

● *Original Contribution*

LOW-REFLECTION-COEFFICIENT LIQUID INTERFACES FOR SYSTEM CHARACTERIZATION

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Abstract—The use of liquid brominated hydrocarbons to form a planar reflecting interface with water is described. Gravity-based planar reflecting surfaces with known reflection coefficients can be used in system characterization for quantitative ultrasonics, and a set of surfaces with a range of reflection coefficients allows calibration of the output power and receiver gain of ultrasonic imaging systems. The substances reported here are immiscible in water and form interfaces with water, resulting in a broad range of acoustic reflection coefficients. Reflection coefficients were measured at temperatures from 18–24°C for “pure” substances and for mixtures of two brominated hydrocarbons. Results show that reflection coefficients are weakly dependent on temperature and that, at a specific temperature, a significant range of arbitrarily small reflection coefficients is available, in the case of the mixtures, by the appropriate choice of weight-percents of the two brominated hydrocarbons. (E-mail: thall@kumc.edu) © 2001 World Federation for Ultrasound in Medicine & Biology.

Key Words: Ultrasound, Tissue characterization, Quantitative imaging, Reflection.

INTRODUCTION

Reference media are required in many quantitative ultrasonic measurements. For example, all methods for measuring the acoustic backscatter coefficient require the measurement of the echo signal from a well-characterized medium. Although some techniques use a 3-D random distribution of scatterers that produce acoustic speckle (Yao et al. 1990; Hall et al. 1996; Wear et al. 1995), most use the echo signal from a planar interface (Sigelmann and Reid 1973; O’Donnell and Miller 1981; Insana and Hall 1990; Chen et al. 1993). Also, a simple reflector geometry is required if both the magnitude and phase of the frequency spectrum from the reference echo signal are to be determined as, for example, in autoregressive spectral estimation (Wear et al. 1993). Reflectors with known reflection coefficients can also be used

to calibrate the pulser and receiver characteristics of an ultrasonic imaging system.

The use of common solids as reference planar reflectors has serious disadvantages when used to calibrate echo signals that are very small in comparison, as is generally the case for echoes from soft tissue. Stainless steel or quartz glass immersed in water results in reflection coefficients that are nearly unity. The large echo amplitudes that result can easily saturate the receiver amplifier on ultrasonic imaging systems, making such materials undesirable for system calibration. The use of electronic attenuation to reduce the reflection amplitude (either before transmission or after echo reception) requires calibration of the attenuating device, and that device might change the frequency content of the original signal. Fluid interfaces can be made with reflection coefficients that are much lower than those involving solid materials. The smaller compensating attenuation changes can result in superior accuracy.

A water-to-carbon tetrachloride interface is sometimes used as a reference reflector (Insana et al. 1994). However, there are significant disadvantages to using carbon tetrachloride. First, it is a toxic mutagen that is readily absorbed through the skin (RTECS 1999). Second, the reflection coefficient for a water-carbon tetra-

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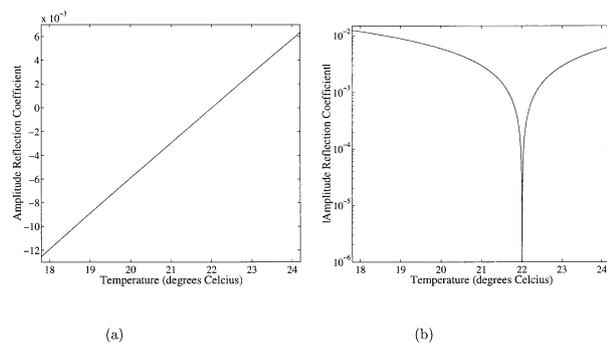


Fig. 1. Plots of the reflection coefficient (r) from a water-to-carbon tetrachloride interface as a function of temperature calculated using published data for sound speeds and densities as a function of temperature (Bilaniuk and Wong 1993; Kell 1975; National Institute of Standards and Technology 1998). The acoustic impedance of carbon tetrachloride is equal to that of water near 22°C, resulting in a reflection coefficient of zero. Near this temperature, the reflection coefficient magnitude is very sensitive to temperature. (a) Linear plot of r ; (b) logarithmic plot of $|r|$.

chloride interface is very sensitive to temperature near the typical room temperature of 22°C, because the acoustic impedances of carbon tetrachloride and water become equal at nearly 22°C (see Fig. 1). Therefore, to avoid large errors in the estimated reflection coefficient, temperatures should be below 21°C or above 23°C. Even with this temperature restriction, to obtain very small reflection coefficient magnitudes, the temperature must be very carefully controlled.

