tion of a number of new sulfides and a greatly improved method for the preparation of *t*-butyl sulfide are described.

Considerable optical interaction is observed when the sulfide function is attached to a benzene ring or to a carbon atom bearing a carbonyl, carbalkoxyl, phenyl, vinyl or alkylmercapto group. The apparent conjugative effect of the sulfide function in these compounds is not destroyed by alkylation of the central carbon atom, but when two methylene groups intervene between the functional groups, the absorption spectra are essentially summations of the spectra of the component chromophores.

An attempt is made to account for the interaction of the sulfide function with a second similar function or with an unsaturated group attached to the same carbon atom by assuming the formation of three-membered rings stabilized by resonance among forms in which sulfur has an expanded valence shell.

PHILADELPHIA, PENNSYLVANIA RECEIVED MARCH 5, 1948

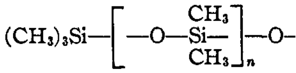
[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. III.[1] Linear Polymethylsiloxanes[2]

BY ALFRED WEISSLER

Certain aspects of the relation between molecular structure and sound velocity in liquids may be studied by means of a polymer series. This has already been done (using four or five members of each series) in the cases of the polyethylene glycols,[3] polychlorotrifluoroethylene,[4] and polyisobutylenes.[5] The last is of special interest because it was in highly viscous polyisobutylenes that Mason found the first unquestionable example of sound velocity dispersion in liquids.

A polymer series in which the liquid state persists up to high molecular weights is the linear polydimethylsiloxanes,[6,7] of type formula



$$(CH_3)_3Si-\left[-O-\underset{CH_3}{\overset{CH_3}{Si}}-\right]_n-O-Si(CH_3)_3$$

where *n* may vary from zero up to several hundred. These materials offer an opportunity for more extensive investigations than the three series mentioned above, where members of moderate molecular weight are already solids. In the present work, the velocity of sound, density and refractive index (D light) at 30° were measured for fourteen linear polydimethylsiloxanes, and the results were used to calculate adiabatic compressibility, ratio of specific heats and molecular weight.

Experimental

The polymers used were those sold by Dow Corning under the name Silicone Fluids DC 500 and 200, viscosity grades from 0.65 to 1000 centistokes. Higher members are polymerization mixtures with the volatiles removed, but the first four fluids are chemical individuals—the dimer, trimer, tetramer and pentamer, respectively. A few measurements were also made on two partially phenylated polymethylsiloxane fluids, of the DC 700 and 702 series.

Sound velocity in these liquids was measured by means of the one-megacycle ultrasonic interferometer previously described.[1] Refractive indices were determined with an Abbe refractometer.

Results and Discussion

The values of sound velocity listed in Table I are lower than for most organic liquids, except that replacing methyl groups by phenyls raises the velocity, as in the 700 and 702 fluids. Figure 1 is a semilogarithmic plot of the data, which shows

TABLE I

PHYSICAL PROPERTIES OF LINEAR POLYMETHYLSILOXANES (DOW CORNING SILICONE FLUIDS)

Fluid	Velocity (meters/sec.)		Temp. coeff. (meters/second/degree)	Refractive index (D)	Density, g./ml.
	at 30.0°	at 50.7°			
DC 500–0.65 cs	873.2	795.3	−3.8	1.3724	0.7535
1.0	901.3	828.5	−3.5	1.3810	.8114
1.5	919.0	849.8	−3.3	1.3856	.8434
2.0	931.3	863.0	−3.3	1.3883	.8652
3.0	942.2	875.2	−3.2	1.3916	.8874
5.0	953.8	892.1	−3.0	1.3943	.9083
10	966.5	909.4	−2.8	1.3972	.9295
20	975.2	918.0	−2.8	1.3992	.9423
50	981.6	925.3	−2.7	1.4007	.9540
200–100	985.2	929.6	−2.7	1.4015	.9579
200	985.7	931.5	−2.6	1.4017	.9611
350	986.2	932.0	−2.6	1.4018	.9628
500	986.4	932.1	−2.6	1.4019	.9632
1000	987.3	933.3	−2.6	1.4020	.9636
702–27	1236.4				
700–50	1054.0				

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[1] Weissler, Part II, THIS JOURNAL, **70**, 1634 (1948).

[2] 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.

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

[4] Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

[5] Mason, Baker, McSkimin and Heiss, *Phys. Revs.*, **73**, 1074 (1948).

[6] Hunter, Warrick, Hyde and Currie, THIS JOURNAL, **68**, 2284 (1946).

