INTERFEROMETRIC STUDIES OF LIGHT SCATTERING : HYPERSONIC VELOCITIES IN LIQUIDS

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Received May 11, 1942

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

One of the outstanding problems connected with the liquid state is the anomalous absorption of sound waves observed at the range of ultrasonic frequencies. Varied suggestions have been put forward (see Bergmann, 1938) to explain the phenomenon; but the one which demands the first consideration is that due to Kneser (1938). According to him, the abnormal increase of the absorption coefficient at high frequencies, which, in some cases, like benzene and chloroform, is about hundred-fold as much as is to be expected from classical considerations, is due to the lowering of the effective specific heat in a manner analogous to what is established for gases for the rapid periodic processes involved in ultrasonics. This would lead to a dispersion of sound velocity in the liquids in the frequency region at which the absorption coefficient shows the maximum anomaly. Numerous papers* have appeared in recent years dealing with this aspect of the problem by the ultrasonic method. The maximum frequency so far attained by the piezoelectric method is less than 10^8 per second, and the increase of sound velocity over the value obtained in the audible region may be expected to be only 1% of the latter. Due to experimental difficulties such as the inconstancy of temperature and variation of the frequency of the oscillator, the measurements of ultrasonic velocities so far obtained have not been able to give a decisive answer to the question, beyond indicating that the dispersion, if at all it exists, is small in the region studied.

Interferometric analysis of the spectral character of the "unmodified" light scattering in liquids provides a method of determining the acoustic velocities in liquids at a frequency of 10^{10} cycles per second, which is 100–1000 times higher than the frequency range employed in the ultrasonic

* For references see Bär, *Proc. Ind. Acad. Sci.*, 1938, **8**, 289; Parthasarathy, *ibid.*, 1935, **2**, 497; Richardson, *Proc. Phys. Soc.*, 1940, **52**, 480; Krishnan, K. G., *Proc. Ind. Acad. Sci.*, 1939, **9**, 382.

investigations. According to Kneser's theory, the velocity reaches its upper limiting value at high frequencies, estimated by him to be of the order of 10^9 Hertz. Accordingly the velocity calculated from the Brillouin displacements in light scattering should be the maximum possible and be systematically higher than the ordinary sound velocity. The percentage increase over the normal value would lie between 10–30% depending on the liquid and should, therefore, be detectable by the interferometric methods.

2. *Experimental Methods*

The accuracy of measurements of the velocity of thermal sound waves in liquids from the frequency shifts of the Brillouin components, depends on using a highly monochromatic incident radiation and maintaining a constant temperature for the liquid under investigation and for the optical system. As mentioned in the earlier papers in this *series*, the latter conditions were secured by surrounding the experimental tube by a water jacket and by enclosing the interferometer and the spectroscope in an asbestos-cement casing. The maximum temperature fluctuation in the liquid was about 5° C. The source used was a mercury-zinc amalgam lamp run at a comparatively low current. The zinc radiations were fairly sharp and the Brillouin components were in most cases well defined. The error due to the angular width of the incident beam is negligible in the backward scattering. Frequency shifts of the displaced components were ascertained for the zinc line, 4722 A.U. and for the mercury radiation, 4078 A.U. for which the hyperfine structure satellites are extremely weak. The separation of the Fabry-Perot plates was ordinarily 5 mm.; a larger separation of 7·5 mm. was employed for liquids like ethyl ether, carbon tetrachloride and chloroform for which the frequency shifts are small. The displacements were measured by a Hilger cross-slide microscope and in cases where the shifts are not great, they were also estimated from the microphotometric curves taken at a magnification of eighty. Considering the breadth of the Brillouin and the central components the error of measurement should be taken to be as high as $\pm$ 25 metres per second. The percentage accuracy is, however, much greater in the case of liquids like water, glycol, etc., for which the displacement is large and the components are sharp.

3. *Results and Discussion*

Seventeen liquids representative of a wide range of physical properties such as viscosity, conductivity and sound absorption are chosen for the investigation. Table I gives the 'hypersonic' velocities in these liquids, calculated from the measured shifts $\delta\nu$ for the 4078 and 4722 A.U., using

