Speed of Sound Results in 2,3,3,3-Tetrafluoropropene (R-1234yf) and *trans*-1,3,3,3-Tetrafluoropropene (R-1234ze(E)) in the Temperature Range of (260 to 360) K

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Speed of sound measurements in high purity samples of two novel candidate refrigerants, 2,3,3,3-tetrafluoropropene (R-1234yf) and *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), are reported along five isotherms in the temperature range of (260 to 360) K and for pressures up to 10 MPa. The experimental technique is based on a double-reflector pulse-echo overlap method. The acoustic path lengths were obtained by a comparison with measurements in pure water carried out at atmospheric conditions. The speed of sound experimental results are characterized by an overall estimated uncertainty of less than of 0.1 %.

Introduction

Driven by international agreements, such as the Montreal and Kyoto protocols as well as a desire for a higher degree of sustainability, agreeing countries showed a renewed interest in the impact of human and industrial activities on climatic equilibrium of the planet. Although the scientific community is still discussing how to distinguish the human contribution from the natural one for climate change, there is a common agreement to gain the highest efficiency in the use of planetary resources.

In this context, industrial refrigerants, playing a vital role in society, can give their aid. Nowadays refrigerants are widely used in preserving food, supporting industrial processes, and realizing heat pump units and fire extinguishers, as well as in the fields of automotive industries, commercial and domestic refrigerators, and air conditioning.

While the need for refrigerants is growing, the world's societies are becoming more concerned about the environmental impact of refrigerants being used and the systems that use them. In the past, many chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were widely used as refrigerants, propellants (in aerosol applications), and solvents, but the manufacturing of such compounds were phased out by the Montreal Protocol, because they have been implicated in the accelerated depletion of ozone in the Earth's stratosphere. The primary substitutes for CFC refrigerants are the hydrofluorocarbons (HFCs), because they do not interact with the ozone layer, but they are "greenhouse gases", and by releasing them into the atmosphere they may contribute to global warming.

In the research for alternatives which have a low global warming potential (GWP), new generation HFCs seem to be able to offer higher performances in refrigeration systems, reducing the impact on atmospheric equilibrium, thanks to their short life when dispersed in the atmosphere. In fact, for example, 2,3,3,3-tetrafluoropropene (R-1234yf) is the first in a new class of refrigerants developed to have almost no environmental impact, with a GWP rating of about 350 times less than that of 1,1,1,2-tetrafluoroethane (R-134a) and an atmospheric lifetime of about 400 times shorter. For these reasons, it has been proposed as a replacement for R-134a as a refrigerant in automobile air conditioners.

Thermodynamic characterization of HFCs constitutes the basis on which their efficiency is determined, but it also constitutes a fundamental tool for designing equipment. A very successful method for the description of the thermophysical behavior of the substances in the fluid phase is by means of a particular function, named equation of state (EoS). This function can be implemented using only few thermophysical quantities directly measured; from here the other properties can be calculated. The accuracy of an EoS depends on many factors, for example, the accuracy of the measured quantities, but also the number of different thermodynamic properties and, not marginally, the personal experience gained in developing an EoS.

There are quantities that are very useful both for building and for checking the predictions of the EoS whatever is the type of EoS (fundamental,[1] empirical,[2] etc.). In particular, aside from density and vapor pressure, speed of sound data are the next most important property for developing excellent EoS's. This type of data has been absolutely crucial, for example, in the recent development of a propane equation.[3]

Speed of sound results obtained in this work are part of a research project originated from the collaboration between the Physical and Chemical Properties Division of the National Institute of Standards and Technology (NIST) and the Thermodynamics Division of the National Institute of Metrological Research (INRiM). The object of this project is the formulation of the properties of R-1234yf and R-1234ze(E) hydrofluorocarbons, implementing two very accurate EoS's, suitable for scientific and industrial purposes.

Experimental Apparatus

Speed of sound was measured by means of an ultrasonic "pulse-echo" technique. The core of the experimental apparatus, used for the determination of the group velocity of the ultrasonic waves (deeply described in ref 4), is a hollow cylindrical stainless steel cell supplied with two reflectors placed at unequal distances from a single piezoelectric transducer.

