and by Green and Day[3]: 2-acetamido-5-nitrotoluene → 2-acetamido-5-nitrobenzoic acid → 2-amino-5-nitrobenzoic acid.

The 2-amino-5-nitrobenzoic acid was then oxidized with Caro's acid as follows:

2-Nitroso-5-nitrobenzoic Acid.—A solution containing 2.5 ml. of water and 10 ml. of sulfuric acid (sp. gr. 1.85) was cooled to 5°. To it was added 4.1 g. of 2-amino-5-nitrobenzoic acid, the mass being broken up with a glass rod. Then 10 ml. more of cold sulfuric acid was poured in, followed by 25 g. of powdered ammonium persulfate. When a uniform paste was obtained, 20 ml. of ice water was added, whereupon the aminonitrobenzoic acid dissolved. The solution was warmed to 40°, and was held at that temperature. A brown precipitate separated after thirty minutes. After one and one-half hours another 10 g. of ammonium persulfate was added, the solution now being allowed to come to room temperature and to stand overnight. Then 50 g. of cracked ice was added and after fifteen minutes the cold solution was filtered with gentle suction through hardened filter paper. The brown product was washed with ice water and, after being dried in warm air, weighed 3.61 g. No more product could be obtained by further diluting and chilling the filtrate. The unpurified acid was cream colored and melted with decomposition at 202°. For recrystalllization 1 g. was dissolved in 20 ml. of 50% ethanol and was chilled, 0.40 g. being recovered.

Anal. Equiv. wt., 0.2770 g. subs. neutd. 14.73 ml. of 0.0957 *N* sodium hydroxide to phenolphthalein end-point. Calcd. for $C_7H_4O_5N_2$: equiv. wt., 196. Found: equiv. wt. 196.6.

2-Nitro-5-nitrosobenzoic Acid.—For the synthesis of this acid a series of reactions corresponding to that given above was carried out: 3-aminotoluene → 3-acetamidotoluene → 3-acetamido-6-nitrotoluene → 3-acetamido-6-nitrobenzoic acid → 3-amino-6-nitrobenzoic acid. The 3-amino-6-nitrobenzoic acid was oxidized as has been described under 2-nitroso-5-nitrobenzoic acid. The sulfate was less soluble than that of 2-amino-5-nitrobenzoic acid, and was oxidized in more dilute solution. The crude, light brown product was recrystallized from dilute ethanol as follows: 1 g. was dissolved in 5 ml. of hot 95% ethanol and 12 ml. of hot water was added. After rapid filtration and cooling of the filtrate, 0.88 g. of 2-nitro-5-nitrosobenzoic acid, m. p. 270–270.5°, was filtered off.

Anal. Equiv. wt., 0.1270 g. subs. neutd. 6.11 ml. of 0.1058 *N* NaOH; 0.1737 g. subs. neutd. 8.42 ml. of 0.1058 *N* NaOH. Calcd. for $C_7H_4O_5N_2$: equiv. wt., 196. Found: equiv. wt., 196.6, 194.9.

Evaporation of the filtrates from the recrystallization yielded about 50 mg. of the nitrosonitro acid, and further evaporation to about 25 ml. yielded a light colored oil, which soon crystallized and proved to be 2,5-dinitrobenzoic acid.

Summary

By alkaline hydrolysis of 2,5-dinitrobenzoic acid either nitro group may be replaced by hydroxyl, giving rise to 2-hydroxy-5-nitrobenzoic acid, and to 5-hydroxy-2-nitrobenzoic acid. Gentisic acid seemed not to be formed. A brown oil also was isolated. This was a mixture probably of azo and hydrazo compounds, which were not identified.

Synthesis of 2-nitroso-5-nitrobenzoic acid and of 2-nitro-5-nitrosobenzoic acid showed these substances to be practically colorless and unlike the colored product formed by the action of alkali upon 2,5-dinitrobenzoic acid. Both nitroso acids were non-reactive toward the 2,5-aminonitrobenzoic acids.

BUFFALO 3, NEW YORK RECEIVED SEPTEMBER 23, 1947

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[3] Green and Day, THIS JOURNAL, **64**, 1167 (1942).

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. II.[1] The Alcohols[1a]

BY ALFRED WEISSLER

Although several investigators[2,3,4,5] have measured the velocity of sound in a variety of liquids, the application of their data to chemical problems has been relatively neglected.[6] Inasmuch as a sound wave is a mechanical impulse transmitted from molecule to molecule, one expects the properties of the molecule to affect the rate of transmission of this impulse.

The use of ultrasonic frequencies permits the apparatus to be of conveniently small size, yet still avoid earlier errors due to wall effect. At one kilocycle the wave length in many liquids is about one meter, while at one megacycle (the frequency employed in this investigation) the wave length is about one millimeter.

For the present work, thirty liquid alcohols were selected as a suitable group of compounds in which correlations could be made between sound velocity and chemical structure. Specifically, sound velocity is of interest in connection with molecular weight, molecular volume, adiabatic compressibility, and the ratio of specific heats.

