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Attenuation of Ultrasound in Silicone-Oil-in-Water Emulsions.

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Abstract. – We report experimental measurements of sound attenuation in silicone-oil-in-water emulsions with varying volume fraction and frequency. These measurements are in good agreement with theoretical predictions for the propagation of ultrasound in inhomogeneous systems. Our results show that attenuation measurements may be used to characterize concentrated emulsions and to investigate ageing phenomena.

1. Introduction.

Colloidal dispersions are ubiquitous in many areas of science and technology [1, 2]. *In situ* characterization of these systems is, however, rather difficult since most of the available techniques are either intrusive or applicable only to dilute systems (*e.g.* quasi-elastic light scattering QELS). Recently there has been interest in the use of ultrasound as nonintrusive technique capable of providing data about concentrated colloidal systems. While theoretical attempts to describe the propagation of acoustic waves through suspensions and emulsions go back over many decades [3-6], experimental studies are still rather scarce [7-9]. In particular, very few attempts were made to determine, using an acoustic technique, the average particle size of concentrated dispersions. In this letter we report ultrasonic absorption measurements in silicone-oil-in-water emulsions over a large range of frequencies and volume fractions. These measurements are compared with theoretical predictions based on the work of Epstein and Carhart [4] and Lloyd and Berry [10]. This study illustrates that ultrasound may provide a useful technique to characterize (noninvasively and without sample dilution) concentrated emulsions and to follow their kinetics of ageing.

2. Experimental.

1) *Materials.* – The silicone-oil-in-water emulsions used in this work were purchased from Hoechst, France. The volume fraction of oil in the original samples was determined

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very accurately ($\pm 0.05\%$) by the producer. A whole range of concentrations (between 2 and $(40 \pm 0.1)\%$) was obtained by dilution with pure water. The mean radius of the oil droplets and the corresponding polydispersity were determined by QELS using a highly diluted sample ($\varphi < 0.01\%$) and were found to be $R = (132.5 \pm 0.5)$ nm and $\sigma^2 \leqslant 0.1$, respectively.

The physical constants of water and silicone-oil are given in table I. Most of the physical constants of the silicone-oil were determined in authors laboratory.

TABLE I. – *Physical constants of water and silicone-oil at* 23 °C.

	Physical constants						
	Density (g/cm^3)	Sound velocity (m/s)	Specific heat (erg/°C/g)	Thermal conductivity (erg/°C/cm/s)	Thermal dilatation ($°C^{-1}$)	Sound attenuation (cm^{-1})	Shear viscosity (g/cm/s)
Water [11]	0.998	1492	$4.18 \cdot 10^7$	$5.9 \cdot 10^4$	$2.38 \cdot 10^{-4}$	$23 \cdot 10^{-17} f^2$	$0.93 \cdot 10^{-2}$
Silicone-oil ([a])	0.974	1004	$1.46 \cdot 10^7$	$1.5 \cdot 10^4$ ([b])	$9.2 \cdot 10^{-4}$	$2 \cdot 10^{-12} f^{1.7}$	$69 f^{-0.33}$

([a]) measured in authors laboratory.
([b]) measured by Hoechst, France.

2) *Ultrasonic measurements.* – The ultrasonic attenuation was determined over a large range of frequencies by using two complementary techniques. At low frequencies ($400\ \text{kHz} < f < 1\ \text{MHz}$) an Eggers resonator [12, 13] was used allowing a determination of the ultrasonic attenuation to a precision of 10% for the lowest frequencies ($f < 700\ \text{kHz}$) and of 5% otherwise. The high-frequency regime ($4\ \text{MHz} < f < 100\ \text{MHz}$) was investigated using a pulse technique (corresponding precision: 5% for $f < 10\ \text{MHz}$ and 1% otherwise). The experiments were performed at temperature $T = (23 \pm 0.1)$ °C.