An alternative is to use other liquids that are immiscible in water having acoustic impedances that are nearly equal to that of water throughout the temperature range of interest. In this paper, we report the reflection coefficients at the boundary of water and solutions of brominated hydrocarbons as functions of hydrocarbon mixture ratio and temperature. The solutions have a low vapor pressure at room temperature. They are described in material safety data sheets as irritants and, therefore, presumably pose significantly lower risk than carbon tetrachloride. (It should be noted that the Registry of Toxic Effects of Chemical Substances, (RTECS 1999) lists a variety of biological responses that should be considered prior to use.) These materials (interfaced with water) provide reflection coefficients that are weakly dependent on temperature. Also, the absolute value of the reflection coefficient can be made to have an arbitrarily small value by suitable choice of weight-percents of solution components.

MATERIALS AND METHODS

Materials

Six brominated hydrocarbons were used in making nine fluid interface reflectors. The manufacturer's values

Table 1. Description of the brominated hydrocarbons used to make water-hydrocarbon interfaces for planar reflectors

Hydrocarbon	Molecular formula	Purity	Density (g/cm ³)
1-bromopropane	C ₃ H ₇ Br	99%	1.354
1-bromobutane	C ₄ H ₉ Br	99%	1.276
1-bromopentane	C ₅ H ₁₁ Br	99%	1.218
1-bromohexane	C ₆ H ₁₃ Br	98%	1.176
1-bromoheptane	C ₇ H ₁₅ Br	99%	1.140
1,6-dibromohexane	C ₆ H ₁₂ Br ₂	96%	1.586

Hydrocarbons were purchased from Aldrich, Milwaukee, WI. Purities and densities (at 25°C) are typical values, as specified by Aldrich.

for mass density and purity of the six hydrocarbons are given in Table 1. Three of the nine reflectors were made using solutions of 1-bromoheptane and 1,6-dibromohexane, the compositions of which are given in Table 2. Each of the other six samples were made using one of the "pure" brominated hydrocarbons listed in Table 1. Note that, in Table 2, 100% 1-bromoheptane is referred to as sample A, 100% 1,6-dibromohexane is referred to as sample B, and samples C, D, and E refer to solutions of the two. Each reflector was made by first pouring approximately 60 mL of the hydrocarbon (solution) into a 50-mm height, 70-mm diameter crystallizing dish. Deionized (to 18 MΩ-cm resistivity) water was then added slowly to avoid mixing with the hydrocarbon. The specific gravity of all the hydrocarbons is greater than unity, so water always is the upper material. Room temperature vulcanizing (RTV) silicone was used to seal the dish with a 25-μm thick layer of Saran wrap (Dow Chemical Co., Midland, MI), air being excluded.

A block of 304 stainless steel (7 cm × 7 cm × 1.5 cm) was ground and lapped to give a surface with irregularities ("surface texture") ≤ 1 μm. The density of this block was determined at 22°C using accurately measured dimensions and mass. The density at other temperatures was calculated using the typical coefficient for thermal expansion for 304 stainless steel (17.3 μm/m-°C at 20°C) (Harvey 1982). Propagation speeds were measured at 18°C and 22°C, using a through-transmission

Table 2. Compositions of the brominated hydrocarbon mixtures used to make water-hydrocarbon interfaces for planar reflectors

Sample	% 1-bromoheptane	% 1,6-dibromohexane
A	100.00	0
B	0.00	100
C	67.00	33.00
D	64.01	35.99
E	61.00	31.00

"Pure" hydrocarbons are those described in Table 1. Components of the mixtures are given in weight percent.

Table 3. Measured mass density and sound speeds for the stainless steel and three of the liquid samples used for planar reflectors in this study

Material	Density (g/cm ³)	Sound speed (m/s)	Acoustic impedance (MRayl)
Stainless steel (304)18.0°C	7.88 ± 0.06	5779 ± 6	45.5 ± 0.3
Stainless steel (304)22.0°C	7.88 ± 0.06	5747 ± 6	45.3 ± 0.3
Sample A 22.0°C	1.1355 ± 0.0023	1135.5 ± 3.4	1.289 ± 0.004
Sample B 22.0°C	1.605 ± 0.003	1158.5 ± 3.4	1.859 ± 0.006
Sample D 22.0°C	1.270 ± 0.003	1139.0 ± 2.8	1.446 ± 0.004

The density of stainless steel was measured at 22°C and the density at 18°C was calculated using the typical coefficient for thermal expansion for 304 stainless steel (17.3 $\mu\text{m}/\text{m}\cdot^\circ\text{C}$ at 20°C) (Harvey 1982). Acoustic impedances were calculated from the measured density and sound speeds.

water-displacement technique (Madsen *et al.* 1982). The results are given in Table 3.

