Proceedings of the Institute of Acoustics

CHARACTERISATION OF EMULSIONS USING A FREQUENCY SCANNING ULTRASONIC PULSE ECHO REFLECTOMETER

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1. INTRODUCTION

Emulsions are important in a wide variety of areas, e.g the food, chemical, petrochemical, cosmetic and agrochemical industries [1]. Many of their physical properties which are of commercial importance, such as stability and rheology, depend on their composition and microstructure and so it is important to have analytical techniques which can be used to characterise these properties. There are a wide range of techniques which can be used for this purpose, each based on different physical principles [2]. It is widely recognised that ultrasonics has considerable potential as a tool for characterising emulsions [3]. Ultrasonics can be used to measure disperse phase volume fractions, particle sizes, creaming profiles, phase transitions and particle compressibilities [3]. To carry out many of these measurements it is necessary to measure the frequency dependence of the ultrasonic properties of an emulsion. For this reason a device has been developed, called a *frequency scanning ultrasonic pulse echo reflectometer* or FSUPER, which can be used to measure the velocity and attenuation of liquids over a range of frequencies (0.2 to 7 MHz).

2. THEORY

To use ultrasound to characterise emulsions it is necessary to relate the physical properties of interest, such as particle concentration or size, to the measurable ultrasonic parameters e.g. velocity and attenuation. There are many theories which attempt to describe ultrasonic propagation in emulsions [4]. The most comprehensive are based on an analysis of the scattering of ultrasound by an emulsion. The ultrasonic properties of an ensemble of scattering particles are described by a complex propagation constant ß (= $\omega/c + j.\alpha$, where ω is the angular frequency, c is the velocity, α is the attenuation coefficient and $j = \sqrt{-1}$) which is calculated by working out the total scattering from all the particles in a system, taking into account their spatial distribution [5]. The complex propagation constant of an ensemble of point scatterers distributed randomly has been calculated by Waterman and Truell [5].

$$(ß/k_1)^2 = (1-3.j.\phi.A_0/(k_1r)^3).(1-9.j.\phi.A_1/(k_1r)^3) \qquad (1)$$

where k_1 is the propagation constant of the continuous phase (= $\omega/c_1 + j.\alpha_1$), c_1 and α_1 are the velocity and attenuation coefficient of the continuous phase, ϕ is the disperse phase volume fraction, r is the particle radius and A_0 and A_1 are the single particle scattering coefficients. The magnitudes of A_0 and A_1 depend on the thermophysical properties of the component

phases, the size of the droplets and the frequency used. Values of A_0 and A_1 for emulsions have been calculated by Allegra and Hawley [6]. The velocity and attenuation of an emulsion are determined from equation 1 using the relationships: $c = \omega/\mathrm{Re}(\beta)$ and $\alpha = \mathrm{Im}(\beta)$.

3. MATERIALS AND METHODS

3.1 Materials.
n-Hexadecane (a hydrocarbon oil) and Tween 20 (a surfactant) were obtained from the Sigma Chemical Company, St. Louis, U.S.A.

3.2 Emulsion preparation.
Emulsions were prepared by homogenising weighed amounts of n-hexadecane and aqueous phase (2 wt% Tween 20 in distilled water) together. Emulsions with varying particle sizes were produced using two different homogenisers. A coarse emulsion was produced using a Warring blender and a fine emulsion using a high pressure laboratory homogeniser (Shields Instruments Ltd, Model S500). The particle size distribution of the emulsions was measured using a Malvern Mastersizer (figure 1).

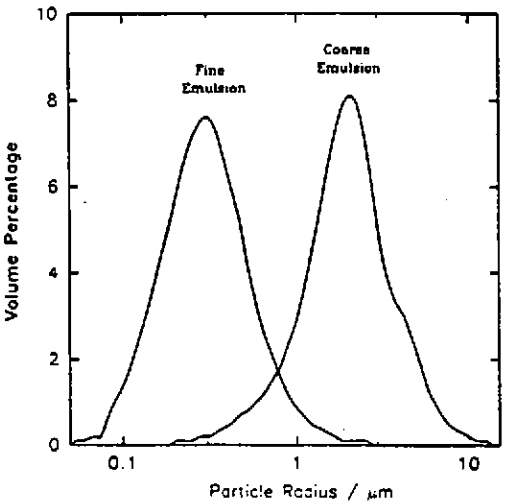

Figure 1. Measured droplet size distributions.