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Table 1. Blowing Agents in R-1234ze(E) and R1234yf Samples

parameter	limit
R-1234ze(E)	
assay as R-1234ze(E)	99.5 % wt. min.
moisture	0.0050 % wt. max.
acidity	
as HCl	0.0001 % wt. max.
as mg KOH/g	0.0015 max.
nonvolatile residues	0.0050 % wt. max.
R-1234yf	
assay as R-1234yf	99.99 % wt. min.

During measurements, the ultrasonic cell was placed within a stainless steel vacuum and pressure-tight vessel. Pressure was generated, and controlled, by a 400 MPa pressure amplifier, connected to a bomb that contains the sample under test. A pressure transducer was used to measure the pressure in the system with a maximum uncertainty value of 0.1 MPa.

The ultrasonic cell and the pressure vessel were placed in a stirred liquid bath thermostat. The temperature was maintained and controlled by a system consisting of a main thermostat, having a stability of ± 0.01 K, and a PID controller, operating with a platinum resistance probe and a control heater. This system has permitted us to achieve a long-term temperature stability within the liquid bath of ± 2 mK, over the whole operating temperature range. The temperature associated with the speed of sound measurements was determined with an accuracy of ± 0.03 K, as the average of the readings of two platinum resistance thermometers (PRTs), attached to the top and bottom parts of the pressure vessel and calibrated by comparison with a standard PRT.

Samples of R-1234f and R-1234ze(E) were supplied by Honeywell International Inc. The declared specific mole fraction purity of these samples was better than 99.5 % wt. The major blowing agents are listed in Table 1; no further analysis or purification was attempted.

Measurement Results and Uncertainties

Results. Measurements of the speed of sound, w_{exp}, in the samples under test have been effected along five isotherms at temperatures equal to (260, 285, 310, 335, and 360) K and at five different pressures (2, 4, 6, 8, and 10) MPa in R-1234ze(E) and (2, 3, 4, 5, and 6) MPa in R-1234yf.

The experimental results were fitted with the following bidimensional polynomial

$$w(p, T) = \sum_{i=0}^{N} \sum_{j=0}^{M} a_{ij}(p - p_0)^i (T - T_0)^j \qquad (1)$$

where the degree of the bidimensional polynomial, N and M, has been chosen so that the differences between experimental values and those calculated are maintained under the experimental uncertainty affecting the speed of sound measurements. In Table 2, the speed of sound experimental values, w_{exp}, together with corresponding experimental temperature and pressure values, are listed. Tables 3 and 4 list the coefficient matrix, a_{ij}, obtained for R-1234ze(E) and for R-1234yf, respectively.

The speed of sound results as a function of pressure are shown in Figures 1 and 2, and the regular trend of the curves reported in these plots is a confirmation of the accuracy of the measurements.

Table 2. Experimental Speed of Sound Results, w_{exp}, as a Function of Temperature, T_{exp}, and Pressure, p_{exp}

R-1234ze(E)			R-1234yf		
T_{exp}	p_{exp}	w_{exp}	T_{exp}	p_{exp}	w_{exp}
K	MPa	$m \cdot s^{-1}$	K	MPa	$m \cdot s^{-1}$
259.98	1.98	715.11	260.00	1.99	632.05
259.98	3.99	728.84	260.00	3.04	640.57
260.00	6.02	742.08	260.00	4.06	648.57
260.00	8.01	754.65	260.00	4.97	655.69
260.00	10.07	767.16	260.00	5.99	663.37
285.00	1.96	606.38	285.01	2.03	525.90
285.00	4.02	624.26	285.01	3.01	536.18
285.00	6.06	640.72	285.00	4.01	546.27
285.00	8.00	655.64	285.01	5.09	556.71
285.00	9.99	670.06	285.00	5.98	565.09
310.00	2.06	497.64	310.01	2.01	415.62
310.00	3.95	519.14	310.01	3.04	430.67
310.00	6.04	540.98	310.01	4.02	444.00
310.00	8.00	559.88	310.00	5.02	456.81
310.00	10.11	578.79	310.00	6.06	469.10
335.01	2.01	379.56	335.00	2.07	293.74
335.01	4.03	413.08	335.00	3.04	317.18
335.01	5.98	440.56	335.00	3.98	336.92
335.00	7.98	465.60	335.00	5.00	355.82
335.00	10.02	488.50	334.98	5.94	371.37
360.02	4.00	296.31	359.96	5.00	248.55
360.00	6.05	340.10	359.94	6.06	275.99
360.03	8.05	373.95			
360.03	10.04	402.50			

