International Journal of Thermophysics, Vol. 16, No. 3, 1995

Identification of Environmentally Acceptable Low-Sound Speed Liquids[1]

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Liquids with unusually low sound speeds are required as filling fluids for sonar targets and acoustic lenses. In this paper, we report on the search for environmentally acceptable fluids for these purposes. A precision variable pathlength interferometer, incorporating some novel features, has been constructed and used to make sound speed measurements on a number of liquids with low speeds of sound. The measurements were made, with a precision of ±0.05% and an uncertainty of ±0.2%, at atmospheric pressure and at various temperatures in the range 273.15 to 303.15 K. The most promising low-sound speed liquid identified was *n*-perfluorohexane, which has a sound speed below 600 $\mathrm{m \cdot s^{-1}}$ in the temperature range of interest here. This liquid forms homogeneous mixtures over at least part of the temperature range with several alkanes including *n*-pentane, *n*-hexane, and 2,2-dimethylbutane. Experimental results for binary mixtures of perfluorohexane isomers with each of the aforementioned alkanes are reported.

KEY WORDS: acoustic interferometer; 2,2-dimethylbutane; *n*-hexane; low-sound speed liquids; *n*-pentane; perfluorohexane; sonar targets.

1. INTRODUCTION

Fluid-filled spherical acoustic lenses are widely used as experimental sonar targets. These objects have a predictable target strength determined mainly by the size of the sphere and the properties of the fluid used to fill it. To maximize the sonar echo, the speed of sound u in the filling fluid should be

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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0195-928X/95/0500-0675$07.50/0

equal to $u_w/1.77$, where u_w is the speed of sound in the surrounding seawater. It is also desirable that the acoustic impedance of the fluid should be close to that of seawater. To achieve precisely the required sound speed, a liquid mixture may be used and the composition adjusted to achieve a match at the specified temperature. Since the anomalous properties of water cause u_w to increase with increasing temperature, rather than decrease as in most liquids, the optimum composition will vary significantly with temperature.

Until recently, the desired properties were obtained by means of a mixture of 1,1,2-trichloro-2,2,1-trifluoroethane (Freon R113) and ethanol, the composition of which was adjusted to "fine-tune" the sound speed to the required value at the operating temperature.

However, R113 is a fully halogenated chlorofluorocarbon (CFC) compound with ozone-depleting potential and, as such, must be phased out of use under the terms of the Montreal Protocol [1] and other international agreements governing the production and use of CFC's. A replacement was therefore required and the objective of this research was to identify and characterise such a fluid. Anticipating future tightening of environmental controls, we decided to seek an entirely chlorine-free replacement.

2. IDENTIFICATION OF SUITABLE LIQUIDS

Sonar targets are generally operated at frequencies f up to about 50 kHz, and as all of the liquids under consideration exhibit no significant dispersion at $f \leqslant 1$ MHz, we are concerned only with the so-called thermodynamic speed of sound. Since the temperature range of interest was 273 to 303 K, one component of the new mixture was required to have a speed of sound less than u_w at 273 K ($820\ \mathrm{m \cdot s^{-1}}$) and the other component a sound speed in excess of u_w at 303 K ($875\ \mathrm{m \cdot s^{-1}}$). Many liquids exhibit sound speeds in excess of $875\ \mathrm{m \cdot s^{-1}}$ at 303 K; however, sound speeds less than $820\ \mathrm{m \cdot s^{-1}}$ in liquids at 273 K are much less common. Nevertheless, a search of the literature [2–4] did reveal a number of chlorine-free compounds with low sound speeds including some fully or partially fluorinated alcohols, alkanes, and ethers. Examples of these substances are listed in Table I.

Unfortunately, most of the possible substances were available only in gram quantities and at very high cost. Trifluoroethanol was a notable exception but the speed of sound in this liquid is too high near to the lower end of the interesting temperature range. The best compromise appeared to be perfluorohexane, which has a sound speed below $600\ \mathrm{m \cdot s^{-1}}$ over the entire range of interest and, provided that a mixture of C_6F_{14} isomers was acceptable, could be obtained at modest cost.