To allow direct computation of reflection coefficients at liquid interfaces, for comparison with measured values, it was necessary to know the acoustic impedances of the liquids. Densities and ultrasonic propagation speeds of water are well documented over a broad temperature range (Bilaniuk and Wong 1993; Kell 1975). Densities of all brominated hydrocarbons and their solutions were measured using a 50-mL volumetric flask (Kimax, Kimble/Kontes, Vineland, NJ) and an electronic balance (Mettler model PM460, Mettler Toledo, Columbus, OH). Accuracy was determined by the ± 0.10 -mL uncertainty in the volume measurement.

Ultrasonic propagation speeds were measured at 2.5 MHz relative to water by monitoring the shift in arrival time of tone burst pulses at a receiver when a known thickness of the material was interposed, displacing water. For the sample C solution, which gives very low reflection coefficients, speed measurements were made at 2.0, 2.5, 3.5, 5.0 and 6.2 MHz; no dispersion was observed. The liquid samples were contained in 3-cm long acrylic tubes with 3-cm inner diameter. The ends were covered with 10- μm thick Saran wrap. Details of the measurement technique are given in a previous publication (Madsen *et al.* 1999).

Measurement of reflection coefficients

Reflector samples were submersed in an acrylic-walled water bath (volume ≈ 75 L) that was thermally insulated on the bottom and sides with 25-mm thick styrofoam. The water surface was thermally insulated with a 5-cm thick layer of styrofoam packaging “pop-corn.”

An external refrigerated circulator (Haake model G, Paramus, NJ) was used to select the temperature of the bath over the range $18 \leq T \leq 24^\circ\text{C}$. The desired temperature was selected and the bath allowed to stabilize for at least 1.5 h prior to reflection measurements. Temperature in the 20–24°C range was measured with an

NIST-certified ASTM 56-C thermometer (19–35°C; 0.02°C divisions, Ever Ready Thermometer Co., Inc., West Paterson, NJ). The 18°C temperature was measured with an NIST-certified $\pm 0.03^\circ\text{C}$ mercury thermometer (model 3D-971, Brooklyn Thermometer Co., Inc., Farmingdale, NY).

The water circulator was shut off during the reflection measurements, to minimize interface motion due to currents in the water. Echo amplitude measurements for all reflector types were performed in less than 10 min at each temperature, and fluctuations in temperature over these 10-min periods were less than 0.1°C.

At each temperature, measurement of the echo amplitude for the first fluid sample measured was repeated at the end to test for changes in reflection coefficient due to temperature drift, and all measurements were repeated if any difference was found. Repeat measurements were needed only initially, as measurement techniques were being developed. In addition, after monitoring the reflection from the center of the interface, the fluid samples were translated about 5 mm laterally and the echo arrival time was measured to check for surface flatness. (Deviations from equal arrival time might indicate a nonflat surface, possibly due to surface tension effects.) A 25- μm thick layer of Saran wrap was suspended over the stainless-steel reflector to cause propagation losses identical to those occurring with the liquid samples.

The measurement apparatus included a 13-mm diameter nominal 5-MHz unfocused transducer (Panametrics model V309, Waltham, MA) mounted in a micrometer-driven gimbal mount manipulator that allowed peaking the echo signal on the reflecting interface. The gimbal mount itself was mounted on a micrometer-driven translator that provided vertical translation. The reflecting surface was positioned in the far field of the transducer and the same distance was used for all interfaces (about 13 cm). The transducer was shock-excited and the broad-band echo signals were received by an ultrasonic analyzer (Panametrics model 5052UA). Echo waveforms were monitored and recorded with a digital

Table 4. Amplitude reflection coefficients for the stainless steel and three of the liquid samples used for planar reflectors in this study

Material	Computed reflection coefficient	Measured reflection coefficient
Stainless steel (304) 18.0°C	0.937 ± 0.013	–
Stainless steel (304) 22.0°C	0.936 ± 0.013	–
Sample A 22.0°C	–0.0688 ± 0.0022	–0.0705 ± 0.0021
Sample B 22.0°C	0.113 ± 0.002	0.112 ± 0.003
Sample D 22.0°C	–0.0131 ± 0.0013	–0.0138 ± 0.0005

Measured values were obtained as described in the text. Computed values were determined from the acoustic impedances in Table 3 and the temperature-dependent acoustic impedance of water. A nearly constant fractional uncertainty was found for the measured reflection coefficients, where the uncertainty is dominated by the uncertainty in the peak-to-peak voltage measurements.

oscilloscope (LeCroy 9310A, Chestnut Ridge, NY). The oscilloscope waveform averaging feature was used to average 50 waveforms to reduce noise, and the peak-to-peak echo voltage was measured on the averaged waveform.

