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Measurements of toluene–water dispersions hold-up using a non-invasive ultrasonic technique

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Abstract

Ultrasound techniques for the characterization of liquid–liquid dispersions have previously shown their value and promise, but still require refinement and careful, preferably non-invasive, implementation. Their combination with drop size distribution measurement techniques is also an important area for further development. A new non-invasive implementation has been developed, studied and evaluated in detail, which leads to accurate hold-up fraction measurements (to within −0.0123 units), surpassing that of most previous techniques. The largest error incurred by the effect of the propagation through the vessel wall glass has been shown to be negligible, the same applying to the effect of the propagation across the agitator shaft. Actual experimental dispersed phase hold-up fractions of up to 40% were tested and successfully correlated, in addition to 100% organic phase.

Keywords: Liquid–liquid systems; Ultrasounds; Hydrodynamics

1. Introduction

Many industrial processes require intimate contact of two immiscible liquids in order to promote either a chemical reaction or the separation of one or more chemical species (solvent extraction). Most often, the mixture is induced by agitation of both phases in order to increase their contact area. Depending on the initial conditions of the mixture (namely the dispersed phase hold-up fraction), one of the phases may form drops (dispersed phase) inside the other (continuous) phase.

Our research team's work has been aimed at the accurate determination of the kinetic parameters of hydrodynamic models used to describe the division and coalescence of dispersed phase drops and at testing their possible universality. As part of this effort, we are now combining the ultrasonic measurement of the dispersed phase hold-up with a previously developed image analysis technique for the measurement of drop size distributions [1], both non-intrusive techniques, in order to test the soundness/applicability of homogeneous two-phase vessel models and develop new non-homogeneous versions of wider applicability.

The use of the ultrasonic technique allows the evaluation of the dispersed phase hold-up in liquid–liquid systems by measuring the sound propagation travel time in dispersions and emulsions. This technique uses the difference between the sound velocities in the organic and aqueous phases to evaluate the dispersed phase volume fraction (hold-up). The experimental results yield the dependence of the sound velocity on the hold-up, by comparing the travel time through the dispersion with that through the pure phases.

Among the pioneering studies in this field, the one by Havliček and Sovová [2] should be particularly mentioned, because the technique was tested with four different physical systems typically used in liquid–liquid extraction processes. Their experiments showed the dependence of the ultrasound velocity on the hold-up and its independence on the size of the droplets forming the dispersion. The experiments contemplated the temperature dependence of the ultrasound velocity in single-phase liquids.

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The ultrasonic technique developed by Bonnet and Tavlarides [3] allowed the measurement of dispersed phase hold-ups by a non-invasive method. Their technique estimated the hold-up exclusively from the ultrasonic waves' time-delays across the dispersion and across each one of the pure phases, thus obtaining estimate errors in the neighbourhood of 27%. Later, Jongheop and Tavlarides [4] proposed a modification of this method, in which the effects of spherical and polydispersed drops on the path length of ultrasound wave transmission are considered, together with the physical properties of both phases. Their experimental results showed that the true hold-up could be predicted with a relative error of up to 7.7%, their experiments having been performed with moderate to high hold-up values.

Tsouris and Tavlarides [5] applied the latter technique to low dispersed phase fractions, for long path lengths. They obtained good results for volume fractions higher than 5% when using a linear model that considers sound reflection and refraction at the drop–continuous phase interface. However, for volume fractions lower than 5%, an empirical model was applied.

In the present work, this same technique was used in transmission mode and different types of time-travel estimates were tested, as explained in Section 5.1.

To determine the hold-up, we developed a new expression for the hold-up based on the dispersion's characteristics that influence the ultrasound velocity.

The propagation velocity (v_h) of a longitudinal perturbation of the ultrasound in liquid–liquid dispersions depends on the compressibility (k_h) and density of the dispersion (ρ_h) according to

$$v_h = (k_h \times \rho_h)^{-1/2}. \tag{1}$$

The density of the dispersion may be related with the values of the density of toluene and water by

$$\rho_h = \rho_a \times (1-h) + \rho_t \times h, \tag{2}$$

and its compressibility by a similar expression

$$k_h = (1-h) \times k_a + h \times k_t, \tag{3}$$

where h is the hold-up fraction. These equations, (1)–(3), have also previously been used in other studies, including ultrasound Doppler velocimetry (Bouillard et al. [6]).

