Physical Properties of Fatty Acid Methyl Esters. IV. Ultrasonic Sound Velocity

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Abstract

The ultrasonic sound velocity of the unsaturated fatty acid methyl esters from acetate to nonadecanoate, methyl oleate, linoleate, linolenate, and erucate have been measured at 20C and 40C in the liquid state. Data of the saturated compounds were correlated with the Smittenberg relation and a reasonable fit was noted. The molar sound velocity according to Rao was computed from the observed values and increments for the CH_2 group and for the double bond are presented.

Introduction

ALTHOUGH THE FIELD of ultrasonics is comparatively new, widespread technical and scientific applications are noted. The velocity of sound in a compound is closely related to many other physical properties, and knowledge of this magnitude has been expediently applied to the evaluation of otherwise more inaccessible values. Reviews on the applicability of ultrasonics to chemical and physical problems have been presented by Richards (18), Bergmann (2), Schaaffs (21), and others.

One of the major applications of ultrasonics in the field of thermodynamics is the derivation of the adiabatic compressibility. The velocity of a wave due to longitudinal vibrations in a liquid is expressed as

$$u^2 = 1/\beta_{ad}\, d = \kappa/\beta_{is}\, d \qquad [1]$$

the propagation taking place adiabatically and independent of the frequency. In this relation, u is the sound velocity, β_{ad} and β_{is} are the adiabatic and isothermal compressibilities of the liquid respectively, κ is the ratio of the specific heats at constant pressure and constant volume ($= C_p/C_v$, which is also equal to β_{is}/β_{ad}), and d is the density. The isothermal compressibility may be derived from relatively simple measurements. C_p, whose direct evaluation entails complicated calorimetric measurements, is now obtained from

$$C_p - C_v = T\,\alpha^2/\beta_{is}\, d \qquad [2]$$

where T is the absolute temp and α the coefficient of thermal expansion. Hence, measurement of the sound velocity, the isothermal compressibility, and the density at two different temp, permits calculation of both C_p and C_v.

There are almost no examples of the application of the sound velocity to structural problems in lipid chemistry. In the field of hydrocarbon analysis, however, a number of papers have been presented on this subject. From the data of pure hydrocarbons and by applying additive functions Geelen (7,8) derived a system in which the structural characteristics of a mineral oil fraction may be calculated from the specific sound velocity and the specific refraction. Use also was made of the percentage hydrogen and the average mol wt. The influence of different structural groups present in mineral oil fractions was also investigated. Cornelissen (5) and Boelhouwer (3) et al. have measured and correlated the sound velocity with other physical constants of mineral oil fractions. Without presenting a detailed physical explanation, graphs and mathematical relationships were proposed from the obtained data which were deemed applicable to uncontaminated oil fractions.

Experimental

Products. The compounds investigated are the saturated fatty acid methyl esters from acetate to nonadecanoate, methyl oleate, linoleate, linolenate, and erucate. Their preparation, purity, density, refractive index, and dispersion have been reported in previous communications (9,10,11).

Measurements. These have been carried out with a commercial interferometer of Steeg & Reuter, Bad Homburg, Germany. The liquid to be measured is placed in a small thermostatically controlled cylindrical container. On the flat bottom a quartz crystal is mounted which is connected to an a.c. generator adjusted at 2 megacycles. The inner surface of the measuring vessel is ribbed to prevent directed reflections. A metal reflector is placed in the liquid perpendicular to the path of the sound waves. It may be moved along the longitudinal axis of the container with the aid of a micrometer screw. If λ is the wavelength of the vibrations generated in the liquid, then at a certain height of the reflector the distance between the reflecting surface and the quartz crystal will be an integer number of ½ λ; a standing wave will result and the ensuing resonance is measured as a deflection on the micro-ammeter measuring the anode current.