ULTRASONIC CHARACTERISATION OF EMULSIONS

3.3 Ultrasonic measurements.
The ultrasonic velocity and attenuation of the emulsions were measured using a frequency scanning ultrasonic pulse echo reflectometer (FSUPER). This device consists of a cylindrical perspex buffer rod set into an aluminium cell, which contains the sample (figure 2). An ultrasonic transducer is fixed to one end of the buffer rod and the other end is fixed parallel to the inside face of one of the cell walls which acts as a reflector plate. A highly damped ultrasonic transducer is used so that a wide range of frequencies can be generated. An ultrasonic flaw detector (Sonatest UFD1) is used to produce a broad band electrical 'spike' which excites the transducer. The signals returning from the sample are analysed using a digital storage oscilloscope (Lecroy 9420). In our experiments *two* highly damped transducers were used in order to cover a wider frequency range: a Sonatest SLH1-25 was used for the frequency range 0.2-1 MHz and a Sonatest SLH5-25 for the range 1-7 MHz.

A pulse of ultrasound is generated by the transducer and this travels along the buffer rod until it reaches the buffer rod/sample interface where it is partly reflected and partly transmitted (figure 2). The transmitted portion travels through the sample until it reaches the sample/reflector plate interface. The pulses reflected from both interfaces return to the transducer where they are detected and displayed on the oscilloscope (figure 2). The magnitude and phase of both echoes are calculated using Fourier Transform analysis. The ultrasonic velocity is then calculated from the phase difference and the attenuation coefficient from the ratio of the magnitudes (see below).

3.3.1 Velocity measurements. The velocity of a sample c is determined from the equation $c = 2d/t$, where d is the sample pathlength and t is the time difference between the two echoes. t is calculated as a function of frequency using the relation:

$$t = (n.360 + \delta\Theta - \Theta_d - 180)/(360.f) \qquad (2)$$

where f is the frequency, n is an integer, $\delta\Theta$ is the difference in phase between the echoes reflected from the sample/reflector plate interface and the buffer rod/sample interface and Θ_d is the phase shift due to diffraction [7]. All these parameters are frequency dependent. The -180 appears in equation 2 because an ultrasonic wave undergoes a 180° phase inversion when the medium it is reflected by has a higher acoustic impedance than the medium it is travelling in (figure 2). If the velocity dispersion in a sample is not large (e.g. $[c_{max}-c_{min}]/c_{max} < (f.t)^{-1}$) then the value of n can be determined by measuring the time difference (δt) between similar positions on the two echoes (e.g. see figure 2) ($n \approx \delta t.f$). If the sample is highly dispersive the value of n can be determined by measuring t at two different pathlengths; $c = 2d_1/t_1 = 2d_2/t_2$ and so the values of n_1 and n_2 needed in equation 2 to satisfy this condition can be determined.

3.3.2 Attenuation measurements. The attenuation coefficient is determined by measuring the magnitudes of the echo reflected from the buffer rod/sample interface (M_1) and from the sample/reflector plate interface (M_2) as a function of frequency.

$M_1 = \exp(-2\alpha' d').R.M_i$

$M_2 = \exp(-2\alpha' d').(R^2-1).R'.M_i.\exp(-2\alpha d)$

Therefore, the attenuation can be calculated by rearranging the following equation:

$$M_2/M_1 = [(R^2-1).R'/R)].\exp(-2\alpha d) \quad (3)$$

Here R and R' are the reflection coefficients from the buffer rod/sample and sample/reflector plate interfaces which can be measured [8], d' and d are the lengths of the buffer rod and the sample, α' and α are the attenuation coefficients of the buffer rod and sample, and M_i is the magnitude of the pulse when it first enters the buffer rod. To obtain accurate results the measurements must be corrected for diffraction effects [7]. With careful design of the instrument the velocity can be determined to better than 1 m s^{-1} and the attenuation coefficient to better than 5% [8]. The ultrasonic properties of the samples are temperature dependent and so all the measurements were carried out at 20.0 ± 0.1 °C in a thermostated water bath.