Table 3. Matrix of Coefficients, a_{ij}, of the Speed of Sound Function for R-1234ze(E)

a_{ij} with $N = 3$ ($i = 0, 1, 2, 3$); $M = 3$ ($j = 0, 1, 2, 3$); $p_0 = 6$ MPa and $T_0 = 310$ K

$a_{00} = 540.6523$	$a_{01} = -3.9722$	$a_{02} = -0.8238 \cdot 10^{-4}$	$a_{03} = -0.2329 \cdot 10^{-4}$
$a_{10} = 9.8859$	$a_{11} = 0.0989$	$a_{12} = 0.1135 \cdot 10^{-2}$	$a_{13} = 0.1087 \cdot 10^{-4}$
$a_{20} = -0.2015$	$a_{21} = -0.5704 \cdot 10^{-2}$	$a_{22} = -0.1240 \cdot 10^{-3}$	$a_{23} = -0.1319 \cdot 10^{-5}$
$a_{30} = 0.0106$	$a_{31} = 0.5292 \cdot 10^{-3}$	$a_{32} = 0.3561 \cdot 10^{-5}$	$a_{33} = 0.6767 \cdot 10^{-7}$

Table 4. Matrix of Coefficients, a_{ij}, of the Speed of Sound Function for R-1234yf

a_{ij} with $N = 3$ ($i = 0, 1, 2, 3$); $M = 3$ ($j = 0, 1, 2, 3$); $p_0 = 4$ MPa and $T_0 = 310$ K

$a_{00} = 443.8703$	$a_{01} = -4.1515$	$a_{02} = -0.3486 \cdot 10^{-2}$	$a_{03} = -0.4339 \cdot 10^{-4}$
$a_{10} = 13.4178$	$a_{11} = 0.1884$	$a_{12} = 0.1927 \cdot 10^{-2}$	$a_{13} = 0.7596 \cdot 10^{-5}$
$a_{20} = -0.4510$	$a_{21} = -0.0190$	$a_{22} = -0.4846 \cdot 10^{-3}$	$a_{23} = -0.4993 \cdot 10^{-5}$
$a_{30} = -0.0330$	$a_{31} = 0.4070 \cdot 10^{-3}$	$a_{32} = 0.2029 \cdot 10^{-3}$	$a_{33} = 0.3702 \cdot 10^{-5}$

Assessment of Measurement Uncertainty. The "pulse-echo" method used to measure the speed of sound $w(p,T)$ basically consists in the determination of two mechanical quantities: the length of the geometric path $2\Delta L(p,T)$ traversed by the acoustic wave and the associated time interval, τ, as it is shown in the following equation:

$$w(p, T) = \frac{2\Delta L(p, T)}{\tau} \qquad (2)$$

The procedure to obtain the uncertainty associated with the speed of sound measurements has been described in ref 4. Table 5 lists the contributions to the overall uncertainty. The measurement of the delay-time uncertainty is assumed to be equal to two oscilloscope sampling intervals, in this case 0.5 ns. Temperature measurements are affected by an uncertainty of 0.03 K, corresponding to the calibration accuracy. The uncertainty in pressure measurements is estimated to be 0.1 MPa, considering the results of the transducer calibration and its repeatability.

