Analysis of Ultrasonic Velocities in Hydrocarbon Mixtures

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Abstract

Ultrasonic velocity data on hydrocarbon mixtures was shown by Wang and Nur [JASA **89**, 2725 (1991)] to agree quite well with the predictions of a simple mixing rule (volume average of velocity). The same data is reanalyzed using Wood's formula and the time average approximation. Wood's formula for acoustic velocity is shown to be always less than the time average formula, which is itself always less than the simple mixing rule result. Although the volume average rule agrees best with the data on binary mixtures of 1-decene and 1-octadecene, all these formulas agree with the data to within 1% and, therefore, it is not possible to distinguish among the formulas using this data set. Similar results are also found for six multicomponent hydrocarbon mixtures.

PACS numbers: 43.35.Bf, 43.20.Bi, 43.20.Hq

Wang and Nur [1] have published a series of measurements on ultrasonic velocities of liquid hydrocarbons and mixtures. They found that their data on hydrocarbon mixtures could be adequately explained using a simple mixing rule having the form of a volume average over the velocities of the pure hydrocarbon constituents

$$\langle V\rangle = \sum x_i V_i, \tag{1}$$

where the x_is are the volume fractions of the constituents and the V_is are their acoustic velocities. This result is somewhat surprising since the formula (1) has no known theoretical standing. We would have expected instead that a liquid mixture should obey Wood's formula [2]

$$V_W = (K_R/\rho)^{\frac{1}{2}}\,, \tag{2}$$

where the effective adiabatic bulk modulus of the fluid mixture is given by the harmonic mean (or Reuss average)

$$\frac{1}{K_R} = \sum \frac{x_i}{K_i} \tag{3}$$

of the constituents' adiabatic bulk moduli ($K_i = \rho_i V_i^2$) and the average density is just

$$\rho = \sum x_i \rho_i. \tag{4}$$

Wood [2] states that the formula (2) is "... applicable to a mixture of any two fluid media, which do not react chemically."

Wood's formula (2) may be seen to be based on the fact that, when written in terms of isothermal moduli, (3) is an exact result for the effective bulk modulus of an immiscible fluid mixture during quasistatic deformations. It has also been shown [3] that, when written in terms of adiabatic moduli (as it is here), (3) is expected to provide a very good approximation to the bulk modulus for immiscible fluid mixtures and suspensions. Wood's formula is therefore known to be correct for immiscible mixtures of Newtonian fluids at low frequencies [4], and should also give an adequate description of the ultrasonic data on hydrocarbons if the acoustic wavelengths in the fluid mixtures are sufficiently large. The center frequency of the transmitter in the Wang and Nur [1] experiments was 2.25 MHz and a typical value of the wave speed was 1.3 km/s, so the wavelength is approximately 0.6 mm. Whether this wavelength is large or small depends on the manner of the fluid mixing: If the fluid is well-mixed at the microscopic level, then this is a large wavelength. However, if the fluid mixture typically contains blobs of one fluid floating in the other liquid, then the largeness of the wavelength depends on the smallness of these blobs. The mixtures were described as being "well-stirred" by Wang and Nur [1]. How this translates into the microstructure of the fluid mixture is unknown to the author, but if the hydrocarbons are miscible and nonreactive (as is most likely [5]) then the blobs should be of molecular size and Wood's formula should apply.

Another well-known estimate that might be expected to work well in describing these data is the time average formula of Wyllie *et al.* [6]

$$\left\langle \frac{1}{V}\right\rangle^{-1} = \left(\sum \frac{x_i}{V_i}\right)^{-1}. \tag{5}$$

Although this formula is not exact in any nontrivial limit, it is based in part on Fermat's principle of least traveltime through a mixture. The average traveltime will generally be greater than the minimum traveltime. It follows that the time average velocity will generally be lower than the actual velocity. Therefore, we expect the velocity estimate (5) to be a lower bound on the true velocity, whenever this formula applies. Successful applications of the formula have been made to solid-solid and solid-liquid mixtures [4,6], but it is known that the formula gives poor results when a gas phase is present. Applicability of the formula depends also on the wavelength. To be consistent with the derivation, the wavelength should be short compared to the inclusion size. Since Fermat's principle may be derived from the eikonal equation which is a high frequency approximation, the wavelength should be small when this formula applies.

Although various numerical comparisons have been made (see for example Kuster and Toksöz [7]), to the author's knowledge general relationships among these three estimates of mixture velocities have not been noted before. The main purpose of this paper is to point out that these estimates are ordered, *i.e.*, Wood's formula always gives a smaller velocity than the time average, which is in turn always smaller than the volume average. The secondary purpose is to show that all three estimates give an adequate description (within 1%) of the ultrasonic data on hydrocarbon mixtures presented by Wang and Nur [1].