The travel time through the dispersion is related with the propagation velocity (v_h) and the path length (L) as

$$t_h = \frac{L}{v_h}. \tag{4}$$

Eliminating v_h between Eqs. (1) and (4), we obtain

$$t_h = L \times (k_h \times \rho_h)^{1/2} \Leftrightarrow t_h^2 = L^2 \times (k_h \times \rho_h). \tag{5}$$

Replacing ρ_h and k_h from Eqs. (2) and (3) in Eq. (5), we obtain

$$t_h^2 = L^2 \times [h^2 \times k_t \times \rho_t + (1-h)^2 \times k_a \times \rho_a + h(1-h) \times (k_t \times \rho_a + k_a \times \rho_t)] \tag{6}$$

and, as $t_a^2 = L^2 \times (k_a \times \rho_a)$ and $t_t^2 = L^2 \times (k_t \times \rho_t)$,

$$t_h^2 = \left[h^2 \times t_t^2 + (1-h)^2 \times t_a^2 + h(1-h) \times \left(\frac{t_t^2}{\rho_t} \times \rho_a + \frac{t_a^2}{\rho_a} \times \rho_t\right)\right]. \tag{7}$$

Solving Eq. (7) for hold-up, a quadratic expression is obtained.

$$h^2 \times \left[t_t^2 \times \left(1 - \frac{\rho_a}{\rho_t}\right) + t_a^2 \times \left(1 - \frac{\rho_t}{\rho_a}\right)\right] + h \times \left[t_t^2 \times \frac{\rho_a}{\rho_t} + \left(\frac{\rho_t}{\rho_a} - 2\right) \times t_a^2\right] + (t_a^2 - t_h^2) = 0. \tag{8}$$

After the substitution of the densities and the measured travel time trough toluene and water, the above equation yields an expression of h as a function of travel time (t_h) only. As the temperature influences the ultrasound travel time (see Section 5.2), this same Eq. (8) could also be expressed as a function of temperature, if the densities (ρ_a and ρ_t) and the travel time (t_a and t_t) for the single saturated phases were expressed as functions of temperature.

2. Experimental set-up and measurement technique

Fig. 1 shows a schematic representation of the mixer vessel and data acquisition equipment used in this investigation. The mixer consists of a glass vessel (0.2 m internal diameter by 0.2 m height) with a flat bottom and four baffles. The agitation was provided by a standard Rushton turbine of 0.1 m diameter (1/2 of vessel diameter) placed at 1/3 of the dispersion's height from the bottom of the vessel (as used in Ribeiro et al. [1]).

The liquid–liquid system used for our experiments consists of toluene as the dispersed phase and distilled water as the continuous phase. The phases were previously equilibrated by mutual contact. Ultrasound transducers with a 1 MHz central frequency were used, mounted outside the vessel in a diametrically opposite configuration. Two contact thermocouple probes were placed on the outside surface of the vessel to measure the temperature in a continuous and non-invasive way.

A computer program was written and used to control and collect the data from the ultrasound board, the stirrer and the pair of thermocouples. With this program, we were able to control the ultrasound board by: (1) setting the energy and duration of the electric pulse to be applied to the emitter transducer, (2) setting the start time, rate and duration of the received signal sampling and (3) setting a broad time interval to visualize the received signal. Based on preliminary work designed and performed to minimize signal noise for a large range of hold-ups, the electric pulse parameters were fixed at the following values: (1) voltage—300 V, (2) high-pass filter—0.5 MHz, (3) low-pass filter—2.5 MHz and (4) energy capacitor—820 pF. The use of a 2.5 MHz low-pass filter is necessary to lower the noise amplitude and, to further decrease that amplitude, the measurement signal is taken as the average of four readings.

The program also implements automatic gain control of the input amplifier, and has the capability to execute a series of mea-