Experimental

Each alcohol (of the highest purity commercially available from such sources as Eastman Kodak Co., Connecticut Hard Rubber Company, and Carbide and Carbon Chemicals Corporation) was fractionally distilled through a 40-cm. Widmer column shortly before using; the higher boiling compounds were fractionated at a reduced pressure of about 1 mm. A middle fraction of narrow boiling range was selected in each case.

Sound velocity measurements were made by means of

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[1] Part I, Weissler, Fitzgerald, and Resnick, *J. Appl. Phys.*, **18**, 434 (1947).

[1a] The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the navy service at large.

[2] Willard, *J. Acoust. Soc. Am.*, **19**, 235 (1947).

[3] Pellam and Galt, *J. Chem. Phys.*, **14**, 608 (1946).

[4] Parthasarathy, *Proc. Ind. Acad. Sci.* (*A*), **3**, 285, 482, 519 (1936); **4**, 59, 213 (1936).

[5] Bergmann, "Der Ultraschall," 3rd ed., Edwards Brothers, Ann Arbor, Mich., 1944, p. 174.

[6] See, however, (a) Freyer, Hubbard and Andrews, THIS JOURNAL, **51**, 759 (1929); (b) Kincaid and Eyring, *J. Chem. Phys.*, **6**, 620 (1938); Kittel, *J. Chem. Phys.*, **14**, 614 (1946).

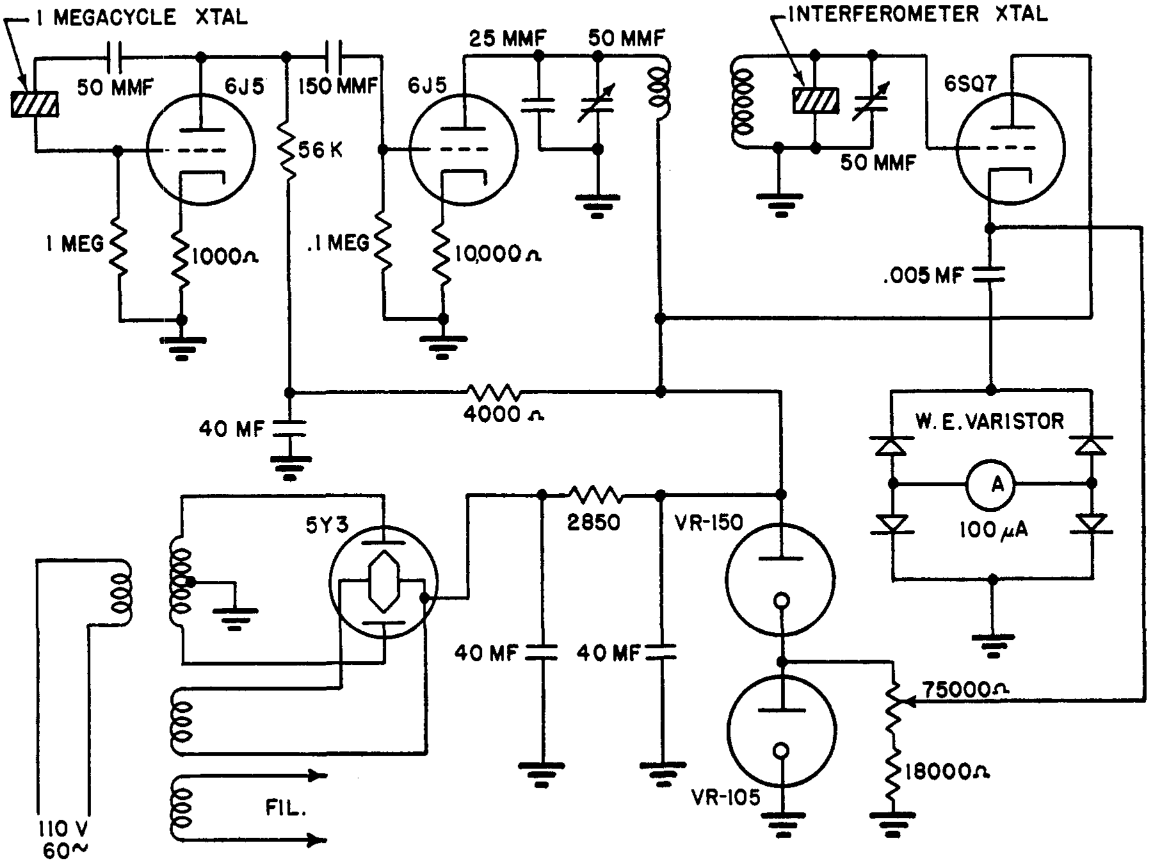

Fig. 1.—Circuit design for interferometer for one megacycle.

an ultrasonic interferometer of conventional type.[6a,7,8] As may be seen in Fig. 1, the circuit includes a power supply, crystal-controlled vacuum-tube oscillator of one megacycle frequency, r. f. amplifier, and microammeter for measuring the current through the interferometer crystal. This latter crystal is the quartz piezoelectric transducer which changes the oscillations from electrical to mechanical.