Data analysis

The reflection coefficient, r , for each liquid interface was calculated as follows:

$$r = r_{ss} \times \frac{A}{A_{ss}} \quad (1)$$

where A and A_{ss} are the echo amplitudes for the liquid and stainless steel interfaces, respectively, and r_{ss} is the reflection coefficient for the water-stainless steel interface. r_{ss} was computed using:

$$r_{ss} = \frac{\rho_w c_w - \rho_{ss} c_{ss}}{\rho_w c_w + \rho_{ss} c_{ss}} \quad (2)$$

where ρ and c are, respectively, the density and sound speed in the medium.¹ ρ_w and c_w were calculated from published values (Bilaniuk and Wong 1993; Kell 1975), and ρ_{ss} and c_{ss} were calculated using values from Table 3. Values for r_{ss} at 18° and 22°C are shown in Table 4.

Estimates of error, Δr , in directly measured reflection coefficients using eqn (1) were made assuming no correlation between r_{ss} , A , and A_{ss} . That is,

¹ Note that, for sufficiently large attenuation coefficients, r_{ss} could be complex, possibly resulting in significant variations in phase with frequency and consequent changes in pulse shape. The attenuation coefficient for steel is far too small to result in significant phase shifts over the frequency spectrum of the pulses used in this study. Thus, a real r_{ss} is acceptable (see Appendix for verification).

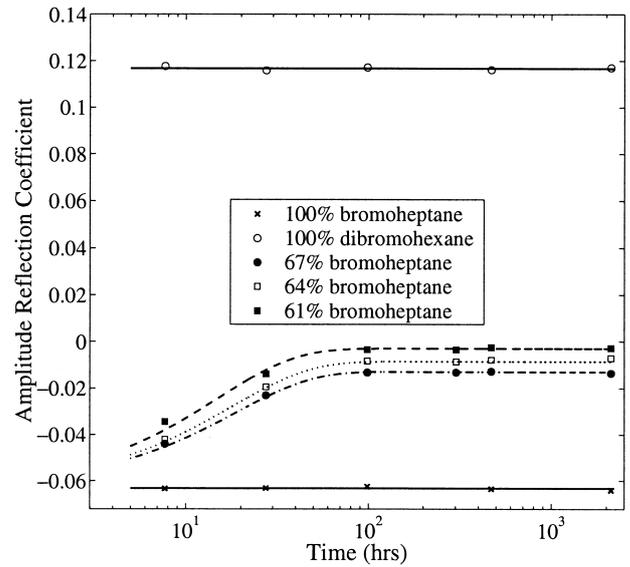


Fig. 2. A plot of the reflection coefficients as a function of time postmanufacture for the fluid interface reflectors. (○) and (x) = data for the 0% and 100% bromoheptane, respectively.

$$\Delta r =$$

$$\left[\left(\frac{\partial r}{\partial r_{ss}} \right)^2 (\Delta r_{ss})^2 + \left(\frac{\partial r}{\partial A} \right)^2 (\Delta A)^2 + \left(\frac{\partial r}{\partial A_{ss}} \right)^2 (\Delta A_{ss})^2 \right]^{1/2} \quad (3)$$

$$\Delta r_{ss} = 0.013 \text{ (Table 4) and}$$

$$\frac{\Delta A}{A} = \frac{\Delta A_{ss}}{A_{ss}} = 0.02 \quad (4)$$

as specified by the manufacturer for the calibrated LeCroy 9310A.

RESULTS

Measured reflection coefficients for samples A–E at 20°C are shown in Fig. 2. Measurements were repeated at various times ranging from about 4–2100 h after manufacture of the samples. The samples containing either 100% 1-bromoheptane or 100% 1,6-dibromohexane show no change in reflection coefficient with time. The solutions of 1-bromoheptane and 1,6-dibromohexane do show a time-dependent reflection coefficient but, after about 100 h (4 days), the reflection coefficients become constant.

Mean reflection coefficients and standard deviations for samples A–E measured at temperatures between 18°C and 24°C are shown in Fig. 3. All measurements are included for samples A and B (100% 1-bromohep-