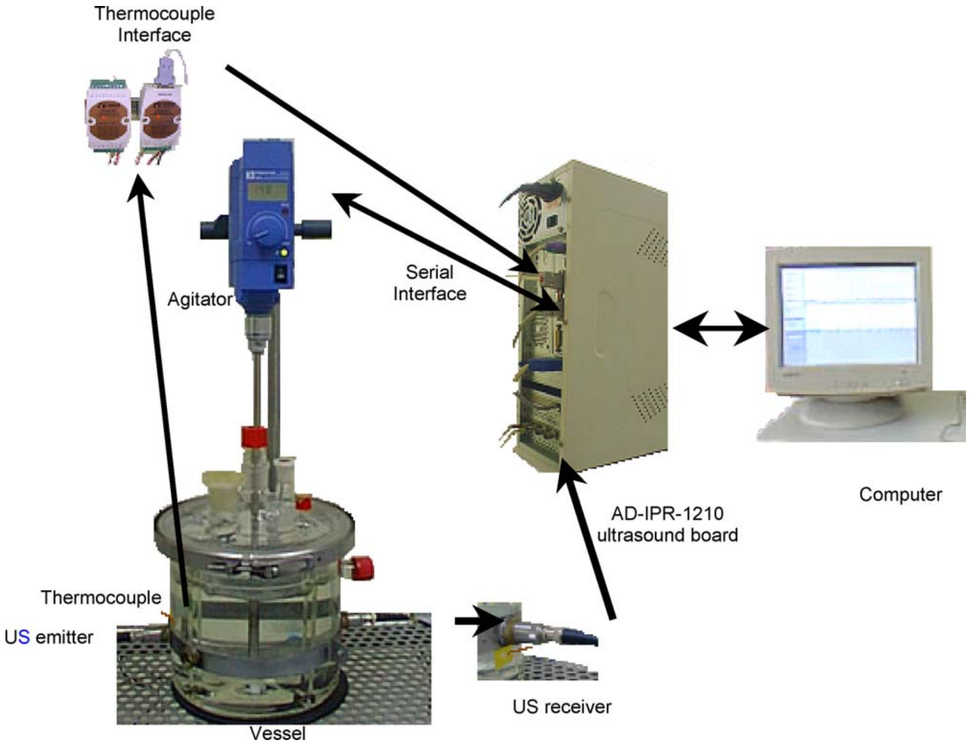


Fig. 1. Schematics of the mixer vessel and data acquisition equipment.

surements, without operator intervention, given the number and the time interval between them. The travel time of the ultrasound pulse is then calculated based on the signal received, using a predefined narrow time window. Using this program, we can also set the stirrer speed and read the actual values of stirrer speed and torque, as well as the temperature measured by one to eight thermocouples. All data collected can be saved on a file for off-line processing.

Due to the signal dispersion, a representative travel time may be calculated in different ways, as explained in Section 5.1. The objective is to choose the travel time definition that fits better the entire working range of hold-up values.

3. Preliminary studies

After acquiring the ultrasound signal, it must be processed in order to extract an accurate dispersed phase hold-up fraction.

3.1. *Influence of the stirrer shaft and glass vessel wall*

As well known, the sound velocity decreases from solids to liquids and is even lower in gases. Table 1 [7] shows the velocity of sound within different materials relevant for the present work.

From the preliminary experimental work, it was found that the stirrer shaft affected the ultrasound signal. The stirrer shaft used is made of steel, and so the results obtained when the sound travels through the vessel (with the liquid–liquid system and the stirrer shaft) are disturbed when compared with those obtained without the stirrer shaft. Another material used in the experimental set-up is the glass of the vessel wall. The manufacture of this type of vessel used standard large diameter glass tubes and flanges that were post-worked, extended and welded. This may introduce irregularities in the thickness and geometry of the glass vessel wall. As we cannot fully characterize these irregularities, it is impossible to accurately quantify the resulting effect.

To understand these two kinds of interferences, two series of experimental tests were conducted, where the glass vessel was filled with 4500 cm^3 of toluene or water (pure phases) and the ultrasound transducers were placed at three different levels, as shown in Fig. 2. For each level, several travel time measurements were carried out in the following conditions: (1) without stirrer shaft, (2) with the stirrer shaft stopped (0 rpm) and (3) with different stirrer speeds (50–150 rpm, in 10 rpm steps). The results obtained are shown in Figs. 3 and 4. Each result is the average of 100 measurements.

As may be seen, at level 1, the travel time with and without stirrer shaft have approximately the same value for the two series of experimental tests (with toluene and water). This is easily explained by the fact that level 1 is below the turbine, so the signal does not pass through the stirrer shaft. For the other two levels, the presence of the shaft causes changes in travel time, because the signal crosses the shaft. Without the shaft, of course,

Table 1
Materials' acoustic properties

Material	Longitudinal velocity (m/s)
Glass	2000–5000[a]
Toluene at 20 °C	1360
Water at 20 °C	1480
Steel	5660–5890[a]

[a] Depending on the material used.

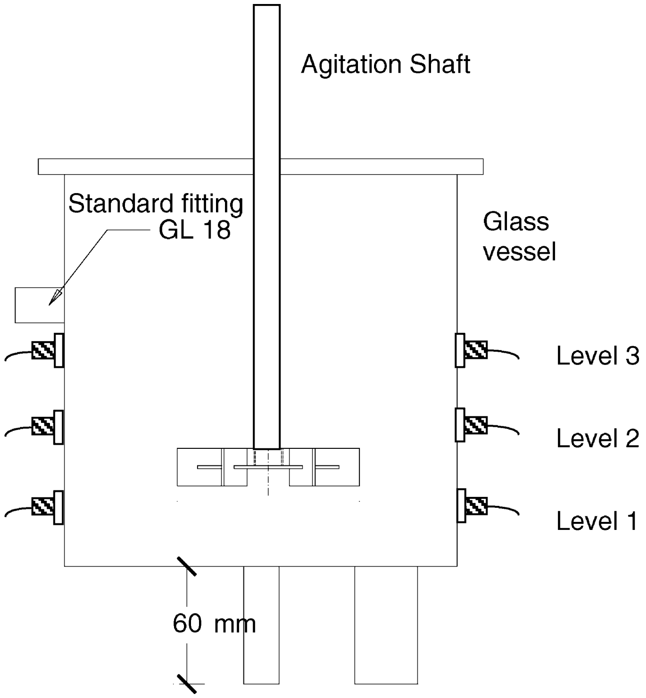


Fig. 2. Schematic drawing of the mixer, identifying the three different levels at which the probes were installed.

