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Measurements of the Speed of Sound for Mixtures of Methane + Butane with a Particular Focus on the Critical State

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The speed of sound in binary mixtures of methane + butane has been measured in the subcritical, near-critical, and supercritical regions as a function of pressure at 311 K. The measurements were based on an acoustic pulse technique using a high-pressure vessel equipped with two 1-MHz transducers to generate and receive the ultrasonic wave. The results showed that the speed of sound decreased with decreasing pressure for mixtures in the subcritical region, whereas it passed through a minimum in the supercritical region.

Introduction

The considerable progress achieved in seismic prospecting and drilling techniques has increased the diversity of produced hydrocarbons. Thus, alongside the standard oil and gas, more specific fluids such as hyperbaric fluids and critical fluids are now increasingly common. However, there is a little experimental data on these fluids, which are found in deep reservoirs at extreme conditions of pressure and temperature. Also, to resolve the numerous problems raised by the petroleum industry in its effort to improve oil field production, it is necessary to be able to characterize the thermophysical behavior of such fluids near the critical conditions. Moreover, a knowledge of thermodynamic properties is of great interest not only for industrial applications but also for fundamental aspects in view of testing the validity of existing models principally near the critical point.

Close to the critical point, large fluctuations leading to thermodynamic anomalies have been reported,[1] making classical fluid models unreliable. Similar observations of nonthermodynamic properties, such as viscosity,[2] have also been reported. Several thermophysical properties of pure components are known to be considerably affected in the critical region. For example, the specific heat at constant volume of argon diverges weakly at the critical point.[3] A direct consequence is that speed of sound tends to zero at the critical conditions, a phenomenon observed experimentally, for instance, in supercritical steam.[4] These similar observations have been reported for binary mixtures of alkanes (methane + ethane or ethane + butane).[5,6] However, the divergence of the specific heat and the reduction of the speed of sound are less pronounced in the case of mixtures.

Among these properties, the speed of sound can be determined experimentally with a high degree of accuracy, even at high pressure.[7] In this context, we have conducted measurements of the speed of sound in model fluids representing real reservoir hydrocarbons.

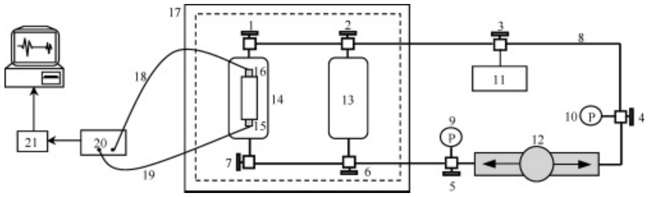

Figure 1. Schematic diagram of the experimental apparatus: 1−7, valves; 8, bypass line capillary; 9 and 10, pressure transducers; 11, vacuum pump; 12, push−pull pump; 13, windowed PVT cell; 14, high-pressure acoustic cell; 15 and 16, piezoelectric transducers; 17, temperature-controlled air bath; 18 and 19, BNC cable; 20, pulse generator; 21, digital oscilloscope.

The first part of this article describes the characteristics of the acoustic cell designed for this purpose. The second part presents the experimental procedure carried out for binary mixtures to characterize the behavior of the speed of sound and also to show the influence of pressure. The speed of sound of three mixtures of methane + butane, showing liquid, near-critical fluid, and gas behavior, has been measured at different pressures.

Experimental Section

Apparatus. The experimental apparatus used in this work is shown in Figure 1. It consists primarily of a high-pressure cell made of 316 stainless steel. There are two piezoelectric ultrasound transducers with a circular cross section of 19 mm and a resonance frequency of 1 MHz. The use of this frequency that is lower than a few tens of MHz, a domain corresponding to the zero-frequency region for most hydrocarbons,[8,9] allows us to neglect dispersive phenomena and then to assimilate the ultrasound speed to the speed of sound, which represents a purely thermodynamic property linked to an isentropic process. Moreover, a frequency of 1 MHz constitutes an acceptable compromise between lower frequencies that give clear signals but reduce the precision and higher frequencies that lead to a better precision of measurements but with a greater attenuation of the acoustic waves.

The transducers are held in their high-pressure housing caps that are used as links between the transducers and the fluid sample and are secured to each end of the cell.

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To ensure a perfect transmission and reception and also to reduce the attenuation phenomenon, an ultrasound couplant was used at the interface between the transducer crystals and the housing caps.