4. RESULTS AND DISCUSSION

In figure 3 the measured ultrasonic velocity and attenuation coefficient of a 10 wt% n-hexadecane-in-water emulsion are compared with the values predicted using multiple scattering theory (equation 1) and the thermophysical properties of the component phases (table 1). The velocity and attenuation per cycle ($\alpha\lambda$) are plotted against $r.\sqrt{f}$ because these parameters give unique curves for any combination of particle size and frequency in the long wavelength limit ($r << \lambda$) (Allegra and Hawley 1972). There is good agreement between theory and

Table 1. Thermophysical properties of n-hexadecane and aqueous phase

Thermophysical property	n-hexadecane	Aqueous phase
Velocity (m s^{-1})	1357.5[1]	1485.7[1]
Density (kg m^{-3})	773.0[1]	999.6[1]
Viscosity (Pa s)	0.0034	0.001
Specific heat capacity (J kg^{-1} K^{-1})	2201	4183
Thermal conductivity (W m^{-1} K^{-1})	0.14	0.59
Coefficient of volume expansion (K^{-1})	0.00094	0.00021
$\alpha/(f^2 \times 10^{-15})$ (Np m^{-1} s^2)	101	25

[1] Measured in the laboratory, all other values were taken from reference [6] assuming that the aqueous phase had the same properties as distilled water.

experiment when a particle size distribution similar to that in the emulsions (figure 1) is used in the predictions. The agreement is significantly worse when it is assumed that the emulsions are monodisperse. This highlights the importance of including the full particle size distribution in the theoretical predictions.

The velocity of ultrasound increases as the particle size and frequency increases, whilst $\alpha\lambda$ is bell shaped. By measuring the velocity and attenuation as a function of frequency it should be possible to determine both the particle size and the disperse phase volume fraction of an emulsion. At low or high values of $r.\sqrt{f}$ the ultrasonic velocity is fairly independent of particle size and so measurements in this region could be used to determine the volume fraction without prior knowledge of r. In the intermediate region the velocity and attenuation are sensitive to r and so measurements in this region could be used to determine the particle size. The accuracy to which the particle size could be determined depends on the accuracy to which the velocity and attenuation can be measured and the magnitude of the change in the velocity and attenuation with particle size (which depends on the degree of scattering). Optimum accuracy would be obtained by making measurements over a range of frequencies and finding the particle size distribution which gave the best agreement between theory and experiments. The frequency range of an instrument sets practical limits to the range of emulsion droplet sizes which could be analysed. The velocity and attenuation are only sensitive to the particle size in the region $0.0002 < r.\sqrt{f} < 0.001$ (figure 3). Thus the FSUPER, which can make measurements in the frequency range 0.2 to 7 MHz, can only be used to determine particle radii from about 0.1 to 2 μm. To extend this range an instrument would have to be used which could measure the velocity and attenuation over a wider range of frequencies.

5. CONCLUSIONS

An ultrasonic device has been described which can be used to measure the velocity and attenuation of emulsions as a function of frequency. Measurements in a series of 10 wt% n-hexadecane-in-water emulsions have shown that there is appreciable velocity dispersion and attenuation due to scattering in this system. There is good agreement between the measurements and theoretical predictions made using multiple scattering theory which suggests that this theory can be used to relate the physical properties of an emulsion to its ultrasonic properties. The possibility of using ultrasonic measurements to determine the particle size and disperse phase volume fraction of emulsions has been discussed and the factors effecting such measurements are highlighted.

Ultrasonics has advantages over many existing techniques for characterising emulsions because it can be used in concentrated systems which are optically opaque or electrically non-conducting. It is also capable of rapid and precise measurements, it is non-destructive, it is relatively inexpensive and it can be used in-line.

6. ACKNOWLEDGEMENTS

The author would like to thank the Department of Trade and Industry and the Ministry of Agriculture, Fisheries and Foods for financial support and Dr MJW Povey and P Fairley for useful advice and discussions.

