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Leslie A. Chambers

Citation: [The Journal of Chemical Physics](#) **5**, 290 (1937); doi: 10.1063/1.1750025

View online: <http://dx.doi.org/10.1063/1.1750025>

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The Emission of Visible Light from Cavitated Liquids

LESLIE A. CHAMBERS

Johnson Foundation for Medical Physics and Department of Pediatrics, University of Pennsylvania

(Received February 6, 1937)

Emission of visible light from a number (14) of pure liquids and from some aqueous and non-aqueous solutions occurs during cavitation by intense sound waves of 8900 c.p.s. The intensity of the visible components of the radiation varies directly with the numerical product of viscosity (in poise) and dipole moment (in Debye units) and inversely with the temperature. In the case of polar solutes in nonpolar solvents the intensity varies with the concentration of the dipole. The light originates in cavitated areas or at the surface of the cavities, and is therefore proportional to the amount of cavitation, and in consequence, to the acoustic power input.

CERTAIN pure liquids emit visible light when cavitated by intense sound waves of audible frequency. The phenomenon was first recognized during the course of an experiment in which it was found that pure water, while sonically agitated, caused blackening of a photographic emulsion. A glow easily perceived by the dark adapted eye issued from the most vigorously cavitated regions in the body of the liquid.

Two similar observations involving ultrasonic frequencies, rather than audible, have appeared recently. Zimakov¹ has reported luminescence from certain aqueous solutions. It is his opinion that the phenomenon results from an electrical discharge between water vapor cavities and the glass walls of the containing vessel. Aqueous solutions of dichloroethanol, dichloroethane, NaI, NaCl, NH_4CNS and $\text{Al}_2(\text{SO}_4)_3$ were reported by Zimakov to emit light, while pure water and solutions of KI, acetic acid, and ethyl acetate did not.

On the other hand Frenzel and Schultes² observed a glow from pure water during ultrasonic treatment. They found that no light was emitted from degassed water and from this concluded that the light results from friction between cavitated gas bubbles and the water itself.

In the present communication some results of an investigation undertaken to determine the nature of the emitted light and the conditions necessary for its production are presented.

APPARATUS AND METHOD

The source of intense audible sound (8900 c.p.s.) used in the experiments was the modified Pierce magnetostriction oscillator previously described by Gaines³ and by Chambers and Gaines.⁴

For each experiment 50 ml of the substance or solution was placed in a cylindrical glass vessel surrounding the nickel vibrator. The dimensions of the vessel were such that the end of the active element was about 3 cm below the liquid surface.

The temperature of the liquid was adjusted previous to placing it in the reaction vessel, and accumulation of heat through sound absorption was prevented by internal water cooling of the nickel vibrator. The latter precaution was unnecessary, however, since the emission of light, when it occurred, could be detected immediately upon the beginning of vibration and before any appreciable temperature rise.

In all cases the oscillator was operated at resonance for maximum acoustic energy output. Thus the conditions of treatment were, as nearly as possible, the same for all the liquids insofar as temperature and energy input were concerned.

Emission of light was detected by visual examination after dark adaptation of the operator for 30 minutes. This qualitative method permitted determination of the emission, or lack of emission, of light sufficiently intense to produce an effect on the retina. Furthermore, it was possible to estimate roughly the relative intensities emitted from the liquids examined.

¹ P. V. Zimakov, *Compt. rendus Acad. Sci. U. S. S. R.* **3**, 450 (1934).

² J. Frenzel and H. Schultes, *Zeits. f. physik. Chemie* **27**, 421 (1934).

³ Newton Gaines, *Physics*, **3**, 209 (1932).

⁴ L. A. Chambers and Newton Gaines, *J. Cell. and Comp. Physiol.* **1**, 451 (1932).