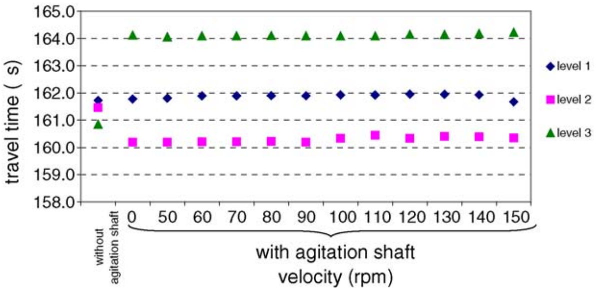


Fig. 3. Experimental results obtained with 4500 cm^3 of toluene and using the hollow shaft.

the travel time values are very similar at the three levels, as the influence of the shaft is then eliminated and only the influence of the wall glass remains. Another expected evidence from these results is that the stirrer velocity does not change the travel time within the range used (50–150 rpm).

It should be mentioned here that these measurements were made on an initial system fitted with a hollow shaft, which would tend to be incompletely filled with liquid, travel times being significantly longer in the air expectedly trapped inside the highest sections of the shaft. This may explain the higher values obtained at level 3 (cf. Fig. 3—possible air trapped inside the shaft), followed by those at level 1 (no shaft), and then by those at level 2.

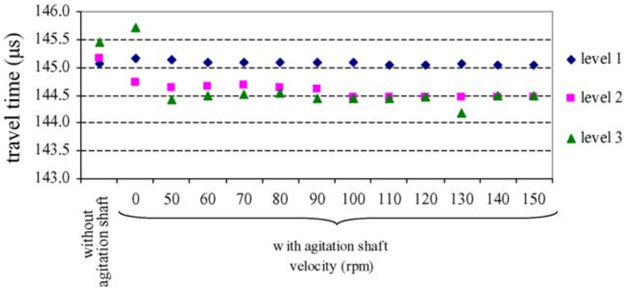


Fig. 4. Experimental results obtained with 4500 cm^3 of water and using the hollow shaft.

In the above two series of experimental tests, the three levels were fixed where the probes were mounted, but the exact position around the vessel perimeter was not well defined and kept unchanged, and so the glass irregularities affected the results. For that reason, the results of Figs. 3 and 4 are not strictly comparable.

3.2. Influence of the ultrasound transducers' setting

In order to study the reproducibility of the ultrasound transducers' assembly, as a result of the way the probes are mounted in the glass vessel (namely the intensity of pressing), another series of experimental tests was performed, dismounting the ultrasound transducers between measurements, and replacing them in the same positions. For these runs, the glass vessel was filled with 4500 cm^3 of distilled water, the ultrasound transducers were placed at level 2, and the stirrer speed was set at 100 rpm.

These results are shown in Fig. 5. In this set of experiments, the influence of the stirrer shaft and the irregularities of the glass vessel were eliminated, as the level and the exact position (around the vessel perimeter) of the probes were fixed. So, the differences between these measurements are due only to the ultrasound transducers' assembly. The results highlight that it is not possible to change the position of the transducers without calibration problems. In future work, we will therefore set the probes in one fixed position and keep them there for all measurements, thus eliminating the interferences from the stirrer shaft, irregularities of the vessel wall and probe mounting.

3.3. Influence of the type of stirrer shaft

For the above measurements, as already mentioned, the shaft used was made from stainless steel hollow pipe, which may bring problems of contamination. For that reason, we decided to change the shaft for a massive stainless steel alternative, and evaluated the results obtained. For these runs, the same

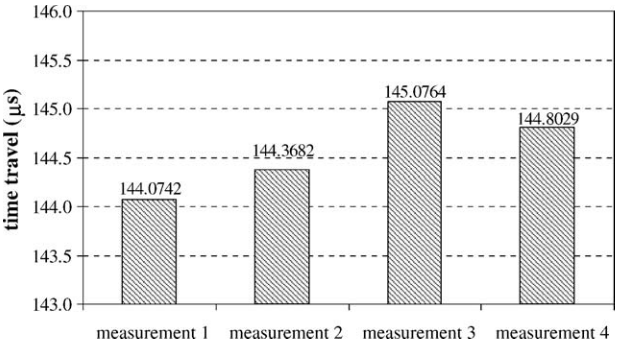


Fig. 5. Experimental results for the reproducibility of the ultrasound transducers assembly (measurements at the same position). Results obtained with 4500 cm^3 of distilled water and 100 rpm of agitation speed.

conditions (as in the study of the influence of the ultrasound transducers' setting) were used, but without agitation (0 rpm). At these conditions, two experimental runs were performed—one using the hollow shaft, and another using the massive one. The travel time results obtained differ by only 0.6059 μs (0.42%). For future work, the decision was taken of always using the massive shaft, in order to prevent contamination problems.