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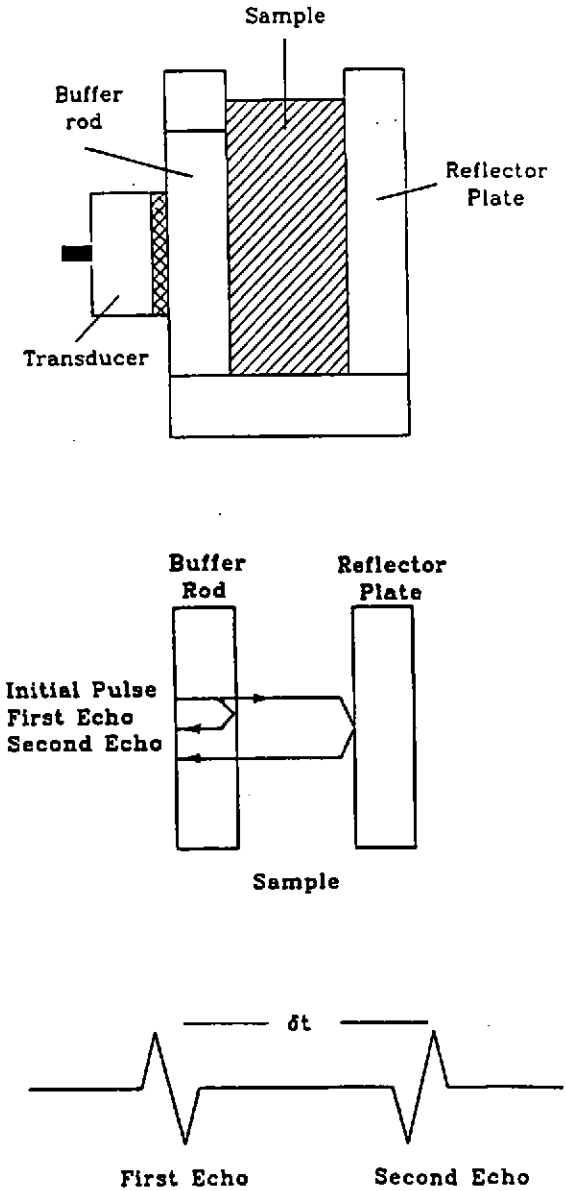

Figure 2. Diagram of ultrasonic pulse echo reflectometer.

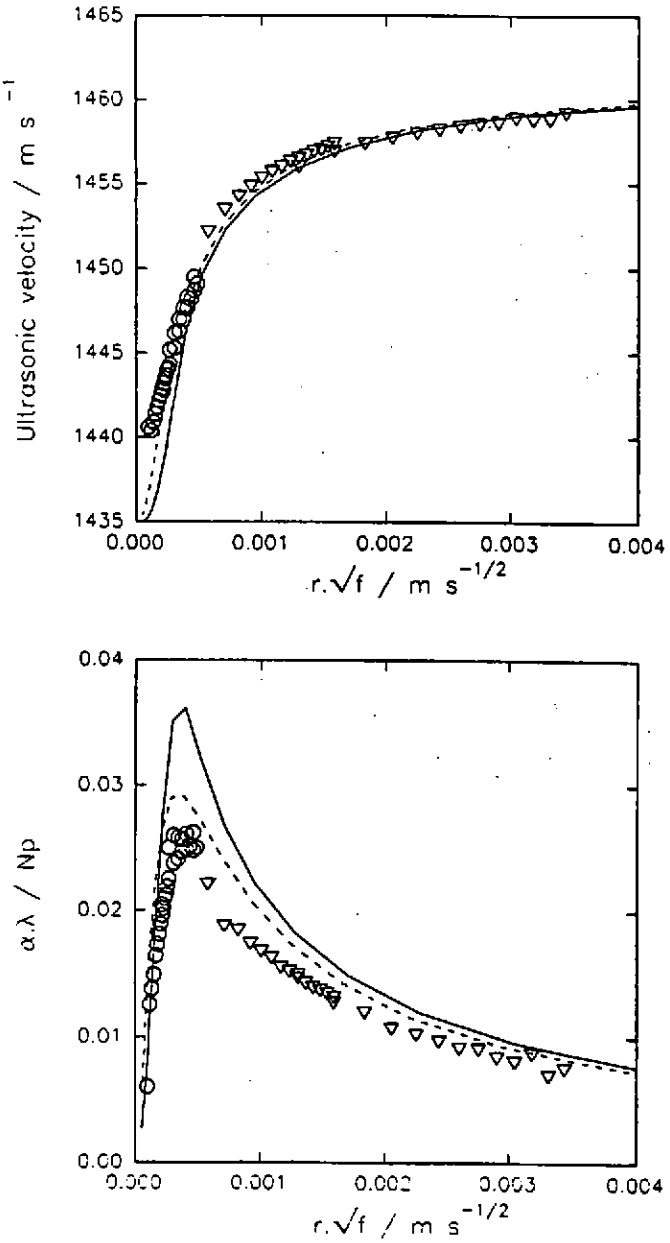

Figure 3. Velocity and attenuation in a 10wt% n-hexadecane-in-water emulsion. Curves are predictions made using multiple scattering theory (equation 1). The full curve assumes that the emulsion droplets are monodisperse and the broken curve that they are polydisperse. The circles represent experimental measurements in the fine emulsions, and the triangles in the coarse emulsions.