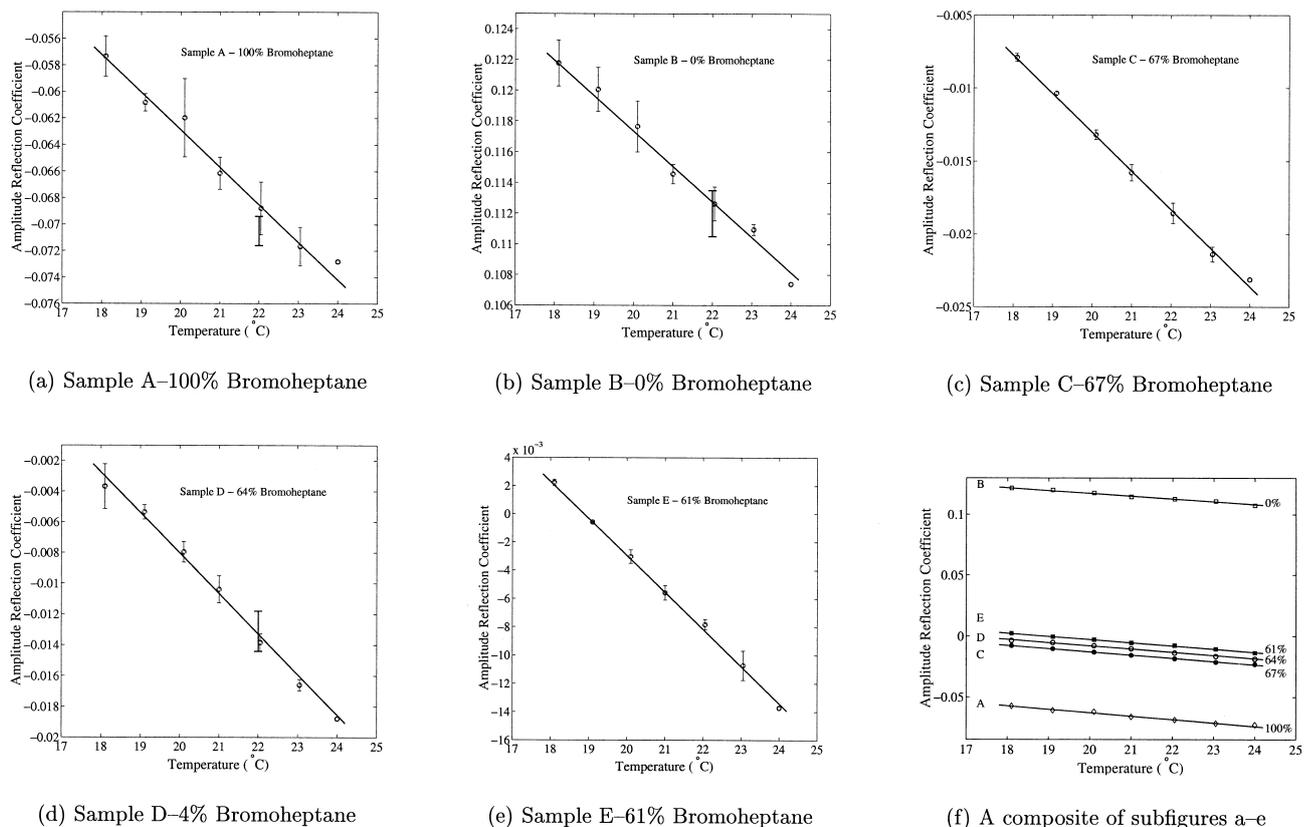


Fig. 3. A plot of the reflection coefficients as a function of temperature for the five samples described in Table 2. The data points indicate the average of measurements for each sample. The error bars represent \pm one SD of the measured values. Only one measurement was performed at 24°C. The lines are calculated using eqn (5). The thick vertical line at 22°C for samples A, B, and D are the mean \pm one SD for the reflection coefficients computed from density and sound speed (Tables 3 and 4).

tane and 100% 1,6-dibromohexane, respectively). Values for samples C–E (solutions of 1-bromoheptane and 1,6-dibromohexane) include only measurements made at least 96 h after manufacture of the samples; thus, stability had occurred, as shown in Fig. 2. Repeated measurements for a single sample at a single temperature demonstrated about a 1% precision.

Curve-fitting provides for prediction of the reflection coefficient in terms of the weight percent of 1-bromoheptane and temperature. A linear least-squares fit for the temperature-dependence of the reflection coefficient was first determined for each sample, using the data shown in Fig. 3. The resulting slopes and intercepts were then fit to a quadratic function of 1-bromoheptane concentration expressed in weight-percent. The resulting relation is:

$$r(B, T) = (-2.290 \times 10^{-5} B^2 - 5.041 \times 10^{-4} B - 2.303 \times 10^{-3}) T + (2.303 \times 10^{-3} B^2 - 4.396 \times 10^{-2} B + 0.1634) \quad (5)$$

where r is the reflection coefficient, B is the weight percent of 1-bromoheptane, and T is temperature in °C. The solid straight lines in Fig. 3 were determined using eqn (5). The good fit to the data corroborates the validity of eqn (5).

Measured reflection coefficients are compared to those calculated from acoustic impedances (Table 3) in Table 4 and Fig. 3.

Measured reflection coefficients for the singly-brominated hydrocarbons listed in Table 1 are plotted in Fig. 4. Reflection coefficients for these “pure” singly-brominated hydrocarbons do not differ significantly as the length of the hydrocarbon chain is increased.

DISCUSSION

The agreement between the measured reflection coefficients and those predicted from measured mass densities and sound speeds is excellent for all samples.