Figure 2 is a sectional view of the brass interferometer cell, diameter 7 cm. and height 11 cm., immersed in a temperature controlled (±0.05°) oil-bath. The cell contains the liquid to be measured, a sensitive thermometer, a manual stirrer for eliminating temperature gradients, the quartz crystal source of ultrasound, and a movable reflecting plate of nickel-plated brass. As the reflector is moved vertically through the liquid by the micrometer head, cyclical variations in the ultrasonic standing wave pattern recur at distances of integral half-wave lengths: depending on its distance from the source, the reflector will sometimes be at a node of the transmitted wave, sometimes at an anti-node. This causes corresponding cycles in the current through the interferometer crystal, which are observed on a suitable microammeter. The micrometer-head travel required for an interval of two current maxima, then, is equal to the wave length; and the velocity of sound is of course the product of this wave length and the frequency. In practice, one uses an interval of twenty maxima, which makes possible a precision of a few hundredths of one per cent.

Although the instrument described requires about 350 ml. of liquid for a measurement, a new three-megacycle interferometer now in use at this Laboratory requires only 15 ml. of sample.

Results and Discussion

The velocity of sound at 30° in each of these thirty alcohols is listed in Table I, together with the density and refractive index. It is apparent that sound velocity increases (but not linearly) with molecular weight in this series,[9] and that it decreases as the molecule becomes more highly branched. A saturated or unsaturated ring, however, causes a considerable increase in velocity.

Also shown in this table are the molar refraction and molar sound velocity of each alcohol. As expected, the observed refractions agree well with those calculated by summing Denbigh's bond refractions,[10] particularly in the absence of extensive branching. The deviation exceeds 1% only in the case of furfuryl alcohol; such anomalous behavior has previously been reported for the furans.[11]

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(7) Pierce, *Proc. Am. Acad.*, **60**, 269 (1925).

(8) Klein and Hershberger, *Phys. Rev.*, **37**, 760 (1931).

(9) Rao, *J. Chem. Phys.*, **9**, 682 (1941), reveals greater irregularities in other series.

(10) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(11) Fajans in "Physical Methods of Organic Chemistry," A. Weissberger, ed., Interscience Publishers, New York, N. Y., 1945, p. 677.