4. Procedure established based on the preliminary studies

To accurately quantify dispersed phase hold-up fractions, it is imperative to run experiments for known dispersed phase fractions, to validate the technique. Such experiments were performed under the following conditions: (1) ultrasound transducers placed at level 2, in a fixed position (the same for all measurements), (2) glass vessel filled with 4500 cm^3 of dispersion with known hold-up fraction and (3) 150 rpm stirrer speed. This agitation intensity is the lowest value for which the well-mixed vessel assumption is reasonably valid.

The experiments were performed and the travel time and fluid temperatures were recorded. The fluid temperature was measured at several time intervals with a glass thermometer immersed just before each series of measurements. The temperatures given by the contact probes (T_0 and T_1) were recorded automatically by the acquisition software, for future correlation of the external surface temperature with the fluid temperature.

This routine was repeated for different vessel contents (saturated single phases, and dispersions with 10, 20, 30 and 40% hold-up fractions), below the limit of phase inversion.

5. Experimental results

As the sound, in this work, also travels through the glass vessel wall, we need to take into account the ultrasound travel time across the glass wall. According to Table 1, the ultrasound velocity in glass is between 2000 and 5000 m/s, depending on the glass type. So we will use, for this purpose, an average value (3500 m/s), as the exact composition and ultrasound velocity for the glass used are not known. Considering this velocity and the thickness of the glass wall, the travel time across the glass wall was calculated and subtracted to each experimental travel time value. This correction for the propagation within the glass turns out not to strongly influence the hold-up results, as shown in Section 5.3. A similar procedure could be adopted to subtract the travel time across the massive stirrer shaft but, based on these results, we decided to neglect the effect.

5.1. Influence of the travel time definition

The travel time was calculated in four different ways, with the objective of choosing the most adequate and representative travel time definition within the entire working range of hold-up values. The following definitions (illustrated in Fig. 6) were tested:

(1) t_{CE}—energy centre, resulting from squared signal integration along a 20 μs window, which is iteratively adjusted until this energy centre and the window centre are coincident, in order to make sure that all significant signal is included in

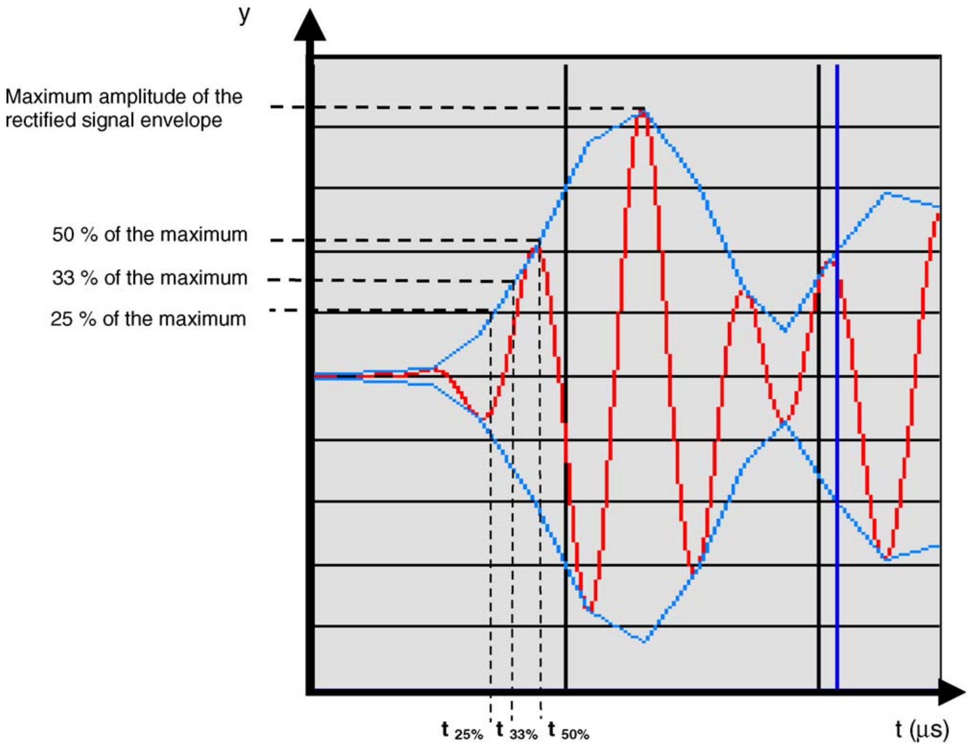


Fig. 6. Three different travel times obtained from the initial part of the signal window.

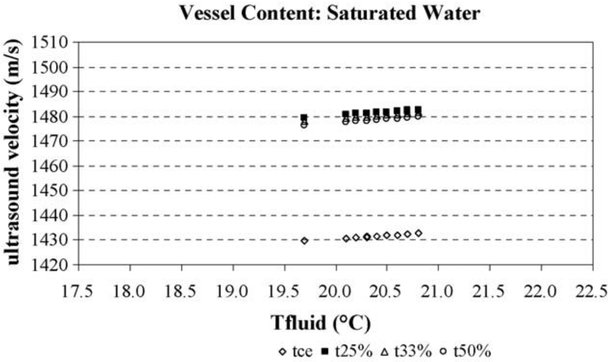


Fig. 7. Variation with temperature of the ultrasound velocity for different travel times, for saturated water.

