L/s for the cylindrical and 0.131 vs. 0.204 L/s for the planar geometry). The lower flow rate corresponds to Reynolds number, Re = 8450, whereas the higher flow rate to Re = 13270.

(3) Viscosity of the dispersed phase (3.0 and 50 mPa.s)

(4) Interfacial tension (from 5.5 to 14 mN/m).

3. Materials and experimental methods.

3.1. Materials. Three emulsifiers were used in different series of experiments, which ensured different interfacial tensions of the oil-water interface: nonionic surfactant polyoxyethylene-20 hexadecyl ether (Brij 58, product of Sigma), anionic surfactant sodium dodecyl sulfate (SDS, product of Acros), and protein emulsifier sodium caseinate (Na caseinate; ingredient name Alanate 180; product of NXMP). All emulsifiers were used as received and their concentration in the aqueous solutions (1 wt % for Brij 58 and SDS, and 0.5 wt % for Na caseinate) was sufficiently high to suppress the drop-drop coalescence during emulsification.

All aqueous solutions were prepared with deionized water, which was purified by a Milli-Q Organex system (Millipore). The aqueous phase contained also NaCl (Merck, analytical grade) in the concentration of 150 mM for the Brij 58 and Na caseinate solutions, and 10 mM for the SDS solutions. The protein solutions contained also 0.01 wt % of the antibacterial agent NaN_3 (Riedel-de Haën).

As dispersed phase we used two oils, which differed in their viscosity, η_D: soybean oil with η_D = 50 mPa.s (SBO, commercial product) and hexadecane with η_D = 3.0 mPa.s (product of Merck). Both oils were purified from surface-active ingredients by passing them through glass column, filled with Florisil adsorbent [1].

3.2. Construction of the homogenizer. Two modifications of the custom-made "narrow-gap" homogenizer – with cylindrical and with planar geometry of the mixing head and the processing element inside it, were used for the emulsion preparation. Both the cylindrical and the planar processing elements contained a single narrow slit with certain gap-width, through which the oil-water mixture was passed under pressure. The dimensions of the cylindrical and the planar homogenizers were chosen to ensure similar hydrodynamic conditions during emulsification. These included (1) same gap-width - 395 μm for the cylindrical and 400 μm for the planar homogenizer; (2) same length of the slit, 1 mm; (3) same slope angle of the slit entrance, 45 °; and (4) same ratio of the cross-sectional areas of the slit and of the inlet before the slit, A_1/A_2 = 0.2663 (see Figure 1).

The mixing head of the planar homogenizer was equipped with glass windows to allow optical observations in the space after the processing element. Note that the planar homogenizer was equipped with the so-called "non-transparent" processing element in all experiments.

3.3. Emulsification procedure. Oil-in-water emulsions were prepared by using a two-step procedure. First, a course emulsion was prepared by hand-shaking a vessel, containing 20 mL oil and 1980 mL surfactant solution. Thus coarse oil-in-water emulsion, with volume fraction of Φ = 0.01 and total volume 2000 mL, was prepared. The second homogenization step was accomplished by passing the emulsion through the narrow-gap homogenizer (cylindrical or planar mixing chamber) in a series of consecutive passes. The driving pressure for this process was provided by gas N_2-bottle. Pressure transducer was mounted close to the homogenizer inlet to measure precisely the driving pressure, which allowed us to control it during the experiment with a precision of ± 500 Pa. The driving pressure was adjusted in advance (in preliminary experiments) to ensure the desired flow rate during the actual emulsification experiments.

After passing through the homogenizer, the oil-water mixture was collected in a container attached at the outlet of the equipment. Then the gas pressure at the inlet was released, and the emulsion was poured back in the container attached to the inlet, by using a by-pass tube. Then the gas pressure at the inlet was increased again to the desired value and the emulsion was allowed to make another pass through the homogenizer.

We performed 100 consecutive passes of the emulsion through the homogenizer to ensure steady-state drop size distribution in the final emulsion.

The experiments were carried out at flow rates $Q = 0.145 \pm 0.001$ L/s and $Q = 0.092 \pm 0.001$ L/s for the cylindrical homogenizer and at $Q = 0.204 \pm 0.004$ L/s and $Q = 0.131 \pm 0.003$ L/s for the planar homogenizer.

3.4. Determination of drop size distribution. The drop-size distribution in the obtained emulsions was determined by video-enhanced optical microscopy [2-4]. The oil drops were observed and video-recorded in transmitted light by means of microscope Axioplan (Zeiss, Germany), equipped with objective Epiplan, ×50, and connected to a CCD camera (Sony) and VCR (Samsung SV-4000). The diameters of the oil drops were measured one by one, from the recorded video-frames, by using custom-made image analysis software, operating with Targa+ graphic board (Truevision, USA). For all samples the diameters of 3000 drops were measured.