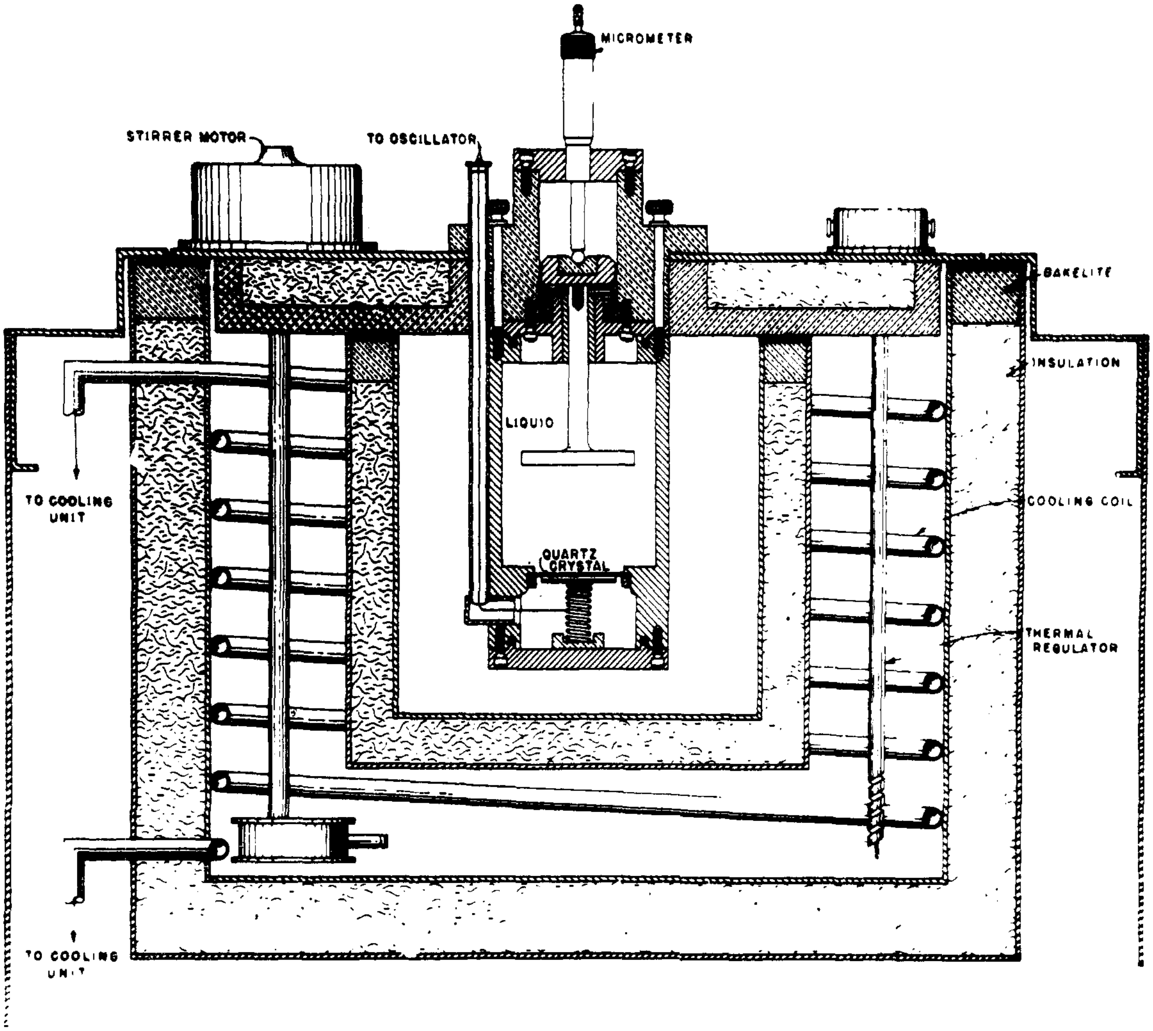

Fig. 2.—Ultrasonic interferometer immersed in thermoregulated oil-bath.

Molar Sound Velocity.—M. R. Rao has proposed[9] the following empirical constant involving sound velocity

$$R = v^{1/3}M/d \qquad (1)$$

where M is the molecular weight, v the sound velocity, d the density, and R may be called the molar sound velocity. For each pure liquid (except a few such as water) R is invariant with respect to temperature. Further, like the other forms of molar volume it is an additive and constitutive property, and is therefore quite analogous to molar refraction except that a theoretical explanation for its constancy has not yet been adduced. An empirical function (the cubic root of sound velocity) which decreases slightly with increasing temperature is used here as a means of correcting the molar volume for thermal expansion. It should be pointed out that R is relatively insensitive to the intermolecular forces which determine the compressibility, since it is inversely proportional to the sixth root of the compressibility.

The observed molar sound velocities computed from equation (1) are compared in Table I with the values calculated by summing Lagemann's bond increments[12] for R. The average deviation is seen to be about 2%, but it is notable that nearly all the errors are in the same direction. This, together with the greater precision of the present measurements, suggests the desirability of a revision of the increment values. For example, changing the R increment for $-CH_2-$ from 195 to 190 would reduce the average deviation to a few tenths of a per cent.

A comparison between the velocity of light (*i. e.*, refractive index) and the velocity of sound is illuminating. Both yield information on the size, shape, and functionality of molecules: the velocity of sound is determined by the distance and elastic forces between them, while the velocity of light depends on their electrical and magnetic characteristics. Both properties can be readily

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[12] Lagemann and Dunbar, *J. Phys. Chem.*, **49**, 428 (1945).