The time-dependent reflection coefficients found for solutions C–E might be due to insufficient mechanical

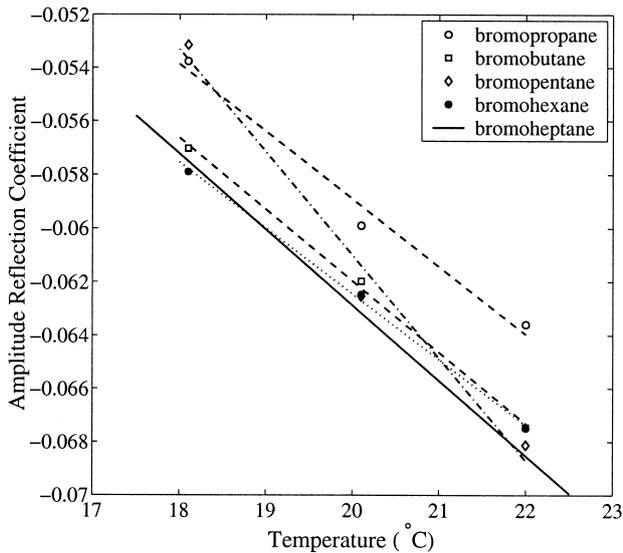


Fig. 4. A plot of the reflection coefficient as a function of temperature for the singly-brominated samples described in Table 1. The data points indicate measurements for each sample. The solid line was calculated using eqn (5).

mixing of the two hydrocarbons. That the initial reflection coefficients are close to that of the less dense material is evidence for this hypothesis because the lower density material would tend to be the uppermost if mixing is not complete. Diffusion processes would then complete the mixing.

The very good agreement between the measured reflection coefficients and those predicted from acoustic impedances suggests that measurements of sound speed and density at two temperatures near the desired temperature for using the reflecting surface (*i.e.*, room temperature) would be sufficient to characterize the reflection coefficient and temperature-dependence of the reflecting surface. This work demonstrates that the sound speed and density measurements, which are more commonly made in acoustics laboratories, are sufficient to estimate the reflection coefficient over a range of temperatures.

Long-term stability of fluid interfaces is expected. A possible cause for a change in the reflection coefficient would be a long-term change in the hydrocarbons due to interaction with light; keeping the reflection samples enclosed in an opaque container when not in use would reduce this possibility.

Equation (5) allows prediction of the bromoheptane concentration necessary to achieve a desired reflection coefficient at a specific temperature. For example, a reflection coefficient of approximately 0.001 would be achieved at 22.0°C with a mixture of 56.2% 1-bromoheptane and 43.8% 1,6-dibromohexane. Alternatively, eqn (5) can be used to predict that a mixture of 54%

1-bromoheptane and 46% 1,6-dibromohexane would result in a surface that would provide noninverted reflections of the incident pulse that are approximately 40 dB down from a perfect reflector at room temperature. Similar calculations could be performed to design a phantom with a series of reflecting surfaces with equally spaced reflection coefficients for system characterization.

As shown in the Appendix, if the magnitude of the reflection coefficient is extremely small (less than about 0.0005), then broad-band pulses might not suffice for measuring reflection coefficients. However, such small reflection coefficients are likely never needed and could also be highly temperature-sensitive through temperature-dependencies of acoustic impedances.

Radiation pressure, acoustic streaming and absorption effects

Note that the shape of the presumed planar reflecting surface and difference in acoustic impedances (water vs. brominated hydrocarbon) could conceivably be influenced by the beam intensity distribution. Variations in radiation pressure could, with reflection at the interface, compromise the gravity-induced planar configuration. Acoustic streaming could have a similar effect. Also, a temperature rise due to acoustic absorption would cause acoustic impedance and, therefore, reflection coefficient, changes. All of these effects, however, are likely limited to relatively high-intensity beams, perhaps with focusing.

Low-intensity, low-repetition rate (100 s^{-1}), pulsed beams were used in this work. No evidence of reflection surface distortion or of temporal variations in acoustic impedances was observed. Regarding acoustic streaming and radiation pressure effects, the act of peaking the echo signal for a water-to-brominated-hydrocarbon interface was indistinguishable from that for the water-to-stainless steel interface. Presumably, if local distortion of the reflecting surface had occurred, then the angular rotation of the transducer relative to the reflector (done to peak the echo signal from the fluid interface) would have caused translating distortion on the interface inducing time-dependent wave motion of the interface with concomitant unexpected fluctuations in the echo signal, even during pauses in angular rotation; no such fluctuations were observed. Also, with the transducer remaining fixed in position and the beam operating for 5 min or more, no changes in echo amplitude were ever observed, indicating no significant temperature rises due to acoustic absorption.

It may be a wise precaution, however, for users of the liquid interface reflectors to be watchful for the described echo signal fluctuations as evidence that acoustic streaming and/or radiation pressure effects are not negligible. A test for slow temporal change in echo

signal might also be done to detect significant thermal effects due to acoustic absorption.