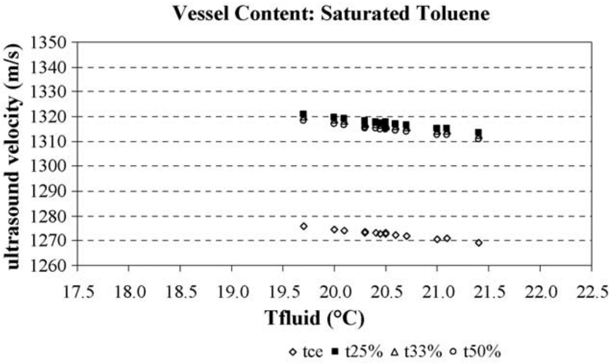


Fig. 8. Variation with temperature of the ultrasound velocity for different travel times, for saturated toluene.

the window. t_{CE} is then approximated by

$$t_{\mathrm{CE}} = \frac{\sum y_i^2 t_i}{\sum y_i^2} \qquad (9)$$

(2) $t_{25\%}$—time to reach 25% of the maximum amplitude of the rectified signal envelope;
(3) $t_{33\%}$—time to reach 33% of the maximum amplitude of the rectified signal envelope;
(4) $t_{50\%}$—time to reach 50% of the maximum amplitude of the rectified signal envelope.

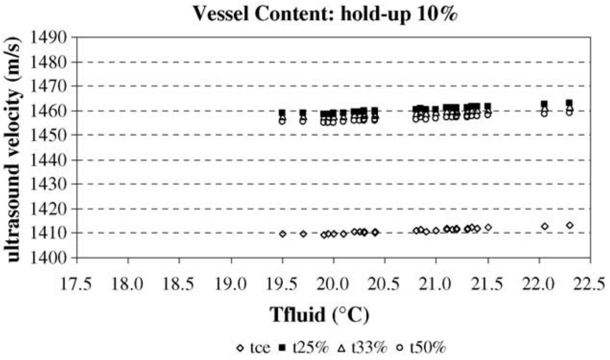


Fig. 9. Variation with temperature of the ultrasound velocity for different travel times, for 10% of toluene in water.

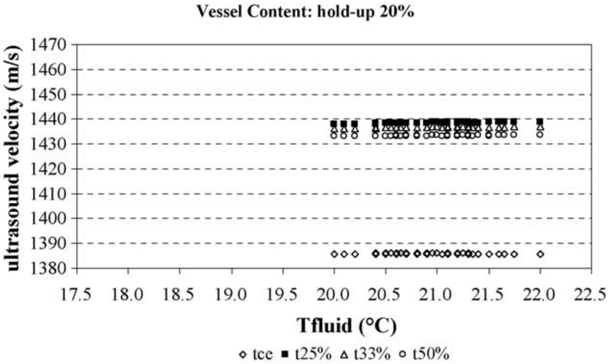


Fig. 10. Variation with temperature of the ultrasound velocity for different travel times, for 20% of toluene in water.

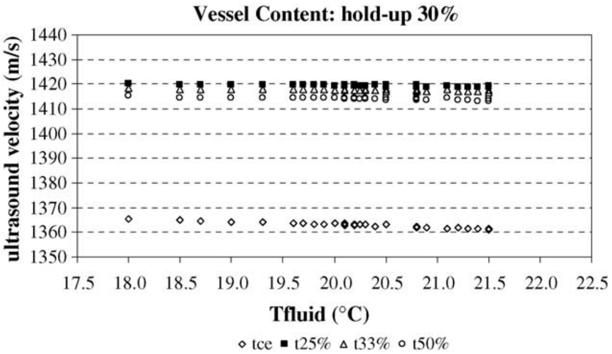


Fig. 11. Variation with temperature of the ultrasound velocity for different travel times, for 30% of toluene in water.

Figs. 7–12 show the experimental results of the ultrasound velocity based on the different travel time definitions (t_{CE}, $t_{25\%}$, $t_{33\%}$ and $t_{50\%}$), as functions of the temperature for each vessel contents (saturated single phases, and dispersions with 10, 20, 30 and 40% hold-up fractions). As may be seen in these figures, an inverse variation of travel time with temperature is obtained for saturated toluene, while for water a direct proportionality is found and, for the other vessel contents, the proportionality changes depending on the amount of toluene in water; as the toluene fraction increases, we eventually obtain an inverse proportionality. The great differences that result between the ultrasound velocity values for the energy centre and the signals