The mean volume-surface diameter, d_{32}, was calculated from the measured drop diameters by using the relation:

$$d_{32} = \frac{\sum_i N_i d_i^3}{\sum_i N_i d_i^2} \qquad (1)$$

where N_i is the number of drops with diameter d_i. The accuracy of the optical measurements was estimated to be ± 0.3 μm [4].

3.5. Measurements of oil viscosity. The viscosity of soybean oil and hexadecane was measured at the temperature of the experiment by using a capillary-type viscometer, after calibration with pure water.

3.6. Measurement of interfacial tension. The oil-water interfacial tension was measured by using a drop-shape-analysis of pendant oil drops, immersed in the surfactant solutions. The measurements were performed on commercial Drop Shape Analysis System DSA 10 (Krüss GmbH, Hamburg, Germany).

4. Experimental results.

All experiments were performed at high surfactant concentration and low oil volume fraction of $\Phi = 0.01$, to suppress the drop-drop coalescence during emulsification. The results from all experiments about the mean drop diameter, d_{32}, are summarized in Table 1 and are briefly described below.

4.1. Relation between the driving pressure and the flow rate.

The experimental data for the relation between the flow rate Q and the driving pressure p are shown in Figure 2A,B for the two processing elements, with cylindrical and planar geometry, respectively. The data were well represented by power law empirical fits, which are shown by curves in Figure 2A,B.

It is seen that at the same flow rate, the driving pressure in the planar homogenizer is about 2 times higher than the driving pressure in the cylindrical homogenizer.

4.2. Effect of hydrodynamic conditions (flow rate and geometry of the processing element).

As expected, the increase of the flow rate results in smaller droplets under equivalent all other conditions. For the SBO + Brij 58 emulsions, the mean drop size decreased almost twice - from 12 to 6.6 μm when increasing Q from 0.092 to 0.145 L/s for the homogenizer with cylindrical geometry and from 12.8 to 7.2 μm when increasing Q from 0.131 to 0.204 L/s for the planar homogenizer.

The experimental results for d_{32} showed that the planar construction produced emulsions with slightly larger mean drop diameter in comparison with the cylindrical one for the same Reynolds number inside the gap. The relative difference in the values of d_{32}, obtained with the planar and with the cylindrical elements, is about 6 % for Re = 8450 and about 7 % for Re = 13270 (see Table 1).

4.3. Effect of oil viscosity.

To study the effect of oil viscosity, η_D, we produced emulsions of two different oils – hexadecane and soybean oil. These emulsions were stabilized with the same surfactant, 1 wt. % Brij 58, to ensure similar (though not exactly the same) interfacial tensions. As seen from Table 1, for both homogenizers higher viscosity of the dispersed phase resulted in larger drops, which shows that the viscous dissipation inside the drops during their breakup was significant and should be taken into account in the data interpretation. For example, in the emulsions prepared with the planar element, larger mean drop diameter, d_{32} = 7.2 μm, is observed for SBO with η_D = 50 mPa.s, whereas smaller diameter, d_{32} = 3.6 μm, is obtained for hexadecane with η_D = 3 mPa.s (see Table 1).

4.4. Effect of interfacial tension.

To study the effect of the interfacial tension we compared the mean drop size of emulsions obtained with soybean oil, when using different emulsifiers. As seen from Table 1, with both homogenizers, largest drops were obtained with Na caseinate (σ_{OW} = 14 mN/m), whereas smallest drops were obtained with SDS (σ_{OW} = 5.5 mN/m). Therefore, the interfacial tension has also effect on the mean size of the drops.

5. Main results and conclusions.

- Experimental results are obtained for the mean drop size after emulsification at various conditions – two geometries of the processing element, two Reynolds numbers, two viscosities of the oil phase, three interfacial tensions. The obtained set of results (see Table 1) can be used for comparison with the numerical simulations performed by our partners from Graz and Warsaw.
- The results show that the effects of oil viscosity, interfacial tension, and Reynolds number are very important for the mean drop size – all these factors should be taken into account when comparing estimating theoretically the drop size during emulsification in the studied homogenizers.
- The comparison of the results obtained with planar and cylindrical homogenizers shows that the mean drop size for the planar homogenizer is systematically (by 7 ± 2 %) larger than that for the cylindrical homogenizer at equivalent all other conditions. The possible reasons for this difference will be discussed during the final meeting of the Project, while comparing the numerical simulations with the experimental results by the partner groups.