EXPERIMENTAL RESULTS

Luminescence has been observed in the following liquids during sonic cavitation (arranged in order of relative light intensity):

- | | |
|------------------------------|-----------------------------|
| 1. Glycerol | 8. Dibutyl phthalate |
| 2. Nitrobenzol | 9. Water |
| 3. Ethylene glycol | 10. <i>n</i> -Butyl alcohol |
| 4. <i>o</i> -Nitrotoluol | 11. Corn oil |
| 5. Isoamyl alcohol | 12. Propyl alcohol |
| 6. <i>n</i> -Butyl phthalate | 13. Isopropyl alcohol |
| 7. Dimethyl phthalate | 14. Ethyl alcohol |

The emission from glycerol and nitrobenzol was visible without any dark adaptation, while the light produced in ethyl alcohol was so feeble as to be barely perceptible under the most favorable conditions.

On the other hand the following liquids showed no visible luminescence under the same conditions:

CCl ₄	Ethyl acetate	Methyl alcohol
CS ₂	Methyl acetate	Acetaldehyde
<i>m</i> -Xylol	Acetone	Amyl acetate
Benzol	Ethyl butyl acetate	Methyl salicylate
Toluol	Ethyl amyl acetate	Mesitylene
Ethyl ether	<i>n</i> -Tetradecane	Oleic acid
CHCl ₃	Aniline	Cotton seed oil
		Chlorobenzol

An interesting empirical correlation between certain physical constants of the liquids and the

relative intensity of visible light emitted has been found. It is that the apparent intensity is directly related to the numerical product of the viscosity (in 100 poise) and the molecular dipole moment (in Debye units) of the substance concerned. Table I illustrates this correlation insofar as reliable measurements of viscosity (η) and moment (μ) are available.⁵

Water seems to be the only exception thus far encountered to the general rule that the intensity of visible emission is related to the product ($\mu\eta$). However, it should be pointed out that the dipole moment given for water is from data involving only the vapor state.

We may conclude from the data of Table I that there is in no case an emission of light of sufficient strength to affect the retina when the product ($\mu\eta$) falls below a limiting value. The emission from ethyl alcohol ($\mu\eta=1.94$) was so feeble as to be barely detectable after 30 minutes of dark adaptation.

Two groups of correlative data have resulted from experiments on a series of liquids for which one or the other of the two variables (μ and η) was the same. In each case the relative intensity of visible radiation was found to be proportional to the free variable thus lending credence to the apparent correlation already drawn.

First, it is possible to select a series of substances in which the dipole moments are of the same magnitude while the viscosities differ.

TABLE I.

SUBSTANCE	100 η	μ	$\eta\mu$	VISIBLE EMISSION (RELATIVE)
Nitrobenzol	2.013 ^(20°)	3.90	7.85	+++++
<i>o</i> -Nitrotoluol	2. (est.)	3.75	7.5	+++++
Isoamyl alcohol	3.865	1.85	7.15	++++
Water	1.005	1.87	1.88	+++
<i>n</i> -Butyl alcohol	2.8 ^(22°)	1.74	4.87	+++
Propyl alcohol	2.23 ^(20°)	1.66	3.70	++
Isopropyl alcohol	1.95	1.78	3.47	++
Ethyl alcohol	1.192 ^(20°)	1.63	1.94	+
Chlorobenzol	0.751	1.52	1.14	0
Methyl alcohol	0.591 ^(20°)	1.64	0.97	0
Acetone	0.3	2.70	0.81	0
Methyl acetate	0.478 ^(0°)	1.67	0.80	0
Ethyl acetate	0.44 ^(20°)	1.74	0.77	0
Chloroform	0.564 ^(20°)	1.10	0.62	0
Acetaldehyde	0.223	2.68	0.60	0
Ethyl ether	0.226	1.22	0.28	0
Toluol	0.552	0.52	0.29	0
Benzol	0.649 ^(20°)	0.06	0.04	0
<i>m</i> -Xylol	0.595	0.06	0.04	0
Carbon disulphide	0.367 ^(20°)	0.06	0.02	0
Carbon tetrachloride	0.96 ^(20°)	0.00	0.00	0

All values of η are at 25° except as noted.

TABLE II.

	μ	100 η	$\mu\eta$	RELATIVE LIGHT INTENSITY
Methyl	1.64	0.591	0.97	0
Ethyl	1.64	1.192	1.94	+
<i>n</i> -Propyl	1.66	2.23	3.70	++
Isopropyl	1.78	1.95	3.47	++
<i>n</i> -Butyl	1.74	2.801	4.87	+++
Isoamyl	1.85	3.863	7.15	++++

TABLE III.