Note that most of the attenuation measurements in emulsions reported in the literature are obtained by using a classical pulse technique which is not very well adapted for the investigation of the low-frequency range ($f < 2\ \text{MHz}$) owing to diffraction phenomena. The resonator technique used in this work allows us to circumvent this limitation and to obtain important information on the physical properties of the system.

3. Results.

1) *Theory.* – There are a variety of theoretical formulations that describe ultrasonic propagation in suspensions of particles in fluids [14]. In this work we use an approach based on the works of Epstein and Carhart [4] and of Lloyd and Berry [10]. Since this approach has been reviewed in detail in ref. [8], we here only outline its essential features.

Consider an oil/water emulsion containing n oil droplets per unit volume. In the long-wavelength limit (*i.e.* for a wavelength in the continuous phase much greater than the droplets size), the ultrasonic propagation in the emulsion may be described by a complex wave number K ($K = 2\pi f/c + i\alpha$, where f is the frequency, c the wave velocity and α the attenuation) given by [10]

$$\left(\frac{K}{k}\right)^2 = 1 + \frac{3\varphi f(0)}{k^2 R^3} + \frac{9\varphi^2}{4k^4 R^6}\left[f^2(\pi) - f^2(0) - \int_0^{\pi} \mathrm{d}\theta \frac{1}{\sin(\theta/2)}\left(\frac{\mathrm{d}}{\mathrm{d}\theta} f^2(\theta)\right)\right], \tag{1}$$

where k is the wave number in the continuous phase, R the droplet radius and φ the droplet volume fraction ($\varphi = 4\pi R^3 n/3$). The far-field scattering amplitude $f(\theta)$ characterizes the asymptotic behaviour of the compressional wave reflected by an individual scattering centre (*i.e.* by a single oil droplet suspended in pure water):

$$\phi_{\rm ref}(r,\theta) \underset{r\to+\infty}{\propto} f(\theta)\,\frac{\exp[ikr]}{r}\,. \tag{2}$$

In terms of Legendre polynomials, $f(\theta)$ may be expanded as

$$f(\theta)=\frac{1}{ik}\sum_{n=0}^{+\infty}(2n+1)\,A_n P_n(\cos\theta)\,. \tag{3}$$

The scattering coefficients A_n can be calculated numerically using the theory of Epstein and Carhart [4]. Usually, only the first two coefficients A_0 and A_1 are important and eq. (1) reduces to (1)

$$\left(\frac{K}{k}\right)^2 \simeq 1-\frac{3i\varphi}{k^3R^3}(A_0+3A_1)-\frac{27\varphi^2}{k^6R^6}(A_0A_1+2A_1^2)\,. \tag{4}$$

The φ^2 term corresponds to the effect of multiple scattering.

From eq. (4) one can deduce the imaginary part of the wave number K, *i.e.* the overall attenuation (α) of the emulsion. This attenuation is due to visco-inertial and thermal scattering mechanisms, as well as to the intrinsic absorption in the two phases composing the system [7]. One can define the «excess attenuation» ($\Delta\alpha$) as the difference between the overall attenuation and that caused by absorption alone:

$$\Delta\alpha=\alpha-(1-\varphi)\,\alpha_1-\varphi\alpha_2\,, \tag{5}$$

where α_1 and α_2 are the intrinsic attenuation of water and oil, respectively.

2) *Results and discussion.* – The experimental measurements of ultrasonic attenuation in the silicone-oil-in-water emulsions are presented in fig. 1 and 2.

In fig. 1*a*) the total attenuation (α) is plotted as a function of the frequency for three different emulsions ($\varphi = 2.05\%$, 5.10% and 10.25%). The solid lines represent the theoretical prediction of sect. 3,1) (using the physical constants of table I and the droplets radius and polydispersity determined by QELS). One can observe a good agreement between theory and experiments over the whole frequency range.