TABLE I

SOME PROPERTIES OF ALCOHOLS AT 30°

Alcohol	Sound velocity, meters per second	Density$^{30}_{4}$	n_D	Molar sound velocity Obs.	Molar sound velocity Calcd.	Molar sound velocity Deviation, %	Molar refraction Obs.	Molar refraction Calcd.	Molar refraction Deviation, %
Methyl	1088.9	0.7816	1.3258	421.7	419.1	+0.63	8.27	8.31	−0.48
Ethyl	1127.4	.7809	1.3578	614.0	613.8	+0.04	12.95	12.94	+ .08
n-Propyl	1193.2	.7966	1.3821	800.2	808.4	−1.02	17.56	17.57	− .06
n-Butyl	1225.3	.8018	1.3956	989.2	1003.0	−1.38	22.19	22.20	− .05
n-Amyl	1254.8	.8089	1.4075	1175.4	1197.7	−1.86	26.85	26.83	+ .07
n-Hexyl	1288.6	.8124	1.4150	1368.6	1392.3	−1.70	31.49	31.46	+ .10
n-Octyl	1331.9	.8182	1.4260	1751.0	1781.6	−1.72	40.78	40.72	+ .15
n-Decyl	1363.8	.8233	1.4340	2131.8	2170.9	−1.80	50.06	49.98	+ .16
n-Dodecyl	1388.0	.8269	1.4400	2513.6	2560.2	−1.82	59.39	59.24	+ .25
Isopropyl	1125.2	.7779	1.3732	803.5	808.4	−0.60	17.61	17.57	+ .23
Isobutyl	1176.5	.7950	1.3921	984.3	1003.0	−1.87	22.21	22.20	+ .05
s-Butyl	1196.8	.7983	1.3932	985.8	1003.0	−1.72	22.17	22.20	− .14
t-Butyl	1101.6	.7756	1.3825	987.0	1003.0	−1.60	22.27	22.20	+ .32
Isoamyl	1220.4	.8028	1.4038	1173.3	1197.7	−2.03	26.84	26.83	+ .04
t-Amyl	1180.4	.8029	1.4001	1160.2	1197.7	−3.13	26.62	26.83	− .78
2-Methylbutyl	1225.3	.8061	1.4055	1170.1	1197.7	−2.31	26.83	26.83	.00
Pentanol-3	1223.7	.8099	1.4058	1164.1	1197.7	−2.81	26.72	26.83	− .41
2-Ethylbutyl	1277.0	.8227	1.4174	1347.3	1392.3	−3.23	31.26	31.46	− .64
4-Methylpentanol-2	1201.3	.8003	1.4087	1357.0	1392.3	−2.54	31.54	31.46	+ .25
Heptanol-2	1266.8	.8098	1.4172	1552.5	1587.0	−2.17	36.10	36.09	+ .03
2,4-Dimethylpentanol-3	1241.1	.8192	1.4189	1524.5	1587.0	−3.94	35.81	36.09	− .78
5-Ethylnonanol-2	1326.5	.8267	1.4362	2290.3	2365.6	−3.19	54.52	54.61	− .16
Benzyl	1508.2	1.0375	1.5363	1195.2	1199.6	−0.37	32.51	32.55	− .12
β-Phenylethyl	1512.6	1.0122	1.5283	1385.3	1394.3	−0.64	37.18	37.18	.00
γ-Phenylpropyl	1523.3	0.9938	1.5231	1576.7	1588.9	−0.77	41.87	41.81	+ .14
Cyclohexanol	1448.3	0.9411	1.4629	1204.1	1206.2	−0.18	29.31	29.33	− .07
Furfuryl	1433.6	1.1238	1.4801	984.3	945.0	+4.16	24.80	25.53	−2.86
Tetrahydrofurfuryl	1467.8	1.0455	1.4490	1110.2	1076.3	+3.15	26.20	26.47	−1.02
Allyl	1215.5	0.8432	1.4090	735.1	742.7	−1.03	17.03	17.10	−0.41
Ethylene glycol	1643.5	1.1068	1.4290	661.8	652.0	+1.50	14.49	14.49	0.00

measured in liquids with an accuracy of five significant figures. In sharp contrast to optical dispersion, sound velocity in liquids does not vary appreciably with frequency, but its relative change with temperature is five to ten times greater than that of refractive index. After thermal equilibrium is established, interferometric determination of the sound velocity requires less than five minutes, but the relatively large sample needed is a disadvantage. For ordinary liquids, the range of sound velocity encountered is 0.8 to 2.0 × 10^5 cm./sec., compared to the refractive index range of 1.3 to 1.8.

Determination of Molecular Weight.—Within a homologous series of liquids, linear relationships exist[12] between any two of several molar constants such as molar sound velocity, molar refraction, parachor and molar viscosity.[13] An example of such a relation is the one involving refraction and sound velocity

$$R = AN + B \qquad (2)$$

where A and B are, respectively, the slope and intercept. Upon substitution of the definitions of R and N, this yields an expression for the molecular weight

$$M = \frac{Bd}{v^{1/3} - A\left(\frac{n^2 - 1}{n^2 + 2}\right)} \qquad (3)$$

in terms of the two "series" constants A and B and the observed sound velocity, density and refractive index. One expects the slope A to be nearly the same for all homologous series, because the difference between successive members is always $-CH_2-$.

In Figure 3 the above-mentioned linearity is verified for the normal primary alcohols up to dodecyl, the highest member which is liquid at room temperature. The slope A of this line is 40.92, and the vertical intercept B is 82.50. Even the branched compounds lie very nearly on the same line,[14] while for the ω-phenylalkanols the slope

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(13) Souders, THIS JOURNAL, 60, 154 (1938).

(14) Dr. Richard K. Cook of the National Bureau of Standards has pointed out that such a result is not surprising, inasmuch as both variables plotted include the factor M, which changes much more rapidly than v, n or d. For a more sensitive test of the linearity, he suggests rearranging equation (3) to

$$\frac{A}{v^{1/3}}\left(\frac{n^2 - 1}{n^2 + 2}\right) + \frac{Bd}{Mv^{1/3}} = 1$$

the graph of which shows appreciable deviations from a straight line,

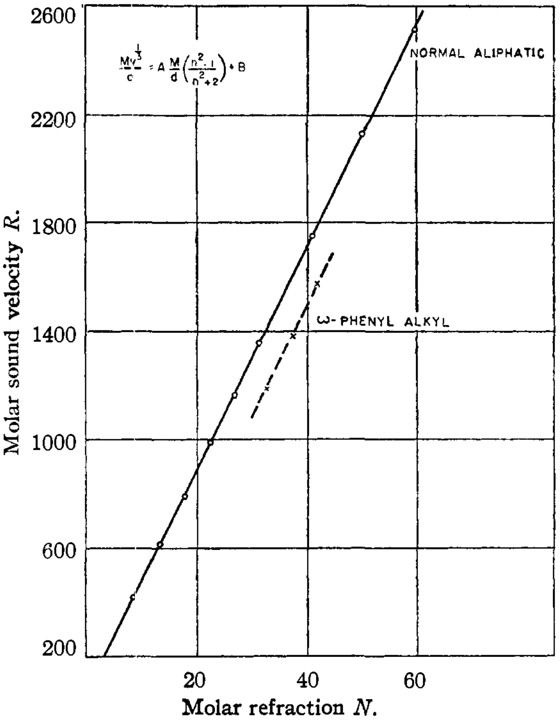

Fig. 3.—Linear relation between molar refraction and molar sound velocity, for primary alcohols.