Table I. Speeds of Sound u in Some Fluorinated Liquids at 298.15 K

Compound	Formula	u $(m \cdot s^{-1})$	Ref. No.
Perfluoropentane	C_5F_{12}	477	2
Perfluorohexane	C_6F_{14}	548	2
Perfluorocyclohexane	C_6F_{14}	590	3
Perfluoro(methylcyclohexane)	C_7F_{14}	579	2
Perfluoro-heptene-1	C_7F_{14}	607	3
Perfluorodecalin	$C_{10}F_{18}$	714	2
2,2,2-Trifluoroethanol	CF_3CH_2OH	835	4
2,2,3,3,3-Pentafluoropropan-1-ol	$C_3F_5H_2OH$	760	4
1,1,1,3,3,3-Hexafluoropropan-2-ol	C_3HF_6OH	696	3

Many substances might be considered as the second (high-sound speed) component of a mixture. However, the phase behavior of several possible candidates with perfluorohexane proved to be unsuitable over at least part of the interesting temperature range. For example, mixtures with *n*-hexane exhibited phase separation at temperatures (dependent on overall composition) below about 293 K. Mixtures of perfluorohexane with *n*-pentane did not suffer from this problem but the boiling temperature of *n*-pentane, 309 K, makes this component unsuitable toward the upper end of the temperature range. The hexane isomer 2,2-dimethylbutane was found to be fully miscible with perfluorohexane at the compositions of interest and temperatures in the range 273 to 303 K; this therefore was the mixture selected for the most detailed study.

3. EXPERIMENTS

A simple two-transducer variable-pathlength interferometer, illustrated in Fig. 1, was specially constructed for this work. One transducer was driven to produce sound at a frequency f, while the other transducer was operated as a detector. Variation of the distance between the two transducers tuned the interferometer through successive resonances spaced one half wavelength apart. The displacement of the movable transducer was measured precisely using a digital micrometer, thereby enabling the wavelength λ of the sound in the liquid to be determined at the operating frequency. The speed of sound u was then determined simply from the product of wavelength and frequency.

The transducers used were piezoelectric devices fabricated from commercially available ceramic elements 5 mm in diameter and 2 mm thick. The fundamental frequency was chosen to be 1 MHz and operation at that

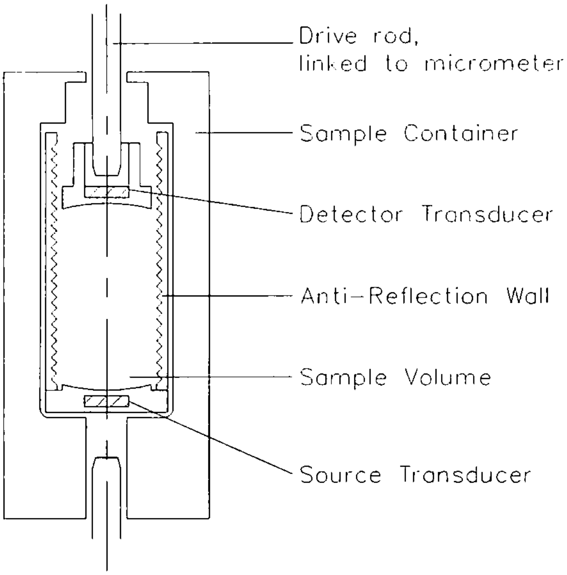

Fig. 1. Schematic diagram of the interferometer.

frequency or any odd harmonic was possible. The transducers were mounted on the center line within the two 20-mm-diameter stainless-steel end faces and were coupled to the liquid through a quarter-wavelength-thick epoxy-resin matching section 3 mm in diameter.

A novel feature of the design was the use of parabolic rather than plane end faces designed to reduce errors in the interferometer due to diffraction and guided-mode dispersion. In the present case, the radius of curvature R of each end face was 50 mm. Numerical simulations of the operation of the interferometer were performed using the methods of geometric acoustics (ray tracing). It was assumed in these calculations that there were no reflections from the side walls so that a ray reflected out of the interferometer path never returned. The results of the calculations showed that resonances occurred at a series of pathlengths L which, provided that $L < 2R$, did not deviate by more than 0.01 % from the simple formula

$$L = n(\lambda/2) \tag{1}$$

At the separation $L = 2R$, this series of resonances was found to end abruptly. The separation $L = 2R$ represents a limit of stability above which any ray, leaving the source in the center of one end face at a nonzero angle to the axis of the interferometer, must eventually be reflected out of the cavity. At smaller separations, there exists a nonzero angle below which rays leaving the source are never reflected out of the cavity; this is the origin of the sharp resonances in that regime.

