Table III. Standard Deviation (σ) and Values of the Constants in Eq 3 at 308.15 K[a]

system	b_0	b_1	b_2	σ
benzonitrile + 1-propanol	−196.01	96.40	−85.39	2
benzonitrile + 1-butanol	−148.71	68.60	−57.21	1
benzonitrile + 1-pentanol	−108.90	43.38	−21.40	1
benzonitrile + 2-propanol	−320.48	150.55	−84.44	1
benzonitrile + 2-methyl-1-propanol	−218.90	66.60	−26.83	1
benzonitrile + 3-methyl-1-butanol	−144.03	37.25	−15.47	1

[a] All values in TPa^{-1}.

these constants are given in Table III along with the standard deviation, σ, which is obtained by using the equation

$$\sigma = \left[\frac{\sum(\Delta K_{s,exptl} - \Delta K_{s,calcd})^2}{n - p} \right]^{1/2} \quad (4)$$

where n is the number of results and p is the number of parameters in eq 3.

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Speed of Sound in Saturated Liquid *n*-Pentane

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The speed of sound in saturated liquid *n*-pentane has been measured in the temperature range −70 to 35 °C from 7.3 to 12 MHz. Two different methods were used, and the agreement of the two data sets is within the experimental error. These data were combined with available density data to obtain the adiabatic compressibilities.

Introduction

Measurements of the speed of sound offer a convenient method for determining certain thermodynamic properties of dense fluids not easily obtained by other means. We have measured the speed of sound W in saturated liquid n-pentane from −70 to 35 °C using the pulse-echo-superposition (PES) and pulse-echo-overlap (PEO) methods at frequencies from 7.3 to 12 MHz. The results have been used with the available density ρ_σ data to obtain isentropic compressibility β_S by means of the relation $W^2 = (\rho_\sigma \beta_s)^{-1}$.

Experimental Procedure

The speed of sound was measured by using two different methods. The first was the pulse-echo superposition (PES), used previously in this laboratory for measurements on trichlorofluoromethane (*1*) and described previously (*1*, *2*). The second method, used widely in solids (*3*, *4*), was the pulse-echo overlap (PEO) described in detail elsewhere (*3*, *5*). Measurements were made by using two 10-MHz X-cut quartz crystals. The first data set was obtained by using the PES method where the crystals vibrated at their resonant frequencies. In the second data set, obtained with the PEO method, at each temperature, the crystals were forced to vibrate around two frequencies, 7.3 and 12 MHz, at which the observed signal on the oscilloscope was clearer. The differences in the overlapping criteria with these frequencies were always less than 10 Hz in the repetition rate frequency. This corresponds to less than 0.02% in the measured speed of sound. This, together with the uncertainties in the acoustic path length and pulse repetition frequency, gives an uncertainty in the measured speed of sound of less than 0.05%, which is comparable with that estimated for the PES method.

The sample cell made of heavy copper was immersed in a thermostated ethanol bath which was controlled with a sensitive proportional temperature regulation. Temperatures were measured by using platinum resistance thermometer calibrated on the IPTS-68. This thermometer was located in a thermowell inside the sample cell in contact with the liquid n-pentane. The temperature could be maintained within ±0.006 °C during the measurements. The n-pentane used was commercially obtained from Merck with reported minimum purity of 99.0% and probable impurities of water and sulfur compounds. The n-pentane was not further purified except for the degassing performed at 25 °C. At each temperature, the sound speed was measured at least twice with some n-pentane being removed from the sample cell between the measurements. Identical sound speed observations indicated that the two-phase condition existed in the sample cell.

Results and Discussion

The speed of sound for the saturated liquid n-pentane has been measured at about 5 °C intervals from −70 to 35 °C for both data sets. These data are shown in Table I. For the PEO method the data are those obtained with the crystals vibrating around 12 MHz. The speed of sound data set measured with the PES method was fitted to a quadratic equation of the form

$$W(t) = a + bt + ct^2 \quad (1)$$

where, a b, and c were found by an unweighted least-squares method. The coefficients obtained are a = 1126.257, b = −4.935006, and c = 0.0016748. Deviations of the two data

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Table I. Speed of Sound W_{exptl} and Derived Values of the Isentropic Compressibility β_S in Saturated Liquid *n*-Pentane[a]