is exactly the same but the intercept is −136.0.

Using the above values for A and B, the molecular weights of the aliphatic alcohols were computed from equation (3). It is evident from Table II that the average error is only 2% for the primary normal members, but is considerably greater where extensive branching occurs. For the three phenylalkanols, taking B as −136, the average error is only 0.3%.

From one point of view, this method may be considered as a determination of molecular weight through linear interpolation or extrapolation, by means of a suitable combination of physical properties.[15] (The molecular weight is not in general a linear or necessarily even a single-valued function of a single physical property.) Volatility or solubility of the liquid is not required, in contrast with other methods.

Because of the association of alcohols, one might suppose that the molecular weights found should be appreciably higher than the theoretical. However, the constants A and B automatically include any correction of this nature which might be involved.

Estimation of van der Waals *b*.—Sound velocities in liquids have been used by Schaafs[16] to estimate the size of molecules, through the value of b in the van der Waals equation of state. According to kinetic theory, this quantity represents four times the actual volume of the molecules in one mole of a fluid in thermal motion.

TABLE II

DETERMINATION OF MOLECULAR WEIGHT BY THE SOUND VELOCITY METHOD

$$M = \frac{82.50d}{v^{1/3} - 40.92\left(\frac{n^2-1}{n^2+2}\right)}$$

Alcohol	Molecular weight Theoretical	Found	Error, %
Methyl	32.04	31.67	− 1.15
Ethyl	46.07	45.15	− 2.00
n-Propyl	60.09	60.74	+ 1.08
n-Butyl	74.12	75.34	+ 1.64
n-Amyl	88.15	94.92	+ 7.68
n-Hexyl	102.17	105.54	+ 3.30
n-Octyl	130.22	130.31	+ 0.07
n-Decyl	158.28	156.86	− 0.90
n-Dodecyl	186.33	184.38	− 1.05
Isopropyl	60.09	59.75	− 0.6
Isobutyl	74.12	80.87	+ 9.1
s-Butyl	74.12	77.75	+ 4.7
t-Butyl	74.12	80.58	+ 8.7
Isoamyl	88.15	96.83	+ 9.8
t-Amyl	88.15	102.54	+16.3
2-Methylbutyl	88.15	100.61	+14.1
Pentanol-3	88.15	102.96	+16.8
2-Ethylbutyl	102.17	123.41	+20.8
4-Methylpentanol-2	102.17	126.98	+24.3
Heptanol-2	116.20	127.25	+ 9.5
2,4-Dimethylpentanol-3	116.20	156.45	+34.6
5-Ethylnonanol-2	172.30	235.98	+37.0
Benzyl[a]	108.13	108.80	+ 0.62
β-Phenylethyl[a]	122.16	122.16	0.00
γ-Phenylpropyl[a]	136.19	135.70	− 0.36

[a] For these compounds, the value of B in equation (3) is −136.0.

Solving the van der Waals equation for the pressure, and substituting M/d for V, gives

$$P = \frac{RT}{M/d - b} - \frac{d^2 a}{M^2} \qquad (4)$$

If one differentiates this with respect to density, remembers that the square of sound velocity is equal to the derivative of pressure with respect to density, and accepts certain approximations made by Schaafs, the result is:

$$b = \frac{M}{d} - \frac{RT}{v^2 d}\left[(1 + Mv^2/3RT)^{1/2} - 1\right] \qquad (5)$$

This method for obtaining b is much easier than the customary evaluation from the critical data; nevertheless, it is sometimes considered unreliable and caution is required in its use. First, the concept of b is not defined with high precision[17]; it is not constant over a range of temperatures and pressures, and different methods for measuring it give divergent results. Thus, the values obtained from equation (5) and listed in Table III show only fair agreement with such

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[15] It has recently been shown by E. L. Warrick, THIS JOURNAL, 68, 2455 (1946), that molecular weight within a polymer-homologous series can be determined from the refractive index alone, without using an additional property such as sound velocity.

[16] Schaafs, *Z. Physik*, **114**, 110, 251 (1939); **115**, 69 (1940).

