Sound Velocity and Chemical Constitution.

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INVESTIGATION on the measurement of sound velocity in liquids was, until 1923, a difficult problem for experimentation, on account of the large quantities of the liquid required and of many uncertain corrections involved therein. The measurements were made by the Kundt's tube method in the audio range, and naturally even for one wave-length, a large column of liquid was required. Sea-water and a few organic liquids formed the whole list of liquids investigated.

The subject took an entirely different turn when Langevin applied the piezo-electric property of quartz and electrical oscillating circuits to the production of high-frequency sound waves. One could then use smaller quantities of liquid and determine the nodes by a probing pin, noting the reaction in the circuit. Of the methods based on the use of the piezo-electric oscillator for the measurement of ultrasonic velocity in liquids we may mention four :—

(1) The acoustic interferometer invented by Pierce[1] and used amongst others by Freyer, Hubbard and Andrews[2] in the United States of America ; and by Boyle[3] and co-workers in Canada.

(2) The method of the diffraction of light by sound waves originated by Debye and Sears[4] in America and by Lucas and Biquard[5] in France ;

(3) The visibility method developed extensively by Hiedemann[6] and co-workers at Köln ;

(4) The periodicity phenomenon[7] first demonstrated almost simultaneously, and independently, by the author[8] and by O. Nomoto.[9]

Amongst these the method of Debye-Sears and of Lucas-Biquard is very simple, precise and rapid. When the author took up the investigation on the relation between sound velocity and chemical constitution data[10] for acoustic velocity in the audible range were availabale for hardly 20 organic liquids and no definite correlation could then have been made. He has now investigated over 125 organic liquids and has drawn some important conclusions therefrom. In this brief article an attempt is made to bring out all the salient points, but for greater details the original papers must be consulted.

1. Aromatic compounds have usually higher velocities than the aliphatics. For the former the range is 1300 m./s. and above at 25° C., while for the latter compounds 1300 m./s. is about the upper limit. Cyclohexane and its derivatives come midway.

2. As the length of the molecule increases, the velocity of sound also increases. This is amply borne out in the case of hydrocarbons,[11] alcohols and ketones, and also in compounds containing two bromine atoms, which are progressively separated, as shown in Table I.

TABLE I.

Liquids	Density	Velocity in m./s.
Alcohols—		
Methyl alcohol	0·792	1130
Ethyl	0·786	1207
Propyl	0·801	1234
Butyl	0·808	1315
Amyl	0·814	1347
Bromine compounds—		
CH_2Br_2	2·453	971
CH_2Br | CH_2Br	2·178	1014
CH_2Br | CH_2 | CH_2Br	1·977	1144

In the case of alcohols the velocity increases in spite of the density increasing, while in the bromine substituted compounds, the increase is regular for a regular diminution in density, which is as it ought to be.

However, esters form a class by themselves.

3. As remarked above, the esters show a diminution in velocity with increasing length of the alcohol radical. This is exemplified in Table II, where the velocities are given for various acetates.

TABLE II.

Liquids	Density	Velocity in m./s.
Methyl acetate	0·928	1211
Ethyl	0·899	1187
Propyl	0·884	1182
Butyl	0·872	1179
Amyl (iso)	0·874	1168

4. Introduction of a heavier atom into the molecule brings down the velocity. Methylene and ethylene halogen substituted compounds form such series where the difference can be easily noticed. It is also remarkable to note that the introduction of a greater number of the same heavy atom also tends to lower the acoustic velocity.

(*a*)	$CH_2 : Cl_2$	1064 m./s.
	$CH_2 : Br_2$	971 ,,
(*b*)	$CHCl_3$	1001 ,,
	$CHBr_3$	930 ,,
(*c*)	$CH_2 : Cl_2$	1064 ,,
	$CHCl_3$	1001 ,,
	CCl_2	928 ,,
(*d*)	$CHCl_2 \cdot CHCl_2$ ..	1155 ,,
	$CHBr_2 \cdot CHBr_2$ ..	1007 ,,

The velocities are comparable among themselves in each group, as the temperature difference is not above 0·5° C.

In the case of methylene iodide the velocity for which is 977·7 m./s. probably greater viscosity compensates for the lowering in velocity due to the iodine atom. There seems to be general agreement throughout.

5. Highly viscous liquids have greater velocities. For example, ethylene glycoll is more viscous than ethyl alcohol and has a higher velocity. Similarly, aniline, anisol, and acetophenone are examples of liquids having higher velocity than their parent compounds.

6. Among isomers, if isomerism is not of the optical kind, there is a difference in acoustic velocity. For example, the xylenes *a*- and *β*-picolines, butyl and *iso*-butyl alcohols show such differences. But the optical isomers, the *d*- and *l*-pinenes possess identical velocity.

7. Speaking of substitution, we may mention here that a methyl radical introduced into an ester or an ether, in place of an ethyl group raises the sound velocity. As examples, we give :

(*a*)	Ethyl chloracetate	1234 m./s.
	Methyl ,, ...	1331 ,,
(*b*)	*o*-Cresol ethyl ether	1315 ,,
	o-Cresol methyl ether.. ..	1385 ,,

Many other examples are given in the original papers.

8. It has been observed that usually the introduction of a double bond favours lowering of the acoustic velocity.

$CHCl = CHCl$ .. 1025 m./s. at 25°·5 C.
$CHCl_2 - CHCl_2$ .. 1155 m./s. at 28° C.

In spite of the fact that acetylene dichloride has only 2 chlorine atoms compared with acetylene tetrachloride, and a lower density it possesses a lower sound velocity. Other examples where it is shown that unsaturation lowers the velocity are allyl chloride and tetrachlorethylene.

9. Similarities in the behaviour of ethers and esters with respect to the sound velocity have been brought out clearly in the original papers which should be consulted for details.

10. It has been shown that molecules possessing an electric moment tend to show enhanced sound velocities. As examples, we give :—

(i)	Benzene	1310 m./s.	at 23° C.
	Nitrobenzene ..	1455 ,,	,, 28° C.
(ii)	Cyclohexane ..	1257 ,,	,, 23° C.
	Cyclohexanone ..	1441 ,,	,, 23°·5 C.

The above are the general findings on the relation between sound velocity and chemical constitution of organic liquids. These have been amply borne out in the investigations carried out by the author.

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[3] Boyle and co-workers, *Trans. Roy. Soc. Canada*, **17,** *et seq.*
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[5] Lucas and Biquard, *C. R.*, 1932, **194,** 2132 ; 1932, **195,** 121 ; and *Journ. de Phys. et la Rad.*, 1932, **3,** 464.
[6] Hiedemann, Asbach and Bachem, *Zeit. f. Physik*, **87, 442, 734** ; and subsequent volumes of *Zeit. Phys.*
[7] Winkelmann, *Ann. d. Phys.*, 1908, 27, 905.
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[8] Parthasarathy, *Proc. Ind. Acad. Sci.*, 1935 and 1936 ; *Curr. Sci.*, Nov., 1937.
[9] Nomoto, *Proc. Phys. Math. Soc., Japan*, 1936, **18,** 402.
[10] See *International Critical Tables*, Vol. VI.
[11] Bergmann and Jænsch, *Sitz. Ber. Schles. Ges. f. Vaterl Kultur*, 1936, **108,** 34.

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