Very importantly, the most conclusive evidence that acoustic streaming and radiation pressure effects were insignificant in our study is the fact that measured reflection coefficients were equal to computed reflection coefficients within experimental error.

CONCLUSIONS

Halogenated hydrocarbons with high purity and having density greater than water can be used to form planar interfaces with water. Such interfaces can be produced with arbitrarily small reflection coefficients using solutions of 1-bromoheptane and 1,6-dibromohexane. Reflection coefficients are weakly temperature-dependent. Accurate values for the reflection coefficient for the solutions can be predicted as a function of temperature and hydrocarbon concentration.

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REFERENCES

- Bilaniuk N, Wong GS. Speed of sound in pure water as a function of temperature. *J Acoust Soc Am* 1993;93(3):1609–1612.
- Chen J-F, Zagzebski JA, Madsen EL. Tests of backscatter coefficient measurement using broadband pulses. *IEEE Trans Ultrason Ferroelec Freq Cont* 1993;40(5):603–607.
- Hall TJ, Insana MF, Harrison LA, Cox GG. Ultrasonic measurement of glomerular diameters in normal adult humans. *Ultrasound Med Biol* 1996;22(8):987–997.
- Harvey PD, (ed.) *Engineering properties of steel*. Metals Park, OH: American Society for Metals, 1982.
- Insana MF, Hall TJ. Parametric ultrasound imaging from backscatter coefficient measurements: Image formation and interpretation. *Ultrasonic Imaging* 1990;12:245–267.
- Insana MF, Hall TJ, Cook LT. Backscatter coefficient estimation using array transducers. *IEEE Trans Ultrason Ferroelec Freq Cont* 1994;41(5):714–723.
- Kaye G, Laby T. *Tables of physical and chemical constants*. New York: Longman, 1973.
- Kell G. Density, thermal expansivity, and compressibility of liquid water from 0° to 150°C: Corrections and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *J Chem Eng Data* 1975;20(1):97–105.
- Madsen EL, Dong F, Frank GR, Garra BS, Wear KA, Wilson T, Zagzebski JA, Miller HL, et al. Interlaboratory comparison of ultrasonic backscatter, attenuation and speed measurements. *J Ultrasound Med* 1999;18:615–631.
- Madsen EL, Zagzebski JA, Frank GR. Oil-in-gelatin dispersions for use as ultrasonically tissue-mimicking materials. *Ultrasound Med Biol* 1982;8(3):277–287.
- National Institute of Standards and Technology. NIST Chemistry Web-Book. URL webbook.nist.gov. 1998.
- O'Donnell M, Miller JG. Quantitative broadband ultrasonic backscatter: An approach to nondestructive evaluation in acoustically inhomogeneous materials. *J Appl Phys* 1981;52:1056–1065.
- RTECS Registry of toxic effects of chemical substances maintained by the National Institute for Occupational Safety and Health, 1999.
- Sigelmann R, Reid JM. Analysis and measurement of ultrasonic backscattering from an ensemble of scatterers excited by sine-wave bursts. *J Acoust Soc Am* 1973;53:1351–1355.
- Wear KA, Garra BS, Hall TJ. Measurements of ultrasonic backscatter coefficients in human liver and kidney in vivo. *J Acoust Soc Am* 1995;98:1852–1857.
- Wear KA, Wagner RF, Insana MF, Hall TJ. Application of autoregressive spectral analysis to cepstral estimation of mean scatterer spacing. *IEEE Trans Ultrason Ferroelec Freq Cont* 1993;UFFC-40:50–58.
- Yao LX, Zagzebski JA, Madsen EL. Backscatter coefficient measurements using a reference phantom to extract depth-dependent instrumentation factors. *Ultrasonic Imaging* 1990;12:58–70.

APPENDIX

Complex reflection coefficients

The reflection coefficient for normal incidence of a plane sinusoidal wave onto a planar interface from medium 1 onto medium 2 is:

$$R = \frac{\rho_2 c_2 - \rho_1 c_1}{\rho_2 c_2 + \rho_1 c_1} \quad (\text{A1})$$

where ρ is density and c is propagation speed. R can be expressed in terms of the frequency and wave number k using the relation $c = \omega/k$ as follows:

$$R = \frac{\rho_2 k_1 - \rho_1 k_2}{\rho_2 k_1 + \rho_1 k_2} \quad (\text{A2})$$

k becomes complex (k_c) if attenuation is present. If plane waves traveling in the positive x direction are represented by $\exp i(k_c x - \omega t)$, then $k_c = k + i\alpha$ (ω) where $k = \omega/c$ is the real part and α is the (amplitude) attenuation coefficient. Thus, R is generally complex, resulting in phase shifts on reflection depending on the values of α_1 and α_2 . If continuous waves are used to measure R , then there is a single phase shift and peak-to-peak amplitude determinations are sufficient to determine $|R|$, which is usually the only quantity of interest. However, the reflection coefficients measured in the reported work were determined with broad-band pulses. Thus, if phase shifts are not small and there is a frequency-dependence, the wave-form (shape) can vary accordingly, compromising the use of peak-to-peak amplitudes in reflection coefficient measurements. The purpose of this appendix is to show that attenuation coefficient effects are negligible for the broad-band pulses used in the reported work. When the reflection coefficients are extremely small, much smaller than any reported and probably much smaller than needed by any investigator, accounting for attenuation may be necessary.