[7] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

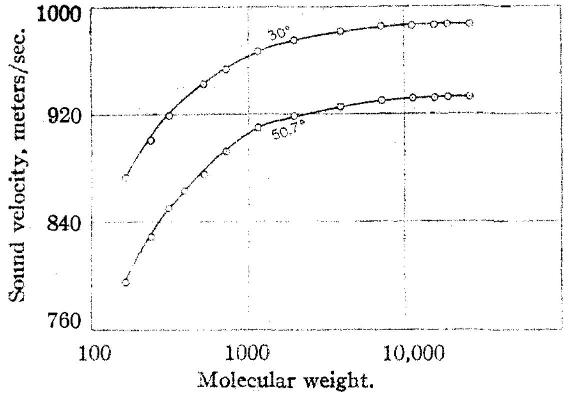

Fig. 1.—Sound velocity in the polydimethylsiloxane fluids.

that the velocity in polydimethylsiloxanes at first increases rapidly with molecular weight, but then levels off in the region of molcular weight 20,000. A similar leveling-off for the higher members is apparent in the refractive indices and densities.

Supplementary measurements at 50.7° showed that the rate of change of sound velocity with temperature decreases from -3.8 to -2.6 meters/second/degree as one goes from the lowest to the highest member (Table I). Such slopes are normal for liquids,[8] in contrast to the unusually flat viscosity–temperature slopes for which these silicone fluids are noted.

Adiabatic Compressibility.—From the sound velocity v and density d, the adiabatic compressibility K_{ad} is readily calculated by means of the equation

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

Table II reveals that the compressibilities so obtained are unusually high. This correlates with other characteristic properties of the silicones: low cohesive forces, low boiling points, and X-ray evidence[9] for large-amplitude oscillations of the methyl groups which sweep out umbrella-like surfaces.

The densities at 50.7°, required in eqn. (1), were computed with the aid of the thermal expansion coefficients supplied by the manufacturer.[10]

Ratio of Specific Heats.—The isothermal compressibility K_{is} can be calculated from the relation

$$K_{\text{is}} = K_{\text{ad}} + T\alpha^2/c_pd \qquad (2)$$

where T is the absolute temperature, α the coefficient of thermal expansion, and c_p the specific heat at constant pressure. The values of c_p at 30° for the first nine fluids were determined by electrical heating in a simple vacuum-bottle calorimeter,[11] with no attempt at high precision; they ranged from 0.45 calorie/gram for the 0.65 cs. fluid, to 0.39 calorie/gram for the 50 cs. fluid.

In Table II, the isothermal compressibilities calculated in this way are seen to be unusually high. A novel use of this property is in an aircraft landing gear developed in Great Britain, in which the spring action results from the compressibility of a silicone fluid.[12]

TABLE II

COMPRESSIBILITY OF LINEAR POLYMETHYLSILOXANES

Fluid	Adiabatic compressibility (10^{-12} sq. cm./dyne) at 30°	at 50.7°	Isothermal compressibility at 30° (10^{-12} sq. cm./dyne)	Ratio of specific heats
500–0.65 cs.	174.1	219.5	228.7	1.31
1.0	151.7	186.4	196.4	1.29
1.5	140.4	169.7	176.6	1.26
2.0	133.3	160.0	165.9	1.24
3.0	126.4	151.2	155.5	1.22
5.0	121.0	141.9	145.6	1.20
10	115.2	133.2	136.6	1.19
20	111.6	128.8	132.3	1.18
50	108.8	125.1	128.3	1.18
200–100	107.6	123.4		
200	107.1	122.5		
350	106.8	122.1		
500	106.7	122.0		
1000	106.5	121.7		
702–27	61.5			
700–50	91.3			

Also listed in Table II is the ratio of specific heats γ, which is equal to the ratio of isothermal to adiabatic compressibilities

$$\gamma = c_p/c_v = K_{\text{is}}/K_{\text{ad}} \qquad (3)$$

This ratio decreases monotonically as the molecular weight increases. Such a result is expected, because of the greater number of degrees of freedom in more complex molecules.

Molecular Weight.—An empirical method[3] for determining molecular weight M within a polymer series (from sound velocity, density, and refractive index n) utilizes the equation

$$M = \frac{Bd}{v^{1/3} - A\left(\frac{n^2 - 1}{n^2 + 2}\right)} \qquad (4)$$

where A and B are two empirical constants characteristic of the series. For the polydimethylsiloxanes, these constants were evaluated at 40.885 and 48.10, respectively.

Equation (4) yielded the molecular weights listed in Table III, which have an average accuracy[13] of 5% for the first twelve of the fluids. It is

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(8) Bergmann, "Der Ultraschall," 3rd ed., Edwards Brothers, Ann Arbor, Mich., 1944, p. 181.

(9) Roth, THIS JOURNAL, **69**, 474 (1947).

(10) Dow Corning Corporation, "New Engineering Materials—DC Silicones," Midland, Michigan, 1946, p. 6.