Table 1: Experimental results for the volume-surface diameter, d_{32}, of emulsions prepared with the cylindrical (Cyl) and the planar (Plan) homogenizers under various conditions: Re is Reynolds number inside the gap, Q is flow rate of the emulsion through the homogenizer; p is driving pressure, η_D is oil viscosity, σ_{OW} is interfacial tension. The different oils are denoted as SBO (soybean oil, η_D = 50 mPa.s and HxD (hexadecane, η_D = 3.0 mPa.s). The relative differences (%) in the values of d_{32}, obtained with the planar and with the cylindrical elements are also shown.

Reynolds number Re	Q, L/s		$p\times10^5$, Pa		η_D, mPa.s	Surfactant	σ_{OW}, mN/m	d_{32}, µm		
	Cyl	**Plan**	Cyl	**Plan**				Cyl	**Plan**	%
8450	0.092	**0.131**	0.46	**0.45**	50	Brij 58	7.4	12.0	**12.8**	6.2
13270	0.145	**0.204**	1.11	**1.03**	3	Brij 58	7.0	3.3	**3.6**	8.3
					50	SDS	5.5	5.5	**5.8**	5.2
						Brij 58	7.4	6.6	**7.2**	8.3
						Na caseinate	14.0	9.7	**10.3**	5.8

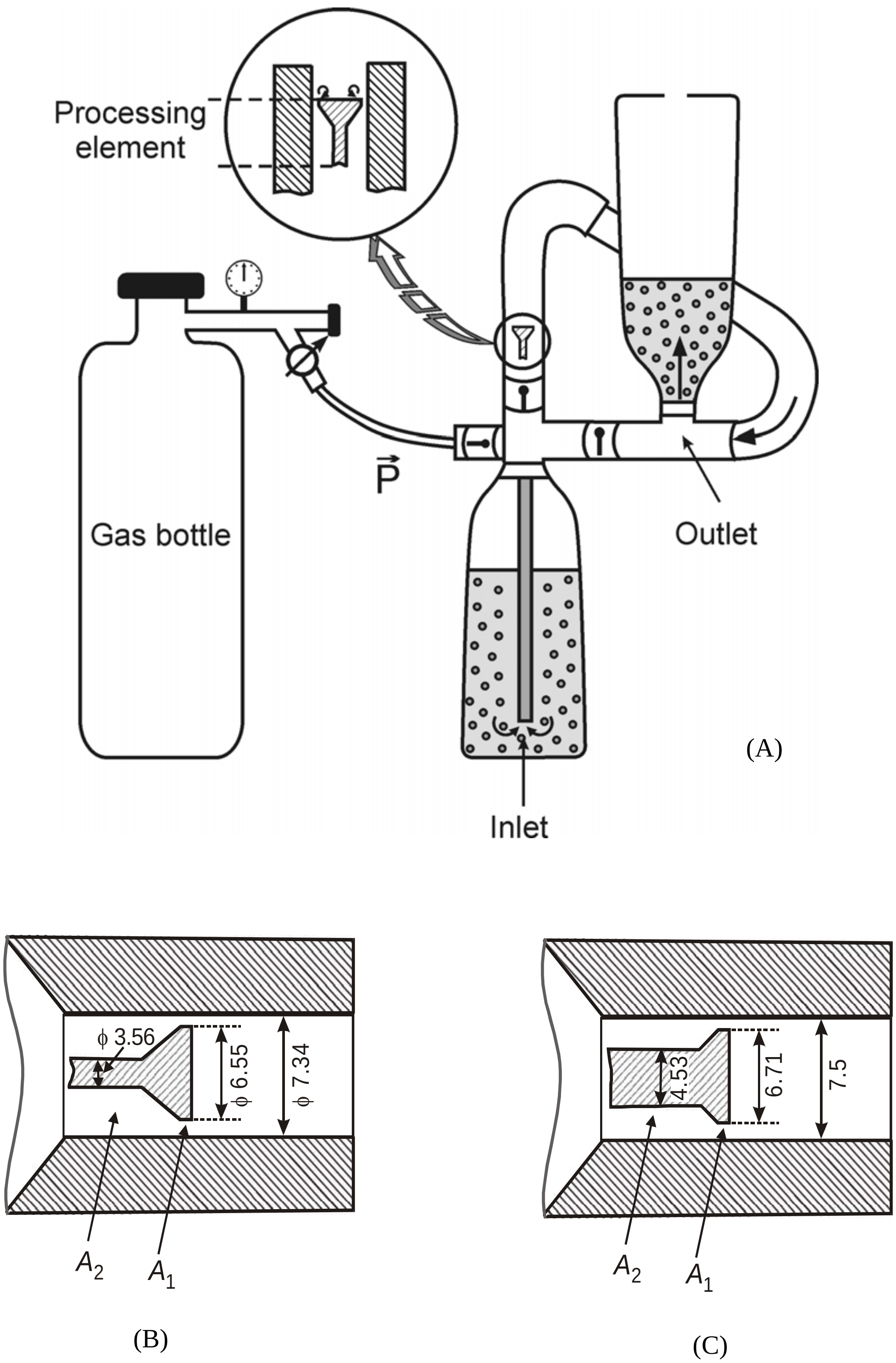

Figure 1. (A) Schematic presentation of the used homogenizer, which was equipped with processing element: (B) of cylindrical symmetry; or (C) of planar symmetry.