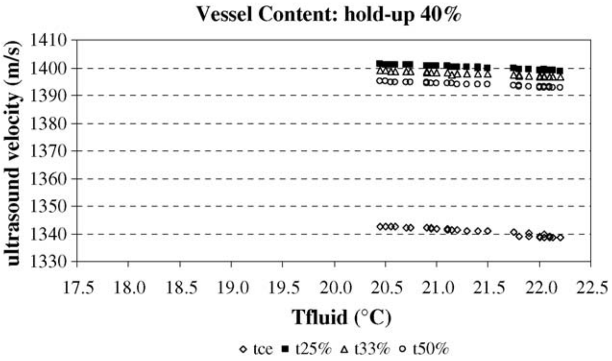
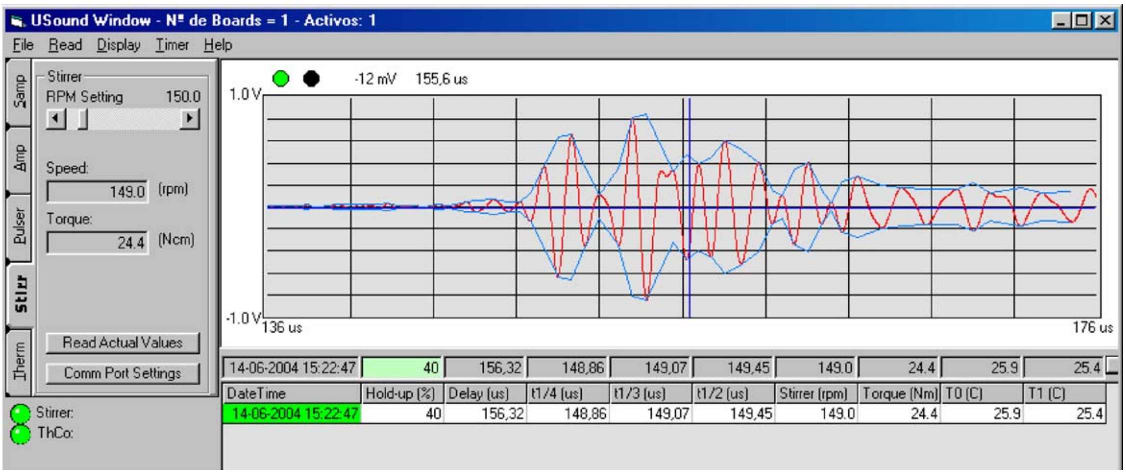


Fig. 12. Variation with temperature of the ultrasound velocity for different travel times, for 40% of toluene in water.



RPM Setting 150.0

Speed: 149.0 (rpm)

Torque: 24.4 (Ncm)

-12 mV 155,6 us

DateTime	Hold-up (%)	Delay (us)	t1/4 (us)	t1/3 (us)	t1/2 (us)	Stirrer (rpm)	Torque (Nm)	T0 (C)	T1 (C)
14-06-2004 15:22:47	40	156,32	148,86	149,07	149,45	149.0	24.4	25.9	25.4

Fig. 13. Signal received on a pre-defined narrower time window (40 μs), for 40% of toluene in water.

for 25, 33 and 50% of the maximum amplitude of the signal envelope are easily justified by the long right tail exhibited by the signal (Fig. 13).

For each fraction of dispersed phase in the vessel (saturated single phases, and dispersions with 10, 20, 30 and 40% hold-up fractions), the correlations of the different ultrasound velocity versus temperature were also studied, and the standard deviations between the experimental and correlated values are shown in Table 2. As may be seen in this table, although the standard deviations for $t_{25\%}$, $t_{33\%}$ and $t_{50\%}$ are very similar, the correlation of $t_{25\%}$ is the one that better fits the experimental data for the whole range of vessel hold-ups (least standard deviation). It seems adequate to point out that the largest standard deviation occurs for t_{CE} at 40% of dispersed phase hold-up. The results of calculating the travel time based on the wave front, namely at $t_{25\%}$, are thus less dependent on this signal spreading.

5.2. *Correlation with temperature of the ultrasound velocity based on the travel time $t_{25\%}$*

Fig. 14 shows the experimental data of the ultrasound velocity based on the travel time $t_{25\%}$ and the correlation with temperature, for different dispersed phase hold-ups. The corresponding equations are given in Table 3.

As previously mentioned, the slope of the regression line has opposite signs for the two saturated phases. Consequently, for higher hold-ups, the toluene effect predominates and the slope is negative. At 20% hold-up the temperature influence is the lowest. For lower hold-ups the ultrasound velocity exhibits a positive slope. Although with different slope and intercept values, these linear regressions always offer excellent fit, and thus very good precision for application in actual measurements.