First, the general relationship between (1) and (5) is trivial, because it is well-known that the harmonic mean is always less than or equal to the mean [8]. Thus, we have

$$\left\langle \frac{1}{V} \right\rangle^{-1} \leq \langle V \rangle . \tag{6}$$

Then, for a binary mixture with $x_1 = x$ and $x_2 = 1 - x$, we consider the difference

$$\left\langle \frac{1}{V} \right\rangle^{2} - \frac{1}{V_W^2} = 2x(1-x)\left[\left(\frac{\rho_1\rho_2}{K_2K_1}\right)^{\frac{1}{2}} - \frac{1}{2}\left(\frac{\rho_1}{K_2} + \frac{\rho_2}{K_1}\right)\right] \leq 0. \tag{7}$$

The fact that the right hand side is less than or equal to zero follows from the fact that the geometric mean is always less than or equal to the mean [8]. This result establishes the general relation for binary mixtures that

$$V_W \leq \left\langle \frac{1}{V} \right\rangle^{-1} . \tag{8}$$

Finally, to establish the result (8) for multicomponent mixtures, we consider

$$\left\langle \frac{1}{V} \right\rangle^{2} = \left[\sum x_i \left(\frac{\rho_i}{K_i}\right)^{\frac{1}{2}}\right]^2 = \left[\sum (x_i\rho_i)^{\frac{1}{2}} (x_i/K_i)^{\frac{1}{2}}\right]^2 \leq \sum x_i\rho_i \sum x_i/K_i = \frac{1}{V_W^2}, \tag{9}$$

where the inequality in (9) follows from Cauchy's inequality [8] for sums $(\sum a_i b_i)^2 \leq \sum a_i^2 \sum b_i^2$. Thus, (9) shows that (8) is a general result for multicomponent fluid mixtures.

Combining these results, we obtain the set of inequalities

$$V_W \leq \langle 1/V \rangle^{-1} \leq \langle V \rangle . \tag{10}$$

These results have been derived for arbitrary multicomponent fluid mixtures, including but not restricted to binary mixtures.

Table 1 presents the velocity data of Wang and Nur [1] on 14 pure hydrocarbons, together with the known densities [9,10], and computed adiabatic bulk moduli at 20° C. The estimated uncertainty in the measured velocities (pure hydrocarbon as well as hydrocarbon mixtures) is stated to be 0.2 %. Including likely errors in the density values of about ±0.1%, an error propagation analysis shows that the error in computing the effective bulk modulus needed in Wood's formula is about 0.5 %. Table 2 compares the measured velocities of binary alkene mixtures as a function of volume fraction to the computed velocities using Wood's formula, the time average estimate, and the volume average estimate. All three computed values lie within 0.6 % of the measured values for all values of volume fraction. The volume average estimate is generally closer to the measured values than either of the other two estimates. However, when measurement errors in both the mixture velocities and the two pure hydrocarbon velocities used to compute these values are considered (0.3 + 0.2 %) together with the fact that the nominally "pure" hydrocarbon samples were actually only 90–96 % pure [11], we see that the remaining differences are in fact too small to allow us to distinguish the three formulas — except for the fact that they are ordered, as we have shown. We note that the time average estimate does appear to be a lower bound on the measured values in all cases. The significance of this observation is unclear however, since we believe the wavelengths to be long compared to the size of the fluid microstructure.

Table 3 compares the measured velocities of multicomponent hydrocarbon mixtures to the same three velocity estimates. (Note that the last mixture in this table contains both 2% of the alkene 1-octene — with chemical formula C_8H_{16} — and 6 % of the naphthene cyclooctane — having the same formula C_8H_{16}, but a different structure and density.) All three estimates are again within 1 % of the measured values, but now the volume average estimate is not always the one closest to that observed. The more complex fluid mixtures seem to agree somewhat better with Wood's formula. In all but one case, Wyllie's time average velocity is again observed to be a lower bound on the measured velocities. However, the main result appears to be that the three estimates are again virtually indistinguishable for this data set.

Our conclusion is that the volume average formula used by Wang and Nur [1] apparently gives good agreement with the velocity data for these hydrocarbon mixtures because in all cases the spread in velocities is so small that Wood's formula, Wyllie's time average, and the volume average all give virtually the same results (within probable experimental error). In general, Wood's formula is expected to give reliable estimates even when the fluid constituents have widely differing acoustic speeds (as in the case of liquid/gas mixtures), whereas the volume average formula is expected to have more limited applicability.

