

The Effect of Volatile Substances on the Chemical Activity of Ultrasonic Cavitation

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The effect of volatile substances on the reactions in ultrasonic-treated water was investigated. It was found that butanol, propanol *etc.* are able to inhibit practically all reactions, the oxidation of luminol being, however, unchanged. The sonoluminescence of pure distilled water could not be observed in the presence of these substances.

In an earlier paper¹ we reported that different volatile substances such as fatty acids, alcohols, *etc.* are able to inhibit nitrogen fixation in water treated with ultrasonics. In the homologous series the inhibition was observed to increase with the length of the carbon chain. When trying to explain this inhibition it seemed at least apparent that the vapour pressure of the substances was not the cause of the inhibitory effect. Since the inhibition generally increased with the length of the carbon chain it seemed reasonable to suppose that the substances caused the inhibition of the reactions by lowering the surface tension of the solution. It is, however, to be observed that other properties also change with the lengthening of the carbon chain.

In the present work attempts were made to elucidate this problem by observing the effect of volatile substances on the oxidation of compounds like luminol during the ultrasonic treatment of distilled water.

EXPERIMENTAL

Ultrasonic vibrations were produced as described previously¹. A sensitive photometer was used for the measuring of the luminescence produced by ultrasonics in distilled water with or without the addition of luminol. The photoelectric cell (RCA 931 A) and the amplifying system were enclosed in a light-tight metal box with a window for the light to be measured. Fig. 1 shows a schematic diagram of the complete electronic circuit². The weak electric current was measured with a sensitive galvanometer (Lange) having a current sensitivity of 3.5×10^{-9} amp/mm.

In the experiments with luminol the following solution was used: 100 ml of the test solution, 0.01 % luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in 0.05 % Na_2CO_3 . The light emitted was measured after it had reached its maximum. Table 1 shows the influence of different substances on the chemiluminescence of luminol.

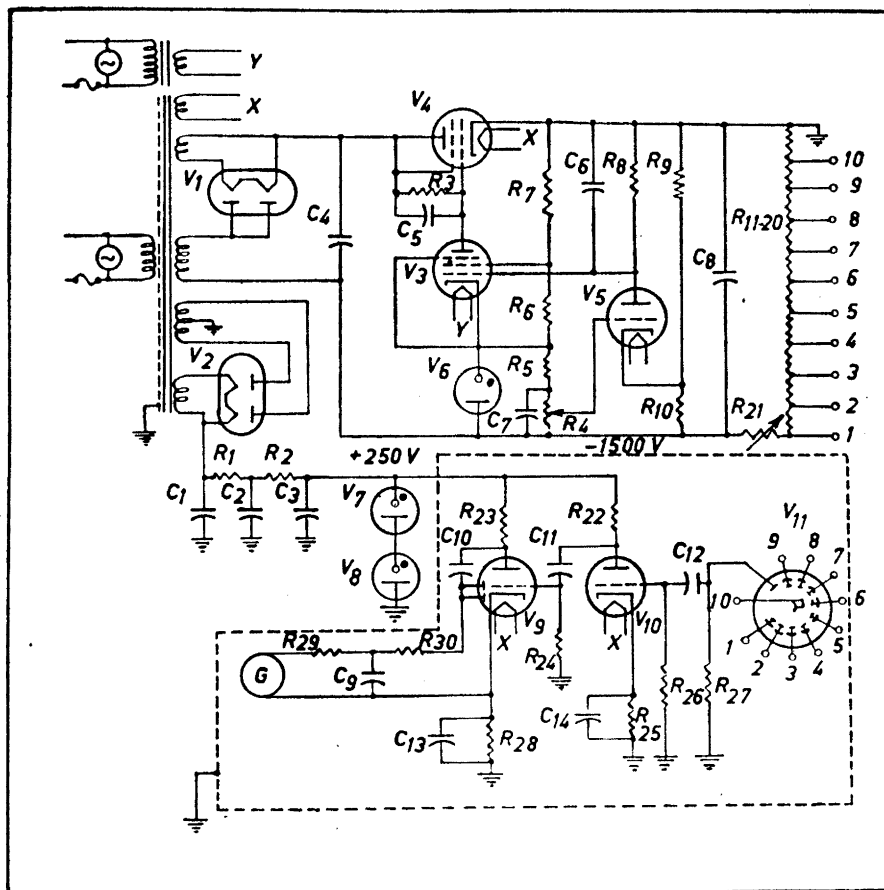


Fig. 1. Circuit of the a-c amplifier and voltage regulated power supply for the phototube.