To take full advantage of the theoretical accuracy of the interferometer, the side walls should either absorb or, at least, scatter sound. In the present case, a series of annular cuts, 1 mm deep, was made on the inside surface of a stainless-steel cylinder surrounding the acoustic cavity in an attempt to scatter sound impinging upon the walls. It appeared that this method was only partially successful and that an improved design will be required to reduce the effects of reflections to a level comparable to the high precision of the instrument.

The interferometer was immersed in a well-stirred fluid bath containing a mixture of water and ethanol. The temperature of this bath was controlled with a precision of ±3 mK using a proportional-integral temperature controller fitted with a thermistor sensor probe and a 1-kW immersion-type bath heater. Cooling was provided by a refrigeration unit fitted with an immersible heat exchanger. The cooler and heater were both located in the bath close to the stirrer. The actual temperature of the interferometer was measured using a platinum resistance thermometer the resistance of which was measured using a precision multimeter. The sensing probe was located in the bath fluid immediately adjacent to the interferometer. The temperature measurements had a resolution of 2.5 mK and an uncertainty (determined by the tolerance of the manufacturer's calibration) of ±0.1 K. Temperature uniformity in the bath was checked by moving the measurement probe to different locations; variation around the interferometer was never more than 5 mK.

Two filling/emptying ports were provided in the wall of the sample container, one located in the lid and the other in the base, and to these were connected lengths of stainless-steel tubing. Prior to filling with a new liquid sample, the sample container was evacuated through the upper port, and to remove any traces of liquid from previous fillings, pumping was continued for some time. A valve in the pumping line was then closed and liquid admitted into the evacuated sample container through the lower port. This appeared to enable us to fill the system completely without trapped bubbles of air or vapour. Following a set of measurements, the bulk of the liquid was forced out through the lower port by means of a flow of compressed gas admitted through the upper port.

In operation, the source transducer was driven at 1 MHz and up to 10 V peak-to-peak (p–p) using a custom-made signal source. The frequency, which was controlled by a quartz-crystal time base, had an accuracy of better than 0.005%. The signal from the detector transducer was fed directly to one input of a two-channel oscilloscope on which it was displayed. Typical signal strengths were 10–50 mV p–p at a resonance of the interferometer. Two modes of operation were possible. In the first, the signal amplitude was observed on the oscilloscope as the pathlength was varied and maxima in the amplitude were taken to correspond to resonance; the corresponding micrometer readings were then noted. In the second method, the horizontal axis of the oscilloscope trace was driven by the source signal and the vertical axis by the received signal. This led to Lissajous' figures, which, in the present case, took the form of ellipses one diameter of which vanished when the two signals were either exactly in phase or exactly out of phase. These conditions should be satisfied at resonances of the interferometer. Thus, in this mode, the pathlength was varied and micrometer readings taken when the phase was either 0 or π; a sensitivity of $\pm 10\ \mu\text{m}$ or better was obtained in this way. In practice, a combination of the two modes was adopted in which each resonance was located roughly by the first method and then precisely by the second method. Groups of resonances over a total displacement of 40 to 50 mm were measured so that full advantage could be taken of the higher reading precision and the long travel of the micrometer.

To validate the performance of the instrument, measurements were made of the speed of sound in both pure ethanol and pure water at 293.15 K and $f = 1$ MHz. The displacements ΔL of the end face required to bring the interferometer into resonance were measured relative to an arbitrary position in which the two end faces were nearly touching and the results were analyzed in terms of the equation

$$\Delta L = L_0 + n(\lambda/2) \tag{2}$$

to determine the wavelength. Fractional deviations $\delta L/L$ of the measured displacements from the fit are shown for ethanol in Fig. 2. The value of λ obtained from this fit was 583.53 μm, with a standard deviation of 0.08 μm or 0.014%, leading to $u = (1167.1 \pm 0.2)\ \text{m} \cdot \text{s}^{-1}$. For water we obtained the value $u = (1489.9 \pm 0.7)\ \text{m} \cdot \text{s}^{-1}$. Clearly the results are of a high precision; however, when compared with values taken form the literature [5, 6], considered to be uncertain to much less than 0.1%, we find that the present results are too high by 0.3% in ethanol and 0.5% in water. We believe that these errors, which increase with the wavelength, are caused mainly by waveguiding effects arising from reflection from the side walls of the interferometer. The results of the trials were used as the basis of an empirical correction factor ϕ by which all subsequent measurements of u were multiplied. The simple one-parameter function $\phi = (1 - b\lambda)$ was adopted with $b = 3\ \text{m}^{-1}$. When applied to ethanol and water, this gave results that agreed with those in the literature to better than 0.1% and we estimate that the uncertainty of our other results is approximately 0.2%.