Rather than using the value of the droplets radius measured by QELS, one can also try to determine it by fitting the experimental data of fig. 1 with the theoretical predictions of sect. 3,1) (the droplets radius being then the only unknown). The best fits are represented in fig. 1 (dashed curves) and the corresponding values of the radius are given by $R = 130$ nm, $R = 136$ nm and $R = 128$ nm for $\varphi = 2.05\%$, $\varphi = 5.10\%$ and $\varphi = 10.20\%$, respectively.

The comparison between these values and the value determined by the QELS technique (on a highly diluted sample) shows clearly the ability of the ultrasonic technique to determine accurately the average size of the droplets in the studied range of concentrations.

Figure 1*b*) shows the variations of the excess attenuation ($\Delta\alpha$) as a function of the oil volume fraction at four different frequencies. The attenuation measurements agree well with the theoretical predictions at lower φ values: however, the measurements fall increasingly below the theoretical curves as the droplet volume fraction increases. One

(1) For the validity of eq. (4) see [8].

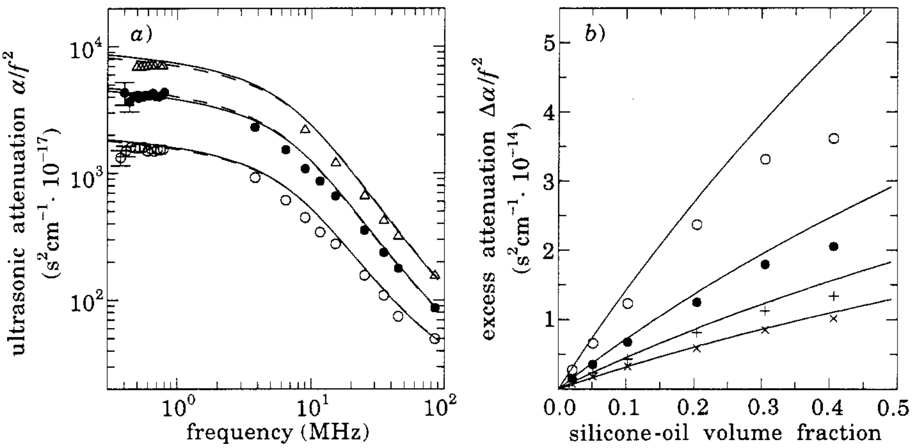

Fig. 1. – *a*) Ultrasound attenuation α divided by the square of the frequency f, *vs.* frequency, for three silicone-oil-in-water emulsions. ○ $\varphi = 2.05\%$, ● $\varphi = 5.12\%$, △ $\varphi = 10.23\%$. —— Theoretical curves calculated using the droplets radius and polydispersity given by QELS; --- best adjustments to the experimental data, by varying the droplets radius R (the polydispersity being neglected). All the theoretical curves are calculated using eq. (4). *b*) Excess attenuation $\Delta\alpha$ divided by the square of the ultrasonic frequency f, *vs.* the oil volume fraction in the silicone-oil emulsions. ○ $f = 15$ MHz; ● $f = 25$ MHz; + $f = 35$ MHz; × $f = 45$ MHz. —— Theoretical curves obtained using eq. (4) with a droplets radius $R = 132$ nm.

possible origin to this discrepancy is that eq. (4) was established assuming the spatial distribution of the scatterers to be random while real emulsions may exhibit correlations between the droplets. Another source of discrepancy could be related to the fact that the medium surrounding the droplets is not defined self-consistently, as pointed out by Sayers [15].