(11) Sturtevant, in "Physical Methods of Organic Chemistry," edited by A. Weissberger, Interscience Publishers, New York, N. Y., 1945, p. 365.

(12) T. K. Cordes, *Engineer's Digest*, March, 1946.

(13) The "theoretical" molecular weights are those kindly furnished by Dr. A. J. Barry of the Dow Chemical Co. in a personal communication. See also *J. Appl. Phys.*, **17**, 1020 (1946). Dr. Barry points out that his figures are not to be regarded as precise standards, because two fluids may have identical viscosities but different number average molecular weights, due to variations in polymerization technique.

evident that the results fall off in accuracy for values above about 15,000, because the computation then involves a very small difference between the two terms in the denominator of eqn. (4).

TABLE III

DETERMINATION OF MOLECULAR WEIGHTS OF POLYDIMETHYLSILOXANES BY THE SOUND VELOCITY METHOD

$$M = \frac{48.10d}{v^{1/3} - 40.855\left(\frac{n^2 - 1}{n^2 + 2}\right)}$$

Fluid	Theoretical molecular weight	Found molecular weight	Deviation, %
0.65 cs.	162.2	141.0	−13.1
1.0	236.3	233.7	− 1.1
1.5	310.4	316.9	+ 2.1
2.0	384.5	371.6	− 3.3
3.0	520	554	+ 6.5
5.0	720	753	+ 4.6
10	1,160	1,208	+ 4.1
20	1,970	1,971	+ 0.1
50	3,900	4,170	+ 6.9
100	7,100	7,680	+ 8.2
200	11,200	11,560	+ 3.2
350	15,800	15,440	− 2.3
500	19,000	23,100	+21.5
1000	26,500	23,200	−12.5

In a paper that came to attention after this work was completed, Warrick[14] has shown how similar results may be obtained from refractive index and density data alone.

Molar Sound Velocity Increments.—Just as in the familiar case of molar refraction, the molar sound velocity $R = v^{1/3}M/d$ of a compound may be calculated by summing the increments[15] for each atom in the molecule, or alternatively for each bond in the molecule. No velocity increment involving silicon has previously been reported. Using the present data on the first four polymers and a value of 95.2 for the C–H bond, the bond increment for silicon–carbon is here determined as 35.4, and that for silicon–oxygen as 61.5. These figures give truly additive molar sound velocities, in which the deviations from experimental values are only a few tenths of a per cent.

Attempts to calculate an atomic increment for silicon gave values of 129, 122, 120 and 117, respectively, for the first four liquids. A corresponding lack of constancy in the atomic *refraction* increments for silicon in these same compounds has been reported[14]; it was necessary to use *bond* refraction increments, again, in order to attain an additive system. This situation was tentatively attributed to wide variations in the ionic character of the bonds in organosilicon compounds.

Acknowledgment.—The assistance of Patricia E. Mortell in the measurements of sound velocity is hereby gratefully acknowledged.

Summary

The variation of sound velocity with molecular weight has been studied in a series of 14 polydimethylsiloxanes, at 30 and 50.7°. These fluids were found to possess remarkably high compressibilities.

Bond increments for the molar sound velocity have been determined for the silicon–carbon and silicon–oxygen bonds.

WASHINGTON, D. C. RECEIVED JULY 2, 1948

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[14] Warrick, THIS JOURNAL, 68, 2455 (1946).

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

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXVI. Effect of Addition Agents on the Conductance of Long Chain Salts[1]

BY GEORGE L. BROWN,[2] PHILIP F. GRIEGER[3] AND CHARLES A. KRAUS

I. Introduction

In previous papers of this series, it has been shown that the addition of methanol to aqueous solutions of long chain salts has marked effect on their properties in the critical region and at higher concentrations.[4]

The present study was undertaken for the purpose of determining the effect of additives in somewhat greater detail in order to ascertain the generality of the phenomena and some of the underlying factors that influence observed results. The present, like the several preceding investigations, has been exploratory in nature. A high precision is not claimed for the results; nevertheless, it is believed that, in the critical region, they are not seriously in error. Precision measurements in the dilute region are now under way in this Laboratory, and the results will be communicated in due course.

The effect of additions of methanol, isopropyl alcohol and *t*-butanol on the conductance of dodecylammonium chloride in water was measured at several concentrations of the additives.

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[1] This paper is based on a portion of a thesis presented by G. L. Brown in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1947.

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[4] Evers and Kraus, THIS JOURNAL, 70, 3049 (1948); Grieger and Kraus, *ibid.*, 70, 3803 (1948); see also Ward, *J. Chem. Soc.*, I, 522 (1939); *Proc. Roy. Soc.* (*London*), 176A, 412 (1940).