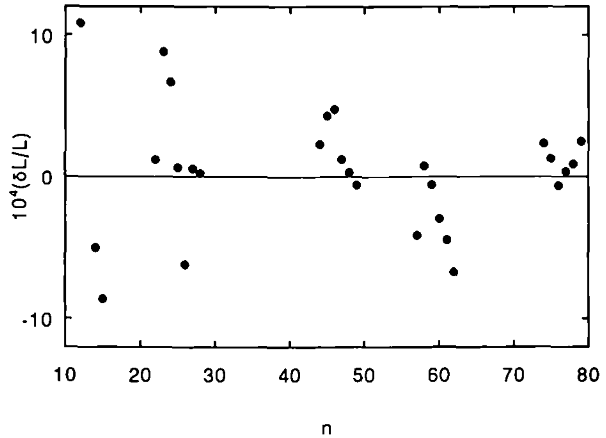

Fig. 2. Fractional deviations $\delta L/L$ from Eq. (2) of displacements measured at resonances of order n for pure ethanol at 293.15 K.

4. RESULTS

The speed of sound was measured in a number of mixtures containing perfluorohexane with the objective of determining, for each mixture studied, the composition that gave the desired speed of sound at various temperatures in the range 273.15 to 303.15 K. Mixtures of perfluorohexane with each of the three alkanes *n*-hexane, 2,2-dimethylbutane, and *n*-pentane in turn were studied at compositions for which a single homogeneous liquid phase was formed.

Perfluorohexane was supplied by the 3M company under the trade name FC-72 Fluoroinert. Information supplied by the manufacturers indicated that the material was 99% C_6F_{14} but that it contained a mixture of isomers dominated by n-C_6F_{14}. Analysis by gas chromatography, using a 30-m capillary column with a nonpolar stationary phase operating at 273 K and a flame-ionization detector, revealed the presence of four significant components with closely spaced retention times. The mole fractions of these components inferred from peak areas were (in order of elusion) 0.017, 0.945, 0.022, and 0.012; the mole fractions of all other components totaled 0.004. These data imply that the material contained approximately 94.5 mol% n-C_6F_{14} and 5 mol% other C_6F_{14} isomers. The source, purity, boiling temperature T_b, and liquid density ρ at 298.15 K of each of the substances used are summarized in Table II. Mixtures were prepared gravimetrically with an estimated uncertainty of 0.001 in the mass fraction.

Table II. Source, Mole-Fraction Purity, Boiling Temperature T_b, and Density ρ at 298.15 K of Materials

Material	Source	Purity	T_b (K)	ρ ($kg \cdot m^{-3}$)
Perfluorohexane	3M Company	—[a]	329	1680
2,2-dimethylbutane	Fluka	0.99	323	649
n-Hexane	BDH	0.99	342	659
n-Pentane	Merck	0.99	309	626

[a] Mixed isomers, 0.99 mole fraction C_6F_{14}. Trade name, FC-72 Fluoroinert.

Table III. Speeds of Sound u in $\{(1-x)\,C_6F_{14} + x\,CH_3C(CH_3)_2CH_2CH_3\}$ at Temperatures T and Mass Fractions x

T (K)	x	u ($m \cdot s^{-1}$)
273.15	1	1113.9
	0.8029	1009.6
	0.5995	896.9
	0.4060	785.6
	0.1970	668.8
	0	588.3
283.15	1	1069.1
	0.8029	964.1
	0.5940	851.0
	0.3975	742.0
	0.1915	628.4
	0	556.8
293.15	1	1022.5
	0.7999	919.5
	0.5949	810.6
	0.3961	702.4
	0.1915	595.2
	0	525.5
303.15	1	976.3
	0.7954	876.4
	0.6045	777.2
	0.4011	666.6
	0.2008	564.5
	0	494.9