Water-to-stainless steel reflection

We take the attenuation coefficient of water to be too small to be of concern. The attenuation coefficient for stainless steel is assumed to be comparable to that for hardened steel ($5 \text{ m}^{-1} = 0.05 \text{ cm}^{-1}$ at 10 MHz) (Kaye and Laby 1973). (Note that propagation speeds for a 10-cm long, 8-cm diameter cylinder of stainless steel were measured in our laboratory at 2.0, 3.5 and 5.0 MHz, and no speed dispersion was found.) Assuming that the attenuation decreases with frequency, the above value can be considered a reasonable upper limit for the frequencies in our nominal 5-MHz pulses. Introducing the speed for stainless steel from Table 3 and an attenuation coefficient of 0.05 cm^{-1} into eqn (A2), we get $R = 0.9365 - 4.5 \times 10^{-5}i$, which corresponds to a negligible phase shift of -0.0027° . Thus, phase shifts are considered unimportant for reflection from stainless steel for the broad-band pulses employed in this work. Also, ignoring the imaginary part of the reflection coefficient is justified.

Water-to-partially brominated hydrocarbon interfaces with very small reflection coefficient magnitudes

When $|R|$ becomes small enough and peak-to-peak amplitudes of broad-band pulses are used to determine R , frequency-dependent attenuation in the partially brominated hydrocarbon can compromise the measurements by causing distortion of the waveforms. However, as

Table 5. Propagation speeds and attenuation coefficients of sample C material at 22°C

Frequency (MHz)	Speed (m/s)	Attenuation coefficient (dB/cm)
2.0	1143 ± 1	0.0 ± 0.1
3.5	1144 ± 1	0.1 ± 0.1
5.0	1143 ± 1	0.2 ± 0.1
6.2	1143 ± 1	0.2 ± 0.1

will be shown, the compromising occurs only for extremely small values of $|R|$, (*i.e.*, $|R| < 0.0005$). The smallest value of $|R|$ measured in this work is about 0.01; thus, attenuation of the partially brominated hydrocarbon solutions had no effect.

Measurements were made of propagation speeds and attenuation coefficients at 22°C in a solution corresponding to sample C. Results are shown in Table 5. The density of the material at 22°C is 1.261 g/cm⁻³. The attenuation coefficient values are so small that they are in the range of the uncertainties.

Assume that the attenuation coefficient for any significant frequencies in our broad band pulse is less than four times the value at 6.2 MHz, *viz.*, 0.8 dB/cm \approx 0.08 cm⁻¹. Using $\alpha = 0.08$ cm⁻¹, the reflection coefficient will be:

$$R = \frac{\rho_2(2\pi f/c_1) - \rho_1[(2\pi f/c_2) + i(0.08\text{cm}^{-1})]}{\rho_2(2\pi f/c_1) + \rho_1[(2\pi f/c_2) + i(0.08\text{cm}^{-1})]} \quad (\text{A3})$$

where we take f to be 10 MHz, $c_1 = 1489$ m/s (water), $c_2 = 1143$ m/s, $\rho_1 = 1.000$ g/cm⁻³, and $\rho_2 = 1.261$ g/cm⁻³. The resulting complex reflection coefficient is:

$$R = -0.0163 - i(0.000075). \quad (\text{A4})$$

The corresponding phase angle is -179.74° . Thus, the shift due to nonzero attenuation is $+0.3^\circ$, which represents an upper bound for the frequencies in the (nominal) 5-MHz pulses. We conclude that attenuation of the partially brominated hydrocarbon in our experiments is negligible and that the values of R can be taken to be real.

Note, however, that when $|R|$ becomes extremely small, it could become necessary to consider attenuation effects. For example, suppose that the real part of the numerator in eqn (A3) is only -0.5 cm⁻¹ instead of -17.6 cm⁻¹, the real part of the denominator remaining at about 1081 cm⁻¹. Then R becomes

$$R = -0.0005 - i(0.000075) \quad (\text{A5})$$

with a possibly significant phase shift due to attenuation of about 8° . Thus, if $|R| < 0.0005$, attenuation effects may be significant when broad-band pulses such as ours are used to determine R . Such low values of $|R|$ are likely unnecessarily small and are likely impractical because temperature variations could become bothersome.