[17] Slater, "Introduction to Chemical Physics," McGraw-Hill, New York, N. Y., 1939, pp. 186, 408.

other values as one-third of the critical volume, or four times the molar refraction (Table I). Second, certain assumptions were employed in the derivation of equation (5), for example that the van der Waals equation of state is applicable to liquids, and that the partial derivative of b with respect to density is equal to $2M/3d^2$.

TABLE III

ADDITIONAL PROPERTIES OF ALCOHOLS AT 30°

Alcohol	van der Waals b, ml. per mole	Adiabatic compressibility, 10^{-12} sq. cm. dyne^{-1}		Ratio of specific heats
		Present work	Other investigators	
Methyl	37.0[a]	107.90	108.6,[b] 107.75,[c] 108.2[d]	1.198
Ethyl	54.0[a]	100.75	100.5,[b] 100.86,[c] 99.7[d]	1.188
n-Propyl	69.9[a]	88.17	89.4[b]	1.180
n-Butyl	86.2	83.07	84.4[b]	1.178
n-Amyl	102.2	78.52		
n-Hexyl	118.6	74.13		
n-Octyl	151.1	68.89		
n-Decyl	183.5	65.30		
n-Dodecyl	215.9	62.77		
Isopropyl	71.3	101.54	100.6[b]	1.178
Isobutyl	86.8	90.88	91.2[b]	1.166
s-Butyl	86.5	87.46		
t-Butyl	88.6	106.25		
Isoamyl	102.9	83.63	84.9[b]	1.157
t-Amyl	102.7	89.38		
2-Methylbutyl	102.5	82.62		
Pentanol-3	102.0	82.45		
2-Ethylbutyl	117.0	74.54		
4-Methyl-pentanol-2	120.0	86.58		
Heptanol-2	135.6	76.95		
2,4-Dimethyl-pentanol-3	133.9	79.25		
5-Ethyl-nonanol-2	199.1	68.75		
Benzyl	99.1	42.37		
β-Phenylethyl	115.1	43.18		
γ-Phenyl-propyl	131.0	43.36		
Cyclohexanol	100.9	50.66	50.3[e]	
Furfuryl	82.6	43.30		
Tetrahydro-furfuryl	92.7	44.39		
Allyl	61.8	80.27	80.8[b]	1.192
Ethylene glycol	52.9	33.45	34.0[b]	1.130

[a] Values of $b = V_c/3$ for these alcohols are 39.3, 55.7, and 73.4, respectively (I. C. T.). [b] Shiba, *Sci. Pap. Inst. Phys. Chem. Research* (*Tokyo*), **16**, 205 (1931). [c] Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914). [d] Fryer, Hubbard and Andrews, THIS JOURNAL, **51**, 759 (1929). [e] Bhagavantam and Rao, *Proc. Ind. Acad. Sci.*, **9A**, 312 (1939).

The additivity of b is demonstrated for the primary normal alcohols in Fig. 4. The values for branched isomers show small changes, but ring compounds of comparable molecular weight exhibit a considerable decrease. Inasmuch as the sound velocity term in equation (5) represents a relatively small correction to the molar volume term, the linearity in Fig. 4 correlates with the familiar additive character of the molar volume.

Determination of Adiabatic Compressibility.—From acoustic theory, the velocity of sound in a medium is

$$v = (1/K_{ad}d)^{1/2} \qquad (6)$$

where K_{ad} is the adiabatic compressibility. The pressure changes which occur during the propagation of a sound wave are so rapid as to prevent heat flow to and from the surroundings.

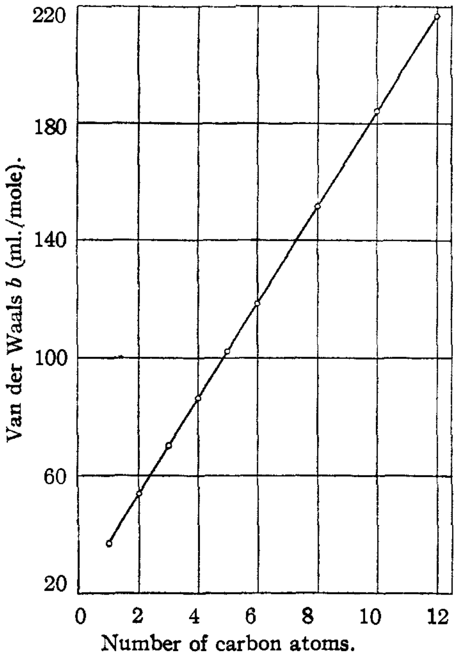

Fig. 4.—Additivity of van der Waals b, for primary normal alcohols.