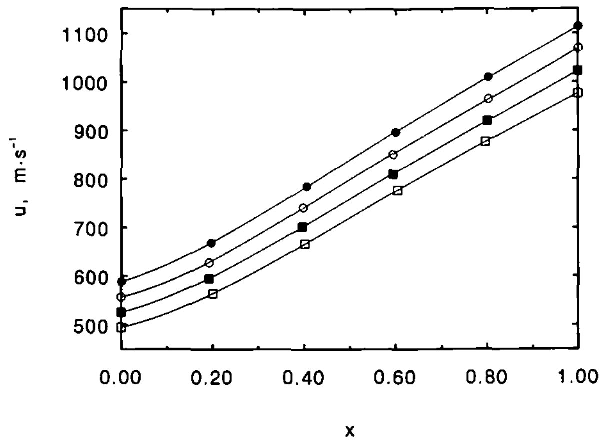

Fig. 3. Speeds of sound u in the mixture $\{(1-x)\,C_6F_{14} + x\,CH_3C(CH_3)_2CH_2CH_3\}$ as a function of mass fraction x. (●) 273.15 K; (○) 283.15 K; (■) 293.15 K; (□) 303.15 K.

Measurements were made on the system (perfluorohexane + 2,2-dimethylbutane) at six compositions with mass fractions x of 2,2-dimethylbutane between 0 and 1 and at four temperatures between 273.15 and 303.15 K. The results are given in Table III and are plotted as functions of x along isotherms in Fig. 3.

Measurements were also made for a more restricted set of conditions on the systems (perfluorohexane + *n*-hexane) and (perfluorohexane + *n*-pentane). The results of these measurements are given in Tables IV and V.

Table IV. Speeds of Sound u in $\{(1-x)\,C_6F_{14} + x\,CH_3(CH_2)_4\,CH_3\}$ at Temperatures T and Mass Fractions x

T (K)	x	u $(\mathrm{m \cdot s^{-1}})$
293.15	1	1099.0
	0.8019	988.0
	0.6023	862.7
	0.5002	802.4
303.15	1	1053.3
	0.7973	942.9
	0.6023	829.5
	0.4995	764.4

Table V. Speeds of Sound u in $\{(1-x)\,C_6F_{14} + x\,CH_3(CH_2)_3CH_3\}$ at Temperatures T and Mass Fractions x

T (K)	x_1	u $(m \cdot s^{-1})$
273.15	1	1124.8
	0.8023	1017.6
	0.6021	902.2
	0.3946	769.7
	0.1997	667.0
283.15	1	1072.8
	0.8042	965.3
	0.6077	862.3
	0.3946	737.2
	0.1994	628.9
293.15	1	1028.0
	0.8133	930.4
	0.6015	815.5
	0.4017	702.5
	0.1994	592.7

5. DISCUSSION

The speed of sound in perfluorohexane is exceptionally low, varying from 588 $m \cdot s^{-1}$ at 273.15 K to 495 $m \cdot s^{-1}$ at 303.15 K. There are few previous results available in the literature for this compound but Pethrick and Teik [7] report (graphically) a value for pure n-C_6F_{14} of $(480 \pm 10)\ m \cdot s^{-1}$ at 303.15 K, while Narayana and Swamy [2] have 502 $m \cdot s^{-1}$ at the same temperature for a sample of mixed C_6F_{14} isomers. Both these values are in fair agreement with the present results.

Mixtures of perfluorohexane with 2,2-dimethylbutane appear to be suitable as filling fluids for sonar targets and may be useful in other applications requiring low-sound-speed liquids. The compositions (expressed as mass fractions x of 2,2-dimethylbutane) required to match the condition $u = u_w/1.77$ at various temperatures were obtained by interpolation and may be represented in the range $273.15 \leqslant T/K \leqslant 303.15$ by the simple formula:

$$x = 0.4638 + 0.01133t - 0.000015t^2 \qquad (3)$$

in which $t = \{(T/K) - 273.15\}$. Values of u_w used in this determination were those for atmospheric pressure and 3.5% salinity [8]. Similar correlations may be devised for the other mixtures studied in this work [9].

ACKNOWLEDGMENTS

The skilled assistance of Mr. A. J. Meredith in constructing the apparatus and financial support from the U.K. Ministry of Defence are both gratefully acknowledged.

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