	μ	100 η	$\mu\eta$	RELATIVE LIGHT INTENSITY
<i>ortho</i>	6.05	(0.649)	3.93	Bright +++
<i>meta</i>	3.81	(0.649)	2.47	Very feeble ++
<i>para</i>	0.32	(0.649)	0.21	None 0

⁵ International Critical Tables and Trans. Faraday Soc. (1934).

TABLE IV.

% Nitrobenzol	Relative light emission (at 28°)	Variation of relative emission with temperature
100	Very bright	Somewhat dimmed at 63°
80	Bright	Somewhat dimmed at 57°
60	Less bright	Dim at 55°
40	Dim	Barely perceptible at 52°
20	Very dim	No light at 52°
0	None	

Such a situation occurs in the homologous primary alcohols indicated in Table II.

With essentially equal moments the emission is proportional to the viscosity, there being graded increase in light intensity from ethyl to isoamyl alcohol, methyl emitting none.

Again, it should be possible to select a series of fluids of essentially equal viscosity but which differ in respect to electric moment. This has proved difficult in the case of pure liquid substances. However, the three dinitrobenzols in benzol solutions of approximately equal viscosity illustrate the principle shown in Table III.

Each test sample consisted in a one-half percent solution of the indicated dinitrobenzol in C. P. benzol. The value taken for viscosity in the table is that of benzol since the addition of the derivatives in such low concentration did not greatly alter the value. In this case with similar viscosities the apparent brightness varied with the moment.

Since viscosity decreases with rise in temperature experiments were devised to determine the relation of the emission intensity to temperature of the substance. In the case of dibutyl phthalate the light was quite bright during vibration at 25°. The cooling arrangement was disconnected so that the liquid rose to 70° in four minutes. As the temperature increased the light intensity gradually decreased until no emission was visible. The liquid was then cooled to 25° whereupon vibration caused luminescence of about the same intensity as at the start of the experiment. Dimethyl phthalate behaved in a similar manner. In the case of glycerol the vibration was continued for 10 minutes without cooling, and the emission of light was never completely inhibited although its intensity was markedly diminished at the final temperature of 80°. The emission was of normal brightness when the liquid was recooled to the starting temperature (25°). A

similar behavior has been noted in all the liquids previously observed to emit light at 25°.

In the case of solutions of polar compounds in nonpolar solvents, there should, under the implications of the empirical rule set forth above, be a relation between the intensity of the emitted light and the concentration of the polar substance. A series of solutions of nitrobenzol in toluol was prepared and vibrated to determine whether or not such a relationship exists. Table IV shows the results of the experiment. It will be seen that the relative intensity in this case is, in fact, directly related to the concentration of polar molecules. The right-hand column of Table IV constitutes further confirmation of the temperature relationship indicated previously.

In addition to the experiments recorded above which relate the phenomenon of acoustic luminescence to certain physical constants of the various systems, direct observation during vibration has revealed some information as to the locale of the light production. No emission has been observed in any liquid in the absence of cavitation. Furthermore, the radiation seems to be localized exclusively at the surface of the cavities. Therefore, it appears brightest in the region immediately adjacent to the end of the vibrator, although not entirely confined to that region.

Two useful reference points are available for estimation of the absolute intensity of the emitted radiation although no quantitatively objective measurements have been made. The emission from ethyl alcohol seems to approach the threshold of human retinal sensitivity, while the brightest observed so far (from glycerol) will blacken a photographic plate (E. K. nitrate) in 4 minutes at a distance of 10 cm.

The duration of the luminescence depends only on the duration of the applied sonic field with exposure times up to ten minutes. There is no persistence or afterglow; all visible emission ceases at once with cessation of cavitation.

No analysis of the spectral characteristics of the radiant emission is available as yet. Obviously the correlations indicated by the data of this paper take into account only the visible components of the radiation, and may therefore require reconsideration if ultraviolet or infrared components are later found to be present.