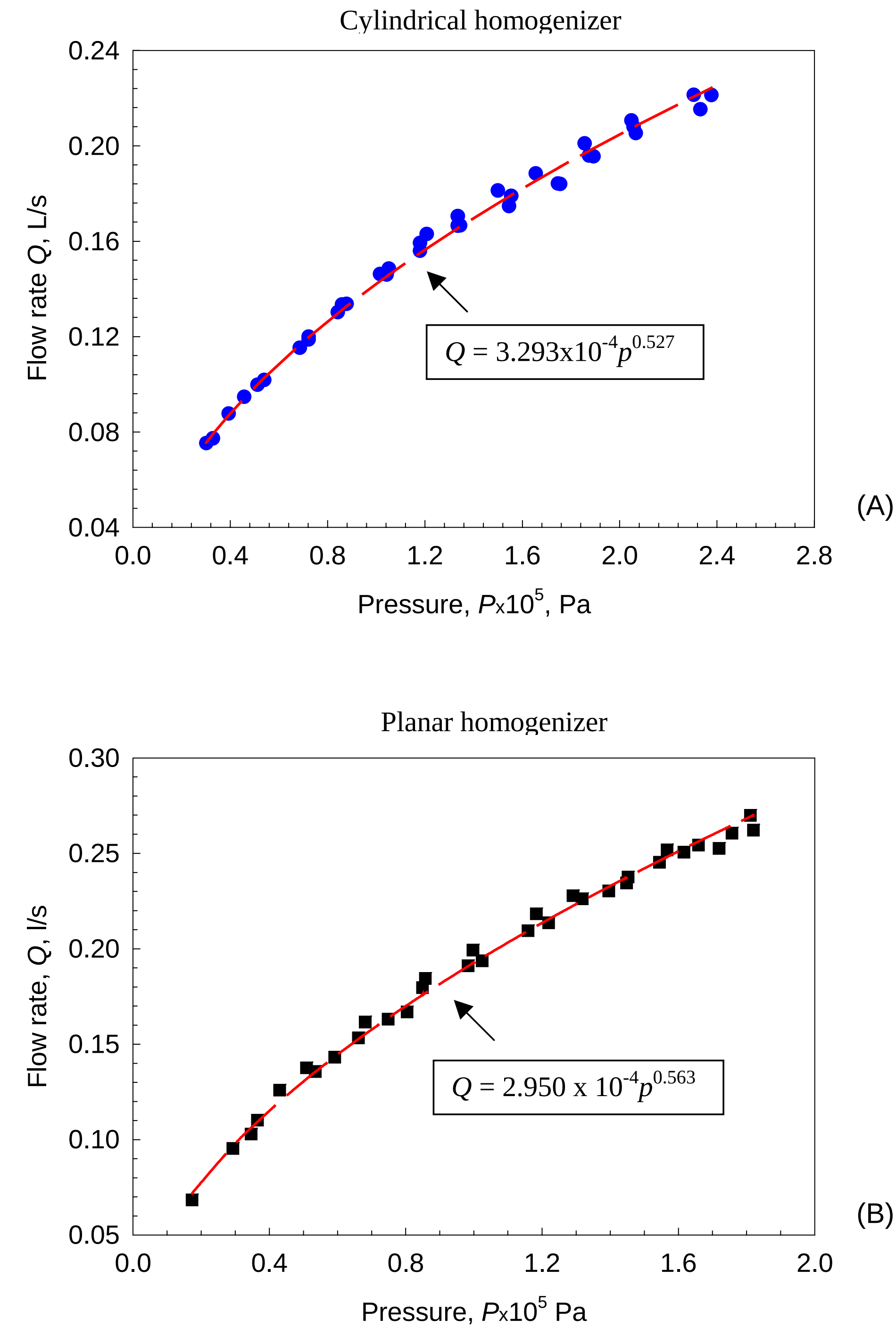

Figure 2. Flow rate, Q, as a function of the applied pressure, p, for processing elements with: (A) cylindrical symmetry, and (B) planar symmetry. The symbols are experimental data, whereas the curves are empirical fits.

References

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