The high-pressure acoustic cell was contained inside a thermally insulated temperature-controlled air bath. This air bath was held at a stable temperature (±0.1 K) of 311 K by a high-precision temperature controller (Eurotherm 905S). The pressure of the fluid within the acoustic cell was applied and controlled by two Ruska pumps, which were also used to circulate the fluid in the acoustic cell to ensure the homogeneity of the mixtures. Pressure was measured by means of two Quartzdyne C20K pressure transducers that can measure the pressure with an uncertainty of ±0.006%.

The technique used to carry out the measurements was based on a pulse transmission/reflection technique. The electronic part of the experimental device used for this purpose consisted of two piezoelectric transducers (detailed previously) connected to a Panametrics pulse transmitter/receiver (model 5077 PR). Its output signal was fed to a digital oscilloscope (Link Instruments, model DSO2102), which could be displayed on the computer, with a measurement error of ±10 ns, which leads to an uncertainty of ±0.02% in the travel time measurements.

Determinations of the speed of sound resulted from a double measurement by direct chronometry of the transit times of pulses by transmission and reflection within the cell containing the fluid sample.[7] In this way, it was possible to deduce the transit time (ΔT_S) through the sample and then to calculate the speed of sound (u) given by

$$u = \frac{L}{\Delta T_S} \tag{1}$$

where L is the travelling distance.

The travelling distance (L) for the wave is affected by the pressure and temperature of the system. Therefore, it is essential to establish the relation between L and these parameters accurately. This was achieved by introducing the following temperature and pressure dependency into the distance L:

$$L(P, T) = L_0[1 + a(T - T_0)][1 + b(P - P_0)] \tag{2}$$

L_0 represents the length L at a reference pressure P_0 = 0.1013 MPa and a reference temperature T_0 = 298.15 K. Coefficients a and b that are linked to the properties of the materials used in the construction of the cell (such as coefficients of thermal expansion and compressibility of stainless steel, Viton O-rings, and transducers) were determined by calibration with water[10,11] and hexane.[12,13]

The uncertainties in our speed of sound measurements stem from several sources. The uncertainty due to the determination of the length L and the transit time ΔT_S is about ±0.05%.[7] However, two additional sources of uncertainty for u have to be taken into account. Indeed, the uncertainties in the temperature and the pressure lead to uncertainties in u of about ±0.03% and ±0.02%, respectively. The uncertainty has been estimated to be ±0.1% and confirmed by comparing the values of the speed of sound determined by our apparatus (for a pure liquid such as n-pentane) with data found in the literature.[14]

Materials. Methane and butane were supplied by Aldrich with a degree of purity higher than 99.9 mol %. The mixtures were prepared as follows.

Table 1. Speed of Sound Values for Methane (1) + Butane (2)

x_1 = 0.158		x_1 = 0.724		x_1 = 0.894			
P/MPa	u/m·s^{-1}	P/MPa	u/m·s^{-1}	P/MPa	u/m·s^{-1}	P/MPa	u/m·s^{-1}
13.790	906.3	17.237	484.4	17.237	438.0	9.653	367.8
10.342	866.0	16.547	464.8	16.547	428.4	8.963	366.0
6.895	817.6	15.858	443.6	15.858	419.4	8.274	365.1
6.205	805.6	15.168	420.7	15.168	410.8	7.584	364.8
5.516	793.5	14.479	395.6	14.479	402.9	6.895	365.2
4.826	778.7	13.845	366.1	13.790	395.6	6.205	366.4
4.137	762.3	13.472	344.0	13.100	388.9	5.516	368.0
3.999	760.7	13.307	329.7	12.411	383.1	4.826	370.1
3.930	760.1	13.231	323.7	11.721	378.0	4.137	372.7
		13.148	316.5	11.032	373.7	3.447	375.5
		13.128	314.6	10.342	370.3	2.758	378.5
						2.068	381.6

First, butane was transferred to a windowed PVT cell, which was kept in the same air bath as the ultrasound cell. Then the cell was pressurized (by means of a pump) to the desire pressure. The mass of butane was calculated from its measured volume and known density.[15] The uncertainties in the volume measurements and density data are estimated to be ±0.01% and ±0.1% respectively. The required quantity of methane was then injected gravimetrically into the PVT cell, with an uncertainty of ±0.001 g, and the mixture was made homogeneous by mixing the fluid under pressure.