TABLE I. *Acoustic Velocities in Liquids*

Liquid	Hypersonics						Supersonics				
	Mean Temp. ° C.	Refractive Index H_γ	$\delta\nu$ cm.$^{-1}$ for 4078	Velocity m./sec.	$\delta\nu$ cm.$^{-1}$ for 4722	Velocity m./sec.	Temp. ° C.	Velocity m./sec.	Author*	Velocity (Partha-sarathy)	Temp. ° C.
Acetone	28	1·364	·254	**1139**	·213	**1129**	28	**1153**	Z.	1203	22·5
Carbon tetrachloride ..	25	1·484	·226	**932**	·195	**938**	23	925	F.H.A.	**929**	23
Chloroform	30	1·450	·229	**966**	·198	**980**	25	**995**	W.	1001	23·5
Cyclohexane	30	1·434	·285	**1201**	·245	**1234**	31·5	**1205**	S.	1257	23
Cyclohexanol	35	1·471	·340	**1414**	·290	**1428**	35	**1442**	B. & R.	1622	23·5
Ethyl ether	30	1·362	·210	**943**	..	..	30	**949**	F.H.A.	..	..
Ethyl alcohol	25	1·365	·261	**1169**	·220	**1166**	25	**1150**	W.	1207	23·5
Ethylene glycol	30	1·427	·390	**1661**	·333	**1670**	..	..	..	**1721**	24
Benzene	28	1·524	·32	**1290**	·268	**1281**	31·5	**1275**	S.	1310	23
Tetralin	30	1·546	·352	**1390**	·304	**1420**	..	..	..	**1465**	24
Phenol	26	1·564	..	..	·346	1568	..	..	..	..	..
Formic acid	25	1·378	·30	1331	·250	1312	..	..	..	..	..
Acetic acid	25	1·386	·257	**1139**	·22	**1153**	26	**1144**	K.	..	..
Iso-butyric acid	28	1·402	·257	1123	·21	1132	..	..	..	..	..
Methyl acetate	28	1·363	·255	**1144**	..	..	28	**1140**	Z.	1211	24
Water	30	1·343	·33	**1518**	·285	**1509**	23	**1492**	B.	1494	24
Conc. KBr solution (700 gm. in 1000 c.c. water)	28	1·38	..	..	·30	**1568**	18	**1570**	Sp.	..	..

* Z. = Zachoval (1939)
W. = Willard (1941)
S. = Suryaprakasa Rao (1940)
B.R. = Bhagavantam and Joga Rao (1939)
F.H.A. = Feyer, Hubbard and Andrews (1929)
K. = Krishnan, K. G. (1941)
Sp. = Spakovskij (1938)
B. = Bär (1938)

the Brillouin's formula $\delta\nu = 2\nu.\frac{v}{c}.\mu \sin \theta/2$, where v and μ are the sound velocity and refractive index of the medium, c is the velocity of light and $\theta = 180°$ for longitudinal scattering. The mean temperature of observation and the refractive index for H_γ are also listed for all liquids. The index used for calculation is corrected for the wavelength used. The velocities determined by the ultrasonic method are entered in columns nine and eleven for comparison. It will be seen that the hypersonic velocities calculated from the shifts for 4078 and 4722 A.U. agree fairly well, within the limits of experimental error.

In comparing the hypersonic and the ultrasonic velocities, it should be borne in mind that the liquids used for light scattering are freshly distilled and kept in vacuum during exposure, whereas it is not clear from the literature, whether sufficient care has been taken by the investigators in ultrasonics to maintain the liquid in a pure state. However, making due allowance for the temperature variation of velocities, the values obtained in the present investigation do not appreciably *exceed* the corresponding ultrasonic velocity in any liquid. Kneser's theory of sound absorption and dispersion of velocity cannot thus be sustained by the experimental facts for the case of liquids. The velocity data obtained by both the methods are *nearly* equal in the case of all liquids given in Table I. The small difference that is observed has to be attributed to the errors of measurement and the slight variations of temperature in the liquids and do not necessitate any special mechanism to be postulated.

The data published by Parthasarathy (1935) are consistently higher than those obtained by subsequent workers. The author is unable to confirm the great divergence between the hypersonic and the ultrasonic velocities reported by Rao (1938) for carbon tetrachloride and acetone. It is probable that the measurements of Rao are vitiated by the hyperfine structure satellites of the mercury radiations and by the uncertainty of the temperature of observation.

Among the liquids studied, water deserves special mention. Ever since Dutta (1938) reported a small dispersion for it, several authors have reinvestigated the liquid with different frequencies. By taking special precautions to eliminate all sources of error, Bär (1939) has been able to demonstrate that the sound velocity for water has a constant value for a wide range of ultrasonic frequencies. As the Brillouin components are sharp and well-separated from the central line, the percentage error in the determination of the hypersonic velocity in water is relatively small.

The observed value for the hypersonic region agrees well with the ultrasonic velocity duly corrected for the differences of temperature. Among the other liquids, Spakovskij (1938) claims that acetic acid shows a slight increase of velocity by about 1% in going from the frequency range of 250 kc./sec., to 2500 kc./sec. A similar dispersion for this acid is also reported by Krishnan (1941). The hypersonic velocity for the acid, however, has nearly the same value as that reported by Krishnan for 7618 kc./sec. Concentrated KBr solution also gives a value which is nearly the same as obtained by Spakovskij for 270–290 kc./sec., thus indicating that there is no dispersion in the case of electrolytic solutions as well.

In conclusion, the author's thanks are due to his Professor Sir C. V. Raman, F.R.S., for his kind interest in the work.

Summary

The 'hypersonic' velocities for eighteen representative liquids are calculated from the Brillouin displacements in the light scattered by these liquids. The data are compared with those obtained by the ultrasonic method. No detectable dispersion of velocity has been observed in any liquid in going over from the frequency range of 10 MHz in the ultrasonic to 10000 MHz in the hypersonic region.

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