Ultrasonic Velocity in a Series of 1Olefins

R. T. Lagemann, D. R. McMillan Jr., and Martha Woolsey

Citation: The Journal of Chemical Physics **16**, 247 (1948); doi: 10.1063/1.1746853
View online: http://dx.doi.org/10.1063/1.1746853
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/16/3?ver=pdfcov
Published by the AIP Publishing

Ultrasonic Velocity in a Series of 1-Olefins

R. T. LAGEMANN, D. R. MCMILLAN, JR., AND MARTHA WOOLSEY
Emory University, Emory University, Georgia

(Received December 18, 1947)

The ultrasonic velocity for the temperature range 10° to 30°C has been measured for seven members of a 1-olefin series. Densities and refractive indices were also measured. From the measurements, values of the molecular sound velocity, adiabatic compressibility, and molecular refractivity were computed. The ultrasonic velocity is found to vary linearly with temperature, while the molecular constant, $MV^{\frac{1}{4}}/d$, remains substantially constant. The constant is found to be strictly additive for the series members studied.

IT is becoming increasingly apparent that measurements of the velocity of ultrasonic waves in liquids can be of valuable aid in the study of molecular structure. In this regard, the velocity and, more especially, its derived molecular constant, will perhaps be found to compare favorably with the parachor and the molecular refractivity, for example. A major contribution in this direction was made by Rao[1] when he showed that there exists a molecular sound velocity characteristic of each substance, which is a function of the ultrasonic velocity, the density, and the molecular weight. Later Lagemann and Dunbar[2] pointed out the simple relationships existing between this new molecular constant and others longer established. The constant has been evaluated by Rao[1,3] for the members of a few series, for which fairly reliable data on velocity are available. These results indicated that the constant is additive, taking on additional increments of about 195 units[3] for the addition of each CH_2 group. The size of this increment varies more within a series and more from series to series than does, say, the parachor increment; whether this is real or due to poor measurement of velocity and density is not yet clear.

In view of the scanty data available on this new property, it seemed worth while to extend ultrasonic and density measurements to a series of olefins which was available. Particularly does this study appear appropriate when it is realized that much of the ultrasonic velocity data now available is not accompanied by accurate density measurements performed on the same sample. Often there is doubt as to the purity of the sample studied.

EXPERIMENTAL

The seven compounds studied are listed in Table I. They were obtained in very pure form through the kindness of Dr. C. T. Lester[4] who had prepared them for a study of the addition of 4-mercaptobiphenyl to a series of 1-olefins. Immediately before the ultrasonic measurements, the compounds were again distilled, all but one boiling within a one degree range.

TABLE I. Measured values of the ultrasonic velocity, density, and refractive index for a series of 1-olefins.

Compound	Ultrasonic velocity (M/sec.) 10°C	20°C	25°C	30°C	Density (g/cc) 10°C	20°C	30°C	Refractive index (D line) 10°C	20°C	30°C
1-Heptene	1189	1128		1082	0.7069	0.6995	0.6910	1.4060	1.4007	1.3953
1-Octene	1229	1184		1146	0.7238	0.7183	0.7100	1.4140	1.4091	1.4037
1-Nonene	1258	1218	1201	1179	0.7411	0.7330	0.7252	1.4209	1.4161	1.4111
1-Decene	1290	1250		1214	0.7510	0.7435	0.7359	1.4260	1.4218	1.4167
1-Undecene	1315	1275	1255	1235	0.7594	0.7523	0.7447	1.4301	1.4260	1.4212
1-Tridecene	1353	1313	1294	1276	0.7739	0.7670	0.7596	1.4373	1.4332	1.4290
1-Pentadecene	1390	1351		1313	0.7867	0.7800	0.7731	1.4436	1.4398	1.4352

[1] M. Rama Rao, Ind. J. Phys. **14**, 109 (1940).
[2] R. T. Lagemann and W. S. Dunbar, J. Phys. Chem. **49**, 428 (1945).
[3] M. Rama Rao, J. Chem. Phys. **9**, 682 (1941).
[4] C. T. Lester, G. F. Rodgers, and E. Emmet Reid, J. Am. Chem. Soc. **66**, 1674 (1944).

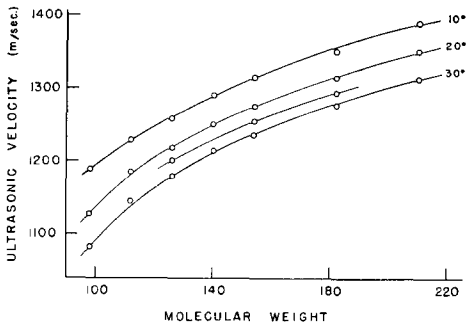

FIG. 1. Plot of the ultrasonic velocity *versus* molecular weight for a series of 1-olefins.

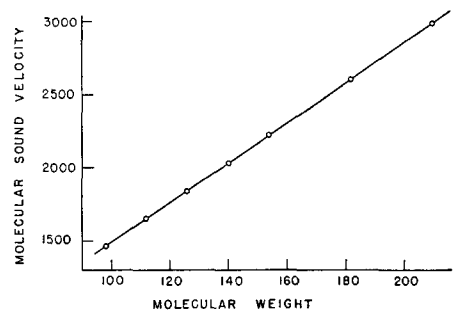

FIG. 3. Plot showing the additivity of the molecular sound velocity.