We note that the error in the composition provides an uncertainty of less than ±0.08% in the measured speed of sound for all of the mixtures.

Results

For methane (1) + butane (2) mixtures at 311 K, the critical pressure is equal to 13.183 MPa with x_1 = 0.724.[16] At a temperature of 311 K, three different compositions were considered: one in the subcritical region (x_1 = 0.158), which is an oil system, one near the critical fluid (x_1 = 0.724), and one in the supercritical region (x_1 = 0.894) for which the temperature of the system (311 K) was above the cricondentherm, hence the remaining single phase at all pressures.

For each composition, the pressure of the mixture inside the acoustic cell was first raised to 17.237 MPa, and then measurements of the transit time were carried out as the pressure was slowly reduced. For the two lowest mole fractions of methane, the minimum pressure for which a measurement was accurately possible was limited to the saturation pressure of the mixture. Where the two-phase boundary was crossed, the appearance of the gas phase made the transmission of the wave difficult. This problem was due to a significant difference between the acoustic impedance of the liquid and gaseous phases.

The values of the speed of sound are displayed in Table 1. On the basis of these data, variations of this property versus pressure are plotted in Figures 2 to 4. Very different trends can be observed in these graphs. First, in the subcritical region (i.e., x_1 = 0.158), the $u(P)$ curve confirms a typical behavior for the liquid state in which the speed of sound increases with pressure (Figure 2). Moreover, as expected, an anomaly appears for x_1 = 0.724 with a rapid decrease in the speed of sound as the critical pressure, P = 13.183 MPa, is approached. This phenomenon is more clearly underlined in Figure 5 in which the gradient of the speed of sound versus pressure ($\delta u/\delta P$) is plotted for x_1 = 0.158 and x_1 = 0.724. For this last mentioned composition, there is a sharp change in the gradient in the vicinity of the critical pressure for T = 311 K.

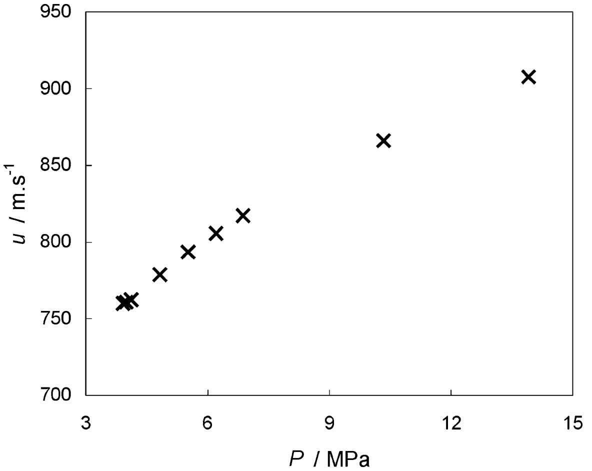

Figure 2. Sound velocity versus pressure for methane (1) + butane (2) and for $x_1 = 0.158$.

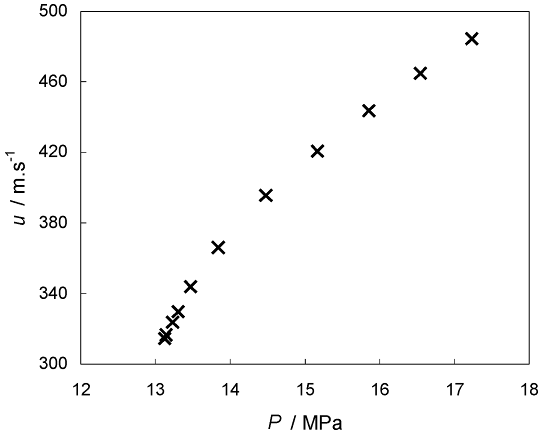

Figure 3. Sound velocity versus pressure for methane (1) + butane (2) and for $x_1 = 0.724$.

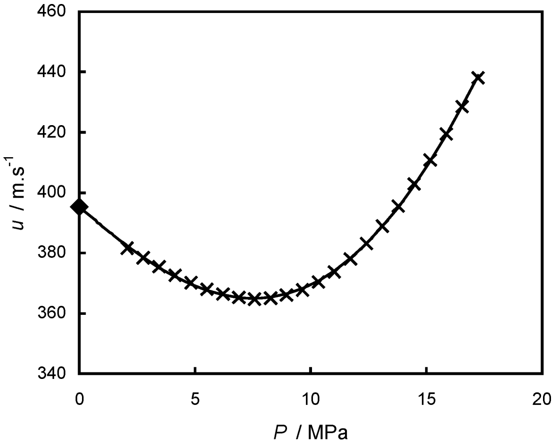

Figure 4. Sound velocity versus pressure for methane (1) + butane (2) and for $x_1 = 0.894$: ×, experimental; −, from a pressure explicit acoustic virial expansion; and ◆, at zero pressure from Boyle's law.