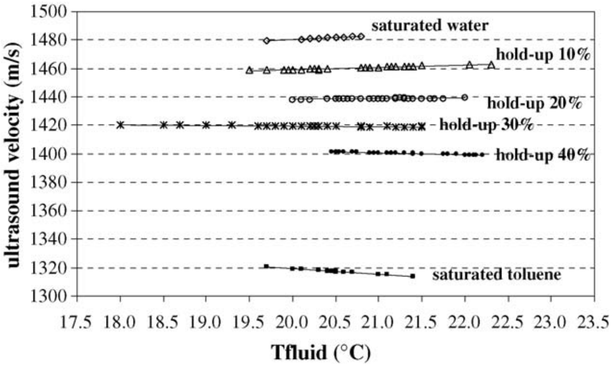


Fig. 14. Variation with temperature of the ultrasound velocity based on the ultrasound travel time ($t_{25\%}$), for different vessel contents.

5.3. *Dispersed phase hold-up fraction calculation*

As already mentioned Eq. (8) may be expressed as a function of temperature and time (t_h). Using the experimental correlations of the ultrasound velocity based on travel time $t_{25\%}$ for the

Table 2
Standard deviation of the differences between experimental and correlated (with temperature) travel time value (μs)

	t_{CE}	$t_{25\%}$	$t_{33\%}$	$t_{50\%}$
Saturated water	0.067	0.075	0.078	0.075
Hold-up				
10%	0.315	0.247	0.254	0.265
20%	0.203	0.149	0.146	0.143
30%	0.256	0.175	0.208	0.254
40%	0.389	0.077	0.113	0.072
Saturated toluene	0.165	0.166	0.168	0.180

Table 3
Correlations for the ultrasound velocity, v (m/s), as a function of temperature, θ (°C)

	Correlation
Saturated water	$v = 2.8965 \times \theta + 1422.4$
Hold-up	
10%	$v = 1.6166 \times \theta + 1426.7$
20%	$v = 0.4266 \times \theta + 1429.5$
30%	$v = -0.3751 \times \theta + 1427.0$
40%	$v = -1.3017 \times \theta + 1427.9$
Saturated toluene	$v = -4.0984 \times \theta + 1401.3$

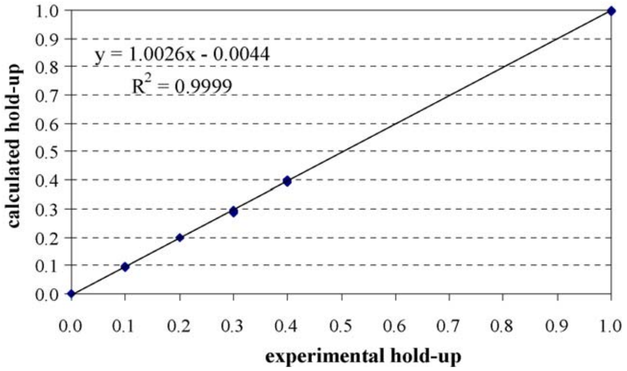


Fig. 15. Calculated and experimental dispersed phase hold-up values (Eq. (8)).

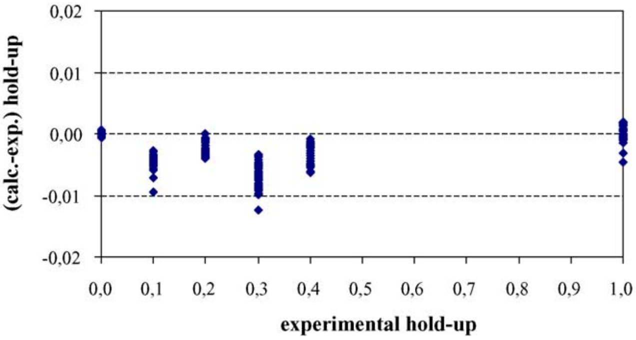


Fig. 16. Differences between the calculated and the experimental hold-up values ($h_{calc} - h_{exp}$) vs. the corresponding experimental values (h_{exp}).

saturated single phases (saturated toluene and saturated water) (see Table 3) and the expressions of the densities as functions of temperature [8], the hold-up values are calculated for each experimental vessel content.

The hold-up values calculated using our own equation (h_{calc}) are plotted versus the correspondent experimental values (h_{exp}) in Fig. 15, and the differences between the calculated and the experimental values ($h_{calc} - h_{exp}$) are plotted versus the correspondent experimental values (h_{exp}) in Fig. 16. If the same calculations are made without glass travel time correction, the greatest error ($h_{calc} - h_{exp}$), which is −0.012317 with glass travel time correction, becomes −0.012351. The results exhibit a very accurate fit.

6. Conclusion

The present non-invasive implementation of the ultrasound technique clearly shows its applicability to accurate dispersed phase hold-up fraction measurements, as an essential component of the full characterization of liquid–liquid dispersions' hydrodynamics. It will easily and effectively combine with a previously developed non-invasive drop size distribution measurement technique for the same type of system and experimental apparatus, for full online characterization of liquid–liquid dispersions. The accuracy that may be achieved in the dispersed phase hold-ups measurements is higher than in most previous implementations of the technique.

Acknowledgements

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