Acknowledgments

I thank Kevin G. Knauss for his help in understanding the notation and terminology for organic molecules. I thank Patricia A. Berge, Francis Muir, and David Nichols for useful comments on the manuscript. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48 and supported specifically by the Geosciences Research Program of the DOE Office of Energy Research within the Office of Basic Energy Sciences, Division of Engineering and Geosciences. Part of the work was performed while the author was visiting the Geophysics Department at Stanford University. Partial support for this visit was provided by the Stanford Exploration

Project, whose sponsors are hereby gratefully acknowledged.

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Table 1. Measured ultrasonic velocities [1] and densities [7,8] at 20° C and computed bulk moduli of various hydrocarbons.

Hydrocarbon	V_{meas} (km/s)	ρ (g/cm^3)	K (GPa)
Alkanes			
C_8H_{18}	1.194	0.7025	1.002
$C_{10}H_{22}$	1.247	0.7301	1.135
$C_{12}H_{26}$	1.294	0.7487	1.254
$C_{14}H_{30}$	1.333	0.7628	1.355
$C_{16}H_{34}$	1.354	0.7734	1.418
Alkenes			
C_8H_{16}	1.188	0.7149	1.009
$C_{10}H_{20}$	1.247	0.7408	1.152
$C_{12}H_{24}$	1.290	0.7584	1.262
$C_{14}H_{28}$	1.321	0.7713	1.346
$C_{16}H_{32}$	1.349	0.7811	1.421
$C_{18}H_{36}$	1.369	0.7888	1.478
Naphthenes			
C_6H_{12}	1.276	0.7785	1.268
C_7H_{14}	1.358	0.8098	1.493
C_8H_{16}	1.402	0.8349	1.641

Table 2. Measured ultrasonic velocities [1] for a sequence of binary hydrocarbon mixtures at 20° C compared to velocities computed using Wood's formula, the time average equation, and a simple mixing rule. Data required for computing Wood's formula may be found in Table 1. The formula for the 1-decene/1-octadecene hydrocarbon mixture is $(C_{10}H_{20})_x(C_{18}H_{36})_{(1-x)}$, where x is the volume fraction of 1-decene. Units of all velocities are km/s.

x	V_{meas}	V_W	$\langle 1/V \rangle^{-1}$	$\langle V \rangle$
0.00	1.369	1.369	1.369	1.369
0.10	1.358	1.354	1.356	1.357
0.20	1.348	1.340	1.343	1.345
0.294	1.336	1.328	1.331	1.333
0.40	1.321	1.314	1.317	1.320
0.50	1.307	1.301	1.305	1.308
0.60	1.298	1.290	1.293	1.296
0.70	1.286	1.279	1.281	1.284
0.80	1.275	1.267	1.270	1.271
0.90	1.260	1.257	1.258	1.259
1.00	1.247	1.247	1.247	1.247

Table 3. Measured ultrasonic velocities [1,12] of six multicomponent hydrocarbon mixtures at 20° C compared to velocities computed using Wood's formula, the time average equation, and a simple mixing rule. Fractional subscripts in chemical formulas refer to volume fractions. Data required for computing Wood's estimate may be found in Table 1. Units of all velocities are km/s.

Hydrocarbon Mixture	V_{meas}	V_W	$\langle 1/V \rangle^{-1}$	$\langle V \rangle$
$(C_{10}H_{22})_{.2}(C_{12}H_{26})_{.2}(C_{14}H_{30})_{.2}(C_{16}H_{34})_{.4}$	1.319	1.313	1.315	1.316
$(C_8H_{18})_{.2}(C_{10}H_{22})_{.2}(C_{12}H_{26})_{.2}(C_{14}H_{30})_{.2}(C_{16}H_{34})_{.2}$	1.286	1.278	1.282	1.284
$(C_{12}H_{24})_{.3}(C_{14}H_{28})_{.3}(C_{16}H_{32})_{.4}$	1.326	1.322	1.322	1.323
$(C_8H_{16})_{.1}(C_{10}H_{20})_{.1}(C_{12}H_{24})_{.2}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.5}$	1.312	1.303	1.306	1.308
$(C_{10}H_{20})_{.1}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.2}\times$				
$(C_6H_{12})_{.1}(C_7H_{14})_{.2}(C_8H_{16})_{.3}$	1.343	1.341	1.341	1.346
$(C_8H_{18})_{.04}(C_{10}H_{22})_{.08}(C_{12}H_{26})_{.08}(C_{14}H_{30})_{.08}(C_{16}H_{34})_{.12}\times$				
$(C_8H_{16})_{.02}(C_{10}H_{20})_{.06}(C_{12}H_{24})_{.1}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.2}\times$				
$(C_6H_{12})_{.02}(C_7H_{14})_{.04}(C_8H_{16})_{.06}$	1.309	1.308	1.312	1.314