Figure 4 plots the speed of sound versus pressure for $x_1 = 0.894$. For this composition, because the mixture temperature is above the cricondentherm of the system, the mixture remains single phase (gaseous) at all pressures. This allows measurements down to a very low pressure. In this particular case, at low pressures the speed of sound decreases as the pressure is lowered and passes through a minimum, after which it increases as the pressure drops further.

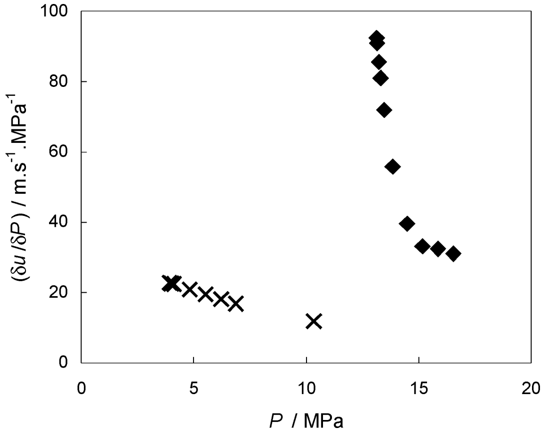

Figure 5. Sound velocity gradient versus pressure for methane (1) + butane (2): ×, for $x_1 = 0.158$; ◆, for $x_1 = 0.724$.

Practically, it was not possible to continue with the measurement of the speed of sound down to zero pressure. However, the values of u^2 along the isotherm considered in this work may be represented by an expansion in powers of pressure (eq 3) and then extrapolated to zero pressure.

$$u^2 = A_0 + A_1 P + A_2 P^2 + A_3 P^3 + \ldots \qquad (3)$$

The value of each coefficient ($A_0 = 156\,421$ m^2·s^{-2}, $A_1 = -5460.45$ m^2·s^{-2}·MPa^{-1}, $A_2 = 220.45$ m^2·s^{-2}·MPa^{-2}, and $A_3 = 12.63$ m^2·s^{-2}·MPa^{-3}) was obtained by a least-squares method leading to an absolute average deviation of less than 0.2% over the whole pressure range. In this equation truncated after the fourth coefficient, A_0 is the zero-pressure limit of u^2. This value can be compared with the square of the speed of sound at the same temperature of 311 K for a perfect gas (u_{pg}^2) deduced from Boyle's law below:

$$u_{\text{pg}}^2(T, P \rightarrow 0) = \frac{\gamma RT}{M} \qquad (4)$$

where γ, R, T, and M are the ratio of the ideal gas specific heat at constant pressure (C_P^0) to that at constant volume (C_V^0), universal gas constant, absolute temperature, and molar mass, respectively.

For the mixture in the ideal gas state, M_{m} and γ_{m} were calculated as follows:

$$M_{\text{m}} = \sum_i x_i M_i \qquad (5)$$

and

$$\gamma = \frac{C_{P\text{m}}^0}{C_{V\text{m}}^0} = \frac{\sum_i x_i C_{Pi}^0}{C_{P\text{m}}^0 - R} \qquad (6)$$

Using eqs 4 to 6 and substituting suitable values of C_{Pi}^0 for each component,[17] we calculated u_{pg}^2 for $x_1 = 0.894$ (data marked by the symbol u in Figure 4).

A comparison between these two values at zero pressure (i.e., A_0 and u_{pg}^2) provides an absolute average deviation of 0.06% in terms of the speed of sound.

Conclusions

Measured data for the speed of sound of three model fluids representing three types of petroleum reservoir fluids has been reported. This work is the first stage of an ongoing program of hyperbaric and supercritical fluids investigation.

In this area, classical equations of state widely used in the petroleum industry fail in the critical region because of fluctuations in density, which dominate the interparticle interactions as the critical point is approached.[18] The generated data near the critical region could be used in development of more robust fluid models such as a crossover equation of state, and a comparison between measured and predicted values will be considered in further work.

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