Table III lists the adiabatic compressibilities of the alcohols, calculated from sound velocity and density as indicated in equation (6). The results agree well with those obtained (mainly from mechanical piezometers) by other investigators. It is apparent that K_{ad} decreases with molecular weight, increases with branching, and is small for ring compounds. The plot of K_{ad} against number of carbon atoms on log–log paper (Fig. 5) reveals more quantitative relations. From the slopes of these lines, adiabatic compressibility is found to be approximately a function of the inverse fourth root of the number of carbons in the molecule, for primary normal alcohols. For iso alcohols, it depends on the inverse 2.6th root; and for tertiary, on the inverse 1.3rd root. The reciprocals of these exponents are in the ratio 3:2:1

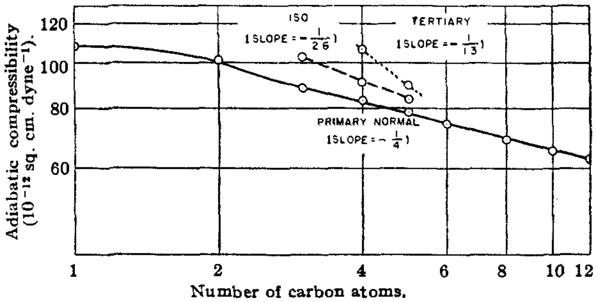

Fig. 5.—Adiabatic compressibility of aliphatic alcohols.

for the cases of no branching, single branching and double branching, respectively, but the precise significance of this result is not apparent.

The compressibility of the methanol molecule estimated from bond force-constants is about 1/1000 as large as the observed compressibility. This indicates that it is the space between the molecules which is compressed, rather than the molecules themselves.

The adiabatic compressibility is of interest in thermodynamics. For example, the ratio of isothermal to adiabatic compressibilities is equal to the ratio of specific heats

$$K_{is}/K_{ad} = c_p/c_v = \gamma \qquad (7)$$

The isothermal compressibility can be obtained either from static measurements or from

$$K_{is} = K_{ad} + T\alpha^2/c_p d \qquad (8)$$

where T is the absolute temperature, α the coefficient of thermal expansion, and c_p the heat capacity at constant pressure.

Sufficient data are available[18] in several cases for calculating[19] the ratio of specific heats from equations (7) and (8). The results in Table III show that γ decreases slightly as the complexity of the molecule increases, as expected because of the larger number of degrees of freedom.

Acknowledgments.—The author is indebted to Dr. G. R. Ringo for many stimulating discussions, to Dr. H. W. Carhart for samples of several of the alcohols, and to The Quaker Oats Company for samples of furfuryl and tetrahydrofurfuryl alcohols.

Summary

The velocity of sound at 30° has been measured in thirty liquid alcohols, using a one-megacycle ultrasonic interferometer. Densities and refractive indices at 30° are also reported.

To illustrate the applicability of sound velocities in chemical studies, these data have been used to calculate molecular weight, van der Waals b, adiabatic compressibility, and the ratio of specific heats. The compressibility has been correlated semi-quantitatively with molecular structure.

The analogy between molar sound velocity and molar refraction has been discussed.

RECEIVED AUGUST 25, 1947

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[18] Shiba, *Sci. Pap. Inst. Phys. Chem. Research (Tokyo)*, **16**, 205 (1931).

[19] It is necessary to avoid using the large body of isothermal compressibility data which has been determined for high pressures, because the excess pressure attained in the ultrasonic interferometer is only a very small fraction of an atmosphere.

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The Accuracy of Estimation of Hydrogen Peroxide by Potassium Permanganate Titration

BY CHARLES E. HUCKABA[1a] AND FREDERICK G. KEYES[1b]

Introduction

The usual method for analyzing aqueous solutions of hydrogen peroxide is by titration in acid solution with a standard solution of potassium permanganate. However the complete reliability of this method for very accurate determinations has been questioned, because of some doubt as to the optimum conditions for carrying out the titration.

A search of the literature revealed varying recommendations as to the proper sulfuric acid concentration, and some uncertainty as to the rate of addition of the permanganate to the peroxide solution. For example, if the rate of addition is too great, some manganese dioxide may be formed due to a local depletion of acid in the solution and bring about catalytic decomposition of a portion of the peroxide.

There are three possible methods for carrying out the determinations of hydrogen peroxide: titration, colorimetry and decomposition. Titration methods using the following reagents have been described in the literature[2]: potassium permanganate, ceric sulfate, potassium iodide–sodium thiosulfate, sodium arsenite and titanium trichloride. However in each case there has been observed either disagreement regarding the best procedure for performing the titration, or uncertainty as to the reliability of the method. The colorimetric method is applicable only for detecting a few parts per million of peroxide.

The method based on the decomposition of the peroxide with a suitable catalyst followed by measuring the amount of oxygen evolved would appear in principle to combine simplicity and reliability. The reaction occurs as follows

$$2H_2O_2 \xrightarrow{\text{catalyst}} 2H_2O + O_2$$

There are no known side reactions to introduce error as is present in some of the titration procedures.

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[1] (a) Results recorded in this article are from a thesis submitted as partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at the Massachusetts Institute of Technology; (b) Department of Chemistry, Massachusetts Institute of Technology.

[2] J. S. Reichert, S. A. McNeight and H. W. Rudel, *Ind. Eng. Chem., Anal. Ed.*, **11**, 194 (1939). This paper surveys the titration procedures for peroxide to date.