All the preceding experimental results have been concerned with freshly prepared emulsions. We now present some results concerning the time evolution of the silicone-oil emulsions. Figure 2 shows low-frequency attenuation measurements performed on the

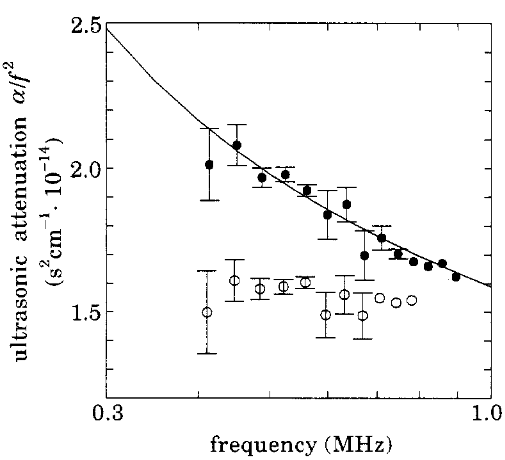

Fig. 2. – Observed attenuation α divided by the square of the ultrasonic frequency f in a 2.05% silicone-oil-in-water emulsion: ○ freshly prepared sample; ● three months aged sample. —— Theoretical adjustment to the data obtained using eq. (4) for the size distribution given by eq. (6).

2.05% silicone-oil emulsion sample, just after its preparation (○) and three months later (●). One can observe in the aged sample a constant increase of α/f^2 as the frequency decreases. On the other hand, we have not observed any significant variation of the attenuation in the high-frequency regime (not presented on the figure). The study by QELS of a diluted sample of the aged 2.05% emulsion did not allow us to detect any variation in the system.

An aged emulsion usually contains primary droplets (*i.e.* original emulsion droplets) as well as a certain number of large oil droplets. If we crudely assume that the latter are monodisperse, the theory of sect. 3, 1) can be readily used to determine their size and their concentration. The best adjustment between the theoretical predictions and the data is represented in fig. 2 (solid line) and corresponds to the following size distribution:

$$(\varphi = 1.88\%,\ R = 132\ \text{nm}) + (\varphi = 0.17\%,\ R = 2360\ \text{nm})\,. \tag{6}$$

According to the acoustical measurements we therefore expect the presence of very large droplets (in comparison with the original ones) in the sample. In order to check whether very large particles were really present or not, the emulsion was observed under an optical microscope. Figure 3 represents a microphotography of the sample. While primary droplets are not visible due to their small size (in comparison with the wavelength of the light), one does observe the presence of large oil droplets. The mean diameter of these large particles is about 1 μm, in good agreement with the acoustical predictions of eq. (6). Note that the prior dilution that was necessary for the study by QELS has probably led to the creaming of the large droplets which therefore became undetectable.

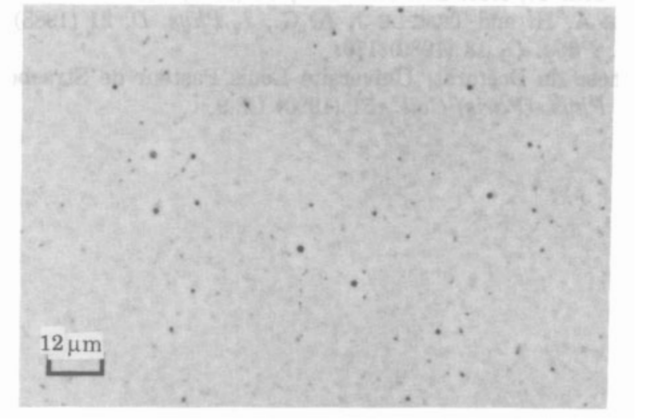

Fig. 3. – Microphotography of the 2.05% aged silicone-oil-in-water emulsion. The scale corresponds to 12 μm. The mean diameter of the visible droplets can be estimated to be about 1 μm.

4. Conclusion.

Our ultrasonic absorption measurements in silicone-oil-in-water emulsions support well the theoretical predictions of Epstein and Cahrhart [4] and Lloyd and Berry [10] over a large range of frequencies and volume fractions. They moreover show the ability of the acoustical measurements to characterize, noninvasively and without sample dilution, concentrated emulsions (up to 10%). More generally, ultrasound may be used for the characterization of various colloidal dispersions [16, 17].

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