By moving the reflector along a distance of exactly ½ λ either upwards or downwards the ammeter will deflect to a min and back again to a max value. The traveled distance is measured by the micrometer screw and the sound velocity is computed from

$$u = \lambda\nu \qquad [3]$$

where ν is the frequency of the vibrations.

For more accurate measurements, the micrometer is moved along a distance of 25–30 wavelengths, depending on the amt of liquid available. Six readings are generally taken and the average value possesses a standard deviation of 0.2–0.3 m/sec. Due to the possible presence of systematic errors and other factors the absolute standard deviation is appreciably higher. It is, therefore, sufficiently accurate to present the

TABLE I

Sound Velocity in Distilled Water

Author	Temp	In m/sec	Ref.
Heusinger	20C	1483.1	13
	40C	1529.3	
Brooks	20C	1483.11	4
Greenspan and Tschiegg	20C	1482.66	12
	40C	1529.18	

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TABLE II

Smittenberg Relation for Saturated Fatty Acid Methyl Esters

	n≧	20C	40C
u_∞	2	1671.03	1551.40
A		−8580.96	−6283.87
B		14.678	10.816
σ		6.364	6.596
u_∞	6	1581.33	1503.38
A		−4510.14	−4167.27
B		7.582	6.487
σ		0.59	0.65

data in integer m/sec. It will be noted that the sound velocity and the derived values in this paper have been given an additional decimal place for statistical considerations.

Calibration. For calibration purposes, distilled water is a substance which is easily available. The following values (Table I) are noted in the recent literature. We used 1483 m/sec at 20C and 1528.5 m/sec at 40C to calibrate our apparatus.

Temperature. Readings were carried out with calibrated thermometers. Temp control was within 0.02C at 20C and 0.1C at 40C.

Results. Except for a few members of the investigated compounds, there are no comparative data available in the literature. The reported values are often quite at variance with each other, probably because of the presence of impurities or systematic errors. The sound velocities of the saturated fatty acid methyl esters are included in Table III and those of the unsaturated members in Table V.

The Smittenberg Relation

The Smittenberg (22) relation

$$u = u_\infty + A/(B + n) \qquad [4]$$

can be applied to the sound velocity of homologous series. In this relation u_∞ is the limiting sound velocity, n the term number, A and B are constants. Geelen (7,8) has already investigated the applicability of this relation to the n-alkanes, n-alkenes-1, and the n-alkynes-1. The observed concurrence was, however, not excellent.

From the data of the saturated fatty acid methyl esters A,B, and u_∞ have been calculated by the method of the least squares without assuming any of these three magnitudes to possess a set value. Values have been computed for $n \geqslant 2$ (all members taken into consideration) and for $n \geqslant 6$ (only methyl caproate and higher). Numerical results show in Table II.

Comparison of the observed values and the predicted data obtained from the first set of values indicates the largest deviations to occur in the first members of the series. This phenomenon has already been noted and discussed before (10). The fact that a significantly better fit is obtained by using the latter set of values may unequivocally be confirmed by applying the Variance Ratio Test to these two sets of values. For our computations we will, therefore, only use the data obtained for $n \geqslant 6$.

TABLE III

Sound Velocity of Saturated Fatty Acid Methyl Esters

Compound	Sound vel. m/sec		Mol sound vel.	
	20C	40C	20C	40C
Acetate	1174.2	1083.4	836.9	838.0
Propionate	1189.0	1099.3	1019.7	1019.9
Butyrate	1202.5	1117.7	1209.1	1209.5
Valerate	1227.6	1145.6	1397.3	1397.2
Caproate	1250.0	1170.0	1585.6	1585.4
Oenanthate	1271.6	1193.6	1775.1	1775.0
Caprylate	1291.7	1215.1	1965.2	1965.1
Pelargonate	1308.5	1234.9	2155.0	2155.6
Caprate	1324.7	1251.8	2345.1	2346.0
Undecanoate	1339.9	1265.9	2535.8	2535.8
Laurate	1350.9	1277.6	2725.3	2725.5
Tridecanoate	1362.0	1288.5	2916.0	2915.2
Myristate	1372.3	1299.4	3106.2	3105.7
Pentadecanoate	1381.6	1309.6	3296.4	3296.0
Palmitate		1318.0		3486.3
Heptadecanoate		1325.5		3676.5
Stearate		1333.4		3867.0
Nonadecanoate		1340.6		4057.5