The ultrasonic velocity of each of the compounds was measured at 10°, 20°, 30°C, and in some cases at 25°C, using the ultrasonic interferometer described by McMillan and Lagemann.[5] The usual precautions to be taken with the interferometer were observed. The frequency used was 500,000±20 cycles per second. The temperature was maintained within ±0.03°C with Bureau of Standards calibrated thermometers. In most cases about 40 ml of each compound were available, giving sufficient nodal points in the interferometer to justify an estimate of 0.1 percent probable error in the measured velocities. In the case of 1-heptene and 1-octene, however, so small a volume was available that only two or three nodal positions could be measured, and for these compounds the error must be larger than that quoted above.

The velocities were measured with the liquids contained in a gold-plated brass cup. Despite the plating, some of the compounds turned lightly blue-green after 6 hours in the cup. Analysis showed the color to be due to copper. Drying with anhydrous sodium sulphate and redistillation yielded samples which remained uncolored on use in the apparatus. New velocity measurements were made, but these did not differ significantly from the earlier ones.

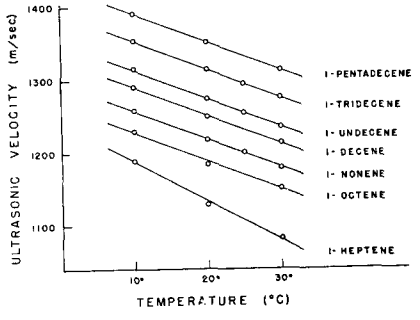

FIG. 2. Graph showing the variation of ultrasonic velocity with temperature for some 1-olefins.

The densities at 10°, 20°, and 30°C were measured using a 5-ml pycnometer such as that described by Lipkin, Davison, Harvey, and Kurtz.[6] Refractive indices were taken on a temperature regulated Abbe refractometer using a wavelength of 5893A.

RESULTS

Table I gives the measured values of the ultrasonic velocity, density, and refractive index. The plots of velocity *versus* molecular weight, shown in Fig. 1, are smooth curves. This is not generally the case within an homologous series.[2] It may be noted that the curve becomes more linear as one goes out the chain.

Figure 2 shows that the temperature coefficient, defined here as $\Delta V/\Delta t$, is constant for the temperature range studied and is the same for the five higher members. For 1-heptene and 1-octene the change of velocity with temperature does not appear linear, or, if assumed linear, the slope for 1-heptene, at least, differs from that of the others. It is unfortunate that larger quantities of these two were not available to check this point.

From the data in Table I it is possible to calculate the values of the molecular sound velocity, $MV^{\frac{1}{3}}/d$, given in Table II. The values for each compound remain substantially constant over the range 10° to 30°C, though there appears a

[5] D. R. McMillan, Jr. and R. T. Lagemann, J. Acous. Soc. Am. 19, 956 (1947).

[6] M. R. Lipkin, J. A. Davison, W. T. Harvey, and S. S. Kurtz, Ind. Eng. Chem. (Anal. Ed.) 16, 55 (1944).

TABLE II. Calculated values of the molecular sound velocity, adiabatic compressibility, and molecular refraction.

Compound	Molecular sound velocity			Molecular refraction (D line)			Adiabatic compressibility (Atm.$^{-1}\times10^6$)		
	10°C	20°C	30°C	10°C	20°C	30°C	10°C	20°C	20°C
1-Heptene	1471	1461	1459	34.13	34.09	34.09	101.4	113.8	125.3
1-Octene	1661	1653	1654	38.74	38.63	38.63	92.69	100.6	108.7
1-Nonene	1839	1839	1839	43.16	43.22	43.23	86.39	92.62	100.5
1-Decene	2033	2032	2033	47.85	47.89	47.90	81.08	87.23	93.43
1-Undecene	2226	2224	2223	52.50	52.55	52.56	77.17	82.86	89.21
1-Tridecene	2606	2603	2604	61.75	61.80	61.87	71.53	76.55	79.67
1-Pentadecene	2985	2982	2980	70.97	71.05	71.03	66.67	71.17	76.03

tendency for them to decrease with increase in temperature. Thus these olefins behave like other normal compounds in that there exists a molecular sound velocity which is constant for changes in temperature.

As CH_2 groups are added in successively building up the series, the constant increases and takes on nearly equal increments. Beginning with 1-heptene, the increase in the molecular velocity per CH_2 group is successively 193, 183, 194, 191, $2\times190/2$, and $2\times189/2$. The linearity between the molecular sound velocity and the molecular weight is well shown in Fig. 3. The average increment is 189 per CH_2 group, slightly less than the average of 195 for several series reported by Rao.[2] Assuming the experimental data used by Rao to be as accurate as the data given here, the change from 195 to 189 appears significant and indicates the constant is constitutive as well as additive.

Included in Table II are values of the adiabatic compressibility calculated by means of the relation

$$V=1/(\rho\beta_{ad})^{\frac{1}{2}},$$

where V is the ultrasonic velocity, ρ is the density, and β_{ad} is the adiabatic compressibility. Values of β_{ad} were converted from cm^2/dyne to atmospheres^{-1} by use of the factor 1,013,000 ($13.590\times76\times980.66$), although g at the location of the experiment was 979.524 cm sec.$^{-2}$.

The CH_2 increments in the molecular refractivities listed in Table II vary more than those of the sound velocity. The average value of 4.620 is in good agreement, however, with the 4.618 proposed by Eisenlohr.[7]

ACKNOWLEDGMENTS

One of us (R.T.L.) wishes to acknowledge support of this work by the Georgia Academy of Science and the Research Corporation. It is also a pleasure to mention that William Woolf and John Evans assisted in the measurements.

[7] F. Eisenlohr, Zeits f. physik. Chemie **75**, 585 (1910).