Finally, the relative uncertainty in sound speed results is estimated to be 0.065 % for R-1234ze(E) over the entire $T-p$

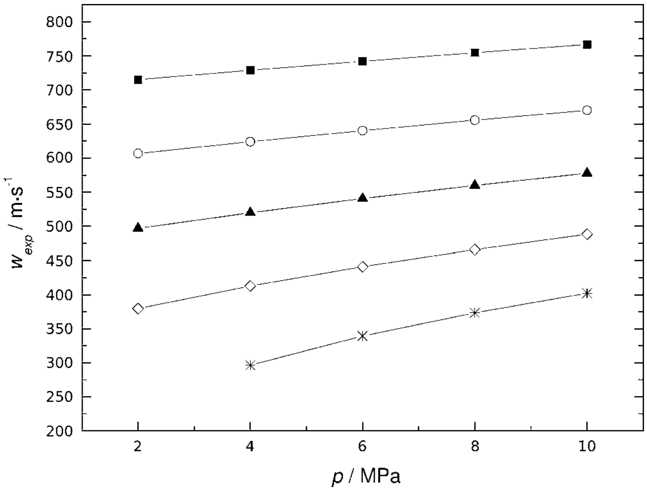

Figure 1. Experimental speed of sound results as a function of pressure in R-1234ze(E): ■, $T = 260$ K; ○, $T = 285$ K; ▲, $T = 310$ K; ◇, $T = 335$ K; ∗, $T = 360$ K.

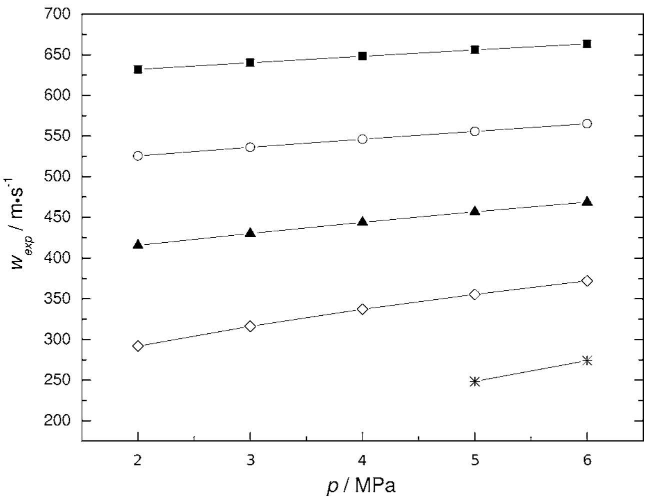

Figure 2. Experimental speed of sound results as a function of pressure in R-1234yf. Symbols show values of each isotherm: ■, $T = 260$ K; ○, $T = 285$ K; ▲, $T = 310$ K; ◇, $T = 335$ K; ∗, $T = 360$ K.

region examined and 0.077 % for R-1234yf, with exception for the isotherm at a temperature equal to 360 K, in which the signal-to-noise ratio was not very good and the estimated overall uncertainty is equal to 0.23 %. Probably this effect is due to the fact that the thermodynamic conditions of this measurement are close to the critical point ($p = 3.38$ MPa, $T = 367$ K), where the bulk modulus decreases quickly with respect to that one in the liquid phase. For these reasons, we have decided to stop the measurements cycle avoiding the last three planned pressure values.

Table 5. Uncertainty Budget

	relative magnitude (%)	
uncertainty source	R-1234ze(E)	R-1234yf
determination of the acoustic path $\sigma(\Delta L)/\Delta L$	0.014	0.013
determination of temporal delay $\sigma(\tau)/\tau$	0.001	0.001
temperature measurements $(\partial w/\partial T)\sigma(T)/w$	0.030	0.036
pressure measurements $(\partial w/\partial p)\sigma(p)/w$	0.056	0.066
estimated overall uncertainty	0.065	0.077

Conclusions

In this work, we have studied the speed of sound behavior, with its uncertainty, for two novel candidate refrigerants (R-1234yf and R-1234ze(E)), with a double-reflector pulse-echo overlap technique. The authors are sure that these results will be useful for the formulation of a new EoS for both fluids and hope that these new compounds become the standard for refrigeration cycles.

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