TABLE IV

Comparative Values of U_{CH_2}

Author	U_{CH_2}	From	Year	Ref.
Rao	195	Atomic increments	1941	17
Lagemann and Corry	194.65	Bond increments of n-alkanes	1942	14
Baccaredda and Pino	192	Radical increments	1951	1
Sakiadis and Coates	195	100 Different compounds	1954	20
Geelen	189–189.7	Higher members of n-alkanes	1956	7
This work	190.15			

Additivity and Sound Velocity

The most well-known additive functions of the sound velocity are those which have been developed by Schaaffs (21), Danusso (6), Wada (23), and Rao (17). Of these four relations only that of Rao has gained wide acceptance, because of the larger degree of accuracy which may be obtained not only for pure compounds but also for mixtures. Geelen (7) calculated the standard deviations of error between predicted and measured values for 28 binary mixtures and found the smallest deviations for the function of Rao. The standard deviation of the CH_2- increment of several homologous series have also been evaluated and the same conclusions have been obtained.

Rao's function

$$U_m = u^{1/3} V_m = \sum_i (z\,A)_i \qquad [5]$$

where V_m is the molar volume, A is the contribution of a certain section of the molecule, and z the number of these increments, is purely empirical. A rigorous physical background which could satisfactorily explain the additive behaviour is still lacking. The dimensions of the function are also rather peculiar. In practice this relation suffices admirably, and is, therefore, widely accepted. In analogy to other additive properties, this relation has been termed the M sound velocity (15), although objections have been presented to the use of their term (2,7).

In a strictly additive property this value may be evaluated from the atomic constituents. Application of the atomic increments originally proposed by Rao, however, does not yield satisfactory results. Bond increments, which were proposed by Lagemann and Corry (14), also were not always accurate. A deficit of both methods is clearly demonstrated in the comparison between branched and straight-chain isomers. The predicted values are the same, contrary to experimental evidence. To surmount this difficulty Baccaredda and Pino (1) introduced increments for radicals. In many cases application of their method does indeed result in a higher accuracy.

TABLE V

Sound Velocity of Unsaturated Fatty Acid Methyl Esters

Compound	Sound vel.		Mol sound vel.	
	20C	40C	20C	40C
Stearate[b]			3866.8	3866.8
Oleate	1407.7	1337.9	3801.6	3800.2
Linoleate	1418.8	1347.9	3732.1	3730.0
Linolenate[a]	1426.8	1356.7	3666.7	3664.8
Behenate[b]			4627.4	4627.4
Erucate	1428.3	1359.3	4560.7	4560.5

[a] Contains 27.5% *trans* double bonds.

[b] Included as reference compound to facilitate comparison.

TABLE VI

Molar Sound Velocities of Alkenes and Alkanes

Compound	u^{20}	d_4^{20}	U_m^{20}	Compound	u^{20}	d_4^{20}	U_m^{20}	U_F	Ref.
n-pentane	1029	0.62624	1163.1	n-pentene-l	1014	0.6405	1100.0	63.1	(7,19,25)
n-hexane	1100.5	0.65937	1349.2	n-hexene-l	1086.5	0.6732	1285.1	64.1	(7,19,25)
n-heptane	1153	0.68376	1536.6	n-heptene-l	1128	0.6970	1466.4	70.3	(7,19,16)
n-octane	1195	0.70252	1725.4	n-octene-l	1184	0.7149	1660.4	65.0	(7,19,16)
n-nonane	1229.5	0.71763	1914.6	n-nonene-l	1218	0.72922	1848.8	65.8	(7,19,16)
n-decane	1253.5	0.73005	2101.3	n-decene-l	1250	0.74081	2039.5	61.8	(16,19,25)