t/°C	W_{exptl}/(m s^{-1})	100$\Delta W/W$	ρ_σ/(kg m^{-3})	β_S/(GPa)$^{-1}$
−67.48	1467.0	0.009	706.89	0.6573
−67.14[b]	1464.9	−0.014	706.60	0.6595
−61.98	1438.5	−0.004	702.17	0.6882
−61.84[b]	1437.8	−0.002	702.05	0.6890
−56.53	1410.7	0.005	697.47	0.7205
−56.49[b]	1410.4	0.001	697.43	0.7208
−56.43[b]	1410.2	0.006	697.38	0.7211
−51.09	1382.3	−0.036	692.72	0.7555
−51.03[b]	1382.5	0.003	692.67	0.7553
−46.15[b]	1357.7	0.011	688.38	0.7880
−45.90	1356.1	−0.014	688.16	0.7902
−40.76[b]	1330.4	0.013	683.60	0.8265
−40.70	1329.9	0.005	683.55	0.8272
−35.50[b]	1303.6	0.001	678.90	0.8668
−35.49	1303.3	−0.016	678.89	0.8672
−30.40[b]	1277.8	−0.004	674.29	0.9083
−30.21	1276.7	−0.011	674.12	0.9101
−25.41	1252.6	−0.009	669.75	0.9516
−25.26[b]	1252.0	−0.000	669.61	0.9528
−20.20[b]	1226.0	−0.006	664.96	1.000
−20.13	1226.2	−0.003	664.89	1.000
−15.15[b]	1201.4	−0.005	660.27	1.049
−15.11	1200.9	−0.022	660.23	1.050
−10.35[b]	1177.5	0.003	655.77	1.100
−10.26[b]	1177.0	−0.010	655.68	1.101
−10.23	1176.6	−0.029	655.65	1.102
−5.46[b]	1153.2	−0.003	651.14	1.155
−5.29	1152.1	−0.031	650.98	1.157
−0.72	1129.5	−0.029	646.60	1.212
−0.58[b]	1129.0	−0.012	646.47	1.214
4.44[b]	1104.2	−0.013	641.62	1.278
5.11	1101.0	−0.010	640.96	1.287
9.90	1077.4	−0.012	636.28	1.354
10.15[b]	1076.5	0.013	636.03	1.357
14.98	1052.5	−0.016	631.25	1.430
15.19[b]	1051.9	0.021	631.04	1.432
20.04	1027.8	−0.020	626.18	1.512
20.23[b]	1027.1	0.003	625.99	1.514
25.16	1002.9	−0.022	620.99	1.601
25.32[b]	1002.4	−0.003	620.82	1.603
30.16[b]	978.9	−0.009	615.85	1.695
30.17	979.0	0.010	615.84	1.694
35.22[b]	954.6	0.004	610.58	1.797
35.25	954.5	0.010	610.55	1.798

[a] Column 3 gives the percent deviation $100(W_{exptl} - W_{calcd})/W_{calcd}$. W_{calcd} from eq 1. [b] Measured with the PES method.

sets from eq 1 appear to be random, as indicated in Figure 1, and the agreement between the two data sets is within 0.04%. The formere indicates the feasibility of applying the PEO method to compressed fluids and also suggests that the frequency dispersion between 7 and 12 MHz is not observable. Also Figure 1 seems to indicate that the differences in the results obtained by the PES and PEO methods are systematic; for the most part, the PEO results are lower than the PES results. This might be due to the different measurement criteria used. In the PES method there is a physical superposition of the pulse and all its echoes in-phase condition that is observed on an oscilloscope as a maximum increase in the amplitude of the leading oscillations of the pulse-echo train. On the other hand, in the PEO there is an overlapping of only any pair of pulse echoes in a train (i.e., pulse and any echo or any two echoes) which is a virtual superposition accomplished with a two-channel "strobe" (see ref *1–5* for details). However because of the estimated uncertainties and lack of sufficient evidence, we cannot give a definite conclusion about the systematic differences. The only published data of the speed of sound in *n*-pentane seem to be those of Otpushchennikov et al. (*6*), but they were unavailable for comparison at the time of writing this report. Qualitatively, the data as a function of temperature show in this region a positive curvature as was observed for Freon (1) and different from those of methane (*7*) and ethane (*8*). The measured speed of sound data have been combined with the orthobaric densities represented by the modified Rackett equation reported by Spencer and Adler (*9*) to calculate adiabatic compressibilities. These are also shown in Table I. The uncertainty in β_S is estimated at about ±0.3% due to the combined uncertainty in the measured sound speed and the average deviation of 0.2% in the density reported by Spencer and Adler (*9*).

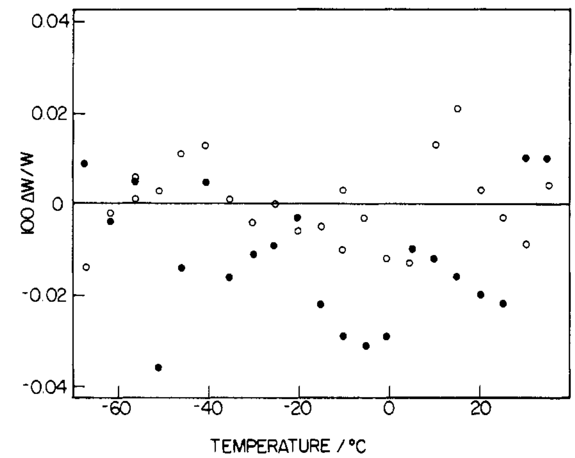

Figure 1. Deviation plot of sound speeds in saturated liquid *n*-pentane compared with values calculated from eq 1: (O) PES and (●) PEO methods.

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