Saturated Fatty Acid Methyl Esters. The computed M sound velocities show in Table III. The M vol ($V_m = M/d$) have already been reported (9). The difference between two consecutive members is U_{CH_2}, the CH_2-increment. This value is not constant but dependent on the chain length. In this respect one is referred to the same problem in the molecular vol and to a smaller extent in the M refraction. For practical purposes, however, U_{CH_2} may be considered constant for methyl caproate and higher homologs.

For the investigated esters one may utilize the general expression

$$U_m = A + n\,U_{CH_2} \qquad [6]$$

where A is a constant and n is the term number.

Assuming U_{CH_2} to be constant, the regression equations have been computed for methyl caproate and higher homologs. Considering the relative magnitudes of A, U_{CH_2}, and the standard error of estimate, it appears that essentially the same regression coefficients are applicable for both temp. The averaged relation reads

$$U_m = 444.1 + 190.15\,n \qquad [7]$$

with a standard error of estimate of 0.37.

Table IV lists some comparative values of U_{CH_2} in the literature.

Limiting Values. The limiting value of the sound velocity may be obtained from the following relationships:

$$\lim_{n\to\infty} U_{sp} = \lim_{n\to\infty} U_m/M = \lim_{n\to\infty} (A + nU_{CH_2})/(B + 14.026\,n) = U_{CH_2}/14.026 = 13.557 \qquad [8]$$

The values of the limiting density have previously been reported as 0.85407 at 20C and 0.84225 at 40C (9). As $U_{sp} = u^{1/3}d$ the limiting sound velocity may be computed as 1552 m/sec at 20C and 1489 m/sec at 40C.

Geelen (7) obtained 1526 m/sec as the limiting value of the n-alkanes at 20C. The values obtained from the Smittenberg relation are 1581.3 and 1503.4 m/sec at 20C and 40C, respectively. These values are quite at variance with each other. It must be noted, however, that all these numbers have been obtained by extrapolating a relatively small number of terms to infinity. Small deviations within the error of measurement, especially in the higher homologs, will induce a large effect in the computed limiting value. The CH_2-increment has been computed as the statistical average from a limited number of terms assuming this value to be invariable in the investigated range. In the presence of a slight trend different limiting values will be obtained.

TABLE VII

Comparative Values of U_F

Author	U_F	From	Year	Ref.
Rao	75	Atomic increments	1941	(17)
Lagemann and Corry	65.7	Bond increments	1942	(14)
Sakiadis and Coates	75	100 Different compounds	1954	(20)
This work	65	Alkenes and alkanes		
	68	Fatty acid methyl esters		

Unsaturation. An estimate of the contribution of the ethylenic double bond, U_F, is obtained from the M sound velocities of the unsaturated compounds. These values show in Table V. Methyl stearate and methyl behenate have been included as reference. Their values have been obtained from the regression equation [Equation 7].

Because of the presence of *trans* double bonds in methyl linolenate, the difference between the M sound velocities of linoleate and linolenate is less than the preceding value. The *trans* modification results in an additional contribution to U_m thereby resulting in a value for methyl linolenate higher than the value expected for the all *cis* linolenate.

For comparison, the double bond increment also has been evaluated from literature data on the n-alkenes-1 and the corresponding alkanes. Values obtained show in Table VI.

The double bond contribution from the alkenes is considerably lower than the value obtained from the fatty acid methyl esters. It must be noted, however, that in the esters the unsaturation centers are situated in the middle of the chain, contrary to the place of the double bonds in the investigated alkenes. Secondly, the ester value has been obtained as the average of mono- and polyethenoic systems. However, the possible errors are large enough to assume no significant difference to exist between these two estimates. Comparative values of the increment of the double bond show in Table VII.

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