- $R_1 = 5.6 \text{ k}\Omega$
- $R_2 = 4 \text{ k}\Omega$
- $R_{3,22,23} = 0.5 \text{ M}\Omega$
- $R_4 = 50 \text{ k}\Omega \text{ pot.m (wire wound)}$
- $R_5 = 0.25 \text{ M}\Omega$
- $R_6 = 25 \text{ k}\Omega$
- $R_7 = 75 \text{ k}\Omega$
- $R_8 = 25 \text{ M}\Omega$
- $R_9 = 0.34 \text{ M}\Omega$
- $R_{10} = 3.4 \text{ k}\Omega$
- $R_{11-20} = 0.1 \text{ M}\Omega$
- $R_{21} = 0.2 \text{ M}\Omega \text{ pot.m (wire wound)}$
- $R_{24,26,27,30} = 1 \text{ M}\Omega$
- $R_{25} = 7 \text{ k}\Omega$
- $R_{28} = 8 \text{ }\Omega$
- $R_{29} = 50 \text{ k}\Omega$

G = 0-70 μ A

- $C_1 = 0.1 \text{ }\mu\text{F}$
- $C_2 = 8 \text{ }\mu\text{F el.kond.}$
- $C_3 = 4 \text{ }\mu\text{F}$
- $C_4 = 16 \text{ }\mu\text{F} \rightarrow 1500 \text{ v (oil filled)}$
- $C_{5-7,13,14} = 1 \text{ }\mu\text{F}$
- $C_8 = 2 \text{ }\mu\text{F el.kond. } 1500 \text{ v (oil filled)}$
- $C_9 = 10 \text{ }\mu\text{F}$
- $C_{10-11} = 0.06 \text{ }\mu\text{F}$

- $V_1 = 5R4G$
- $V_2 = 5Y4$
- $V_3 = 6AC7$
- $V_4 = 6L6$
- $V_{5,10} = 6SF5$
- $V_{4-5} = VR150$
- $V_9 = 6SQ7$
- $V_{11} = 931-A \text{ (phototube)}$

Table 1. Effect of volatile substances on the chemiluminescence of luminol.

| Substance | Added in % | Galvanometer reading in mm n-n ₀ |
|-------------------------|------------|---|
| No addition | — | 700 |
| Ether | 0.2 | 0 |
| <i>iso</i> -Amylalcohol | 0.2 | 700 |
| <i>n</i> -Butanol | 1 | 700 |
| Propanol | 1 | 680 |
| Ethanol | 2 | 700 |
| Benzene | 0.2 | 20 |
| Xylene | 0.2 | 450 |
| Toluene | 0.2 | 150 |

These experiments show that alcohols are hardly competing for oxygen with nitrogen because practically no decrease in light intensity can be observed in the presence of luminol. On the other hand we have previously found that nitrogen fixation does not take place in the presence of alcohol¹. This question will be reverted to below.

To elucidate the interrelationship between the chemiluminescence of luminol and the luminescence of distilled water, treated with ultrasonics, experiments were made with pure distilled water in the same way as with luminol, *i. e.* measuring luminescence after the maximum had been developed. Table 2 shows the influence of different substances on luminescence.

Table 2. Luminescence of water with volatile substances without luminol.

| Substance | Added in % | Galvanometer reading in mm n-n ₀ |
|-------------------|------------|---|
| No addition | — | 30 |
| Ether | 0.2 | 0 |
| Butyric acid | 1 | 0 |
| <i>n</i> -Butanol | 1 | 0 |
| Propanol | 1 | 0 |

A KI solution was treated in the ultrasonic field (100 ml of a solution made up of 50 ml of 1 % KI, 45 ml of 1 % H₂SO₄, and 5 ml of 0.1 % starch solution). The liberated iodine was titrated with thiosulphate. It can be seen in Fig. 2 that no oxidizing substances are produced in the solution in presence of *n*-butanol.

When 1 ml of chloroform is added to this solution some oxidizing substances are still produced in the presence of *n*-butanol as can be seen from the liberation of iodine (Fig. 3). An experiment was made to find out if a change in the physical structure of water possibly causes changes in the chemical activity of cavitation. No effect was observed in 1 M NaCl solution.

DISCUSSION

If oxygen containing water with or without luminol is treated with ultrasonics, molecular nitrogen is fixed under the formation of nitrite, but if for instance 1 % butanol is added nitrogen fixation is completely inhibited. So is also the formation of hydrogen peroxide. Butanol does not, however, notably decrease the chemiluminescence of luminol, a fact which shows that easier

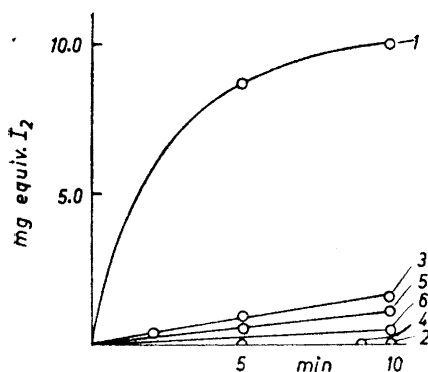


Fig. 2. Inhibitory effect of volatile substances on liberation of iodine from KI. 1) Control without *n*-butanol addition, 2) addition of 1% *n*-butanol, 3) 1% butyric acid, 4) 0.2% toluene, 5) 0.25% caproic acid, 6) 0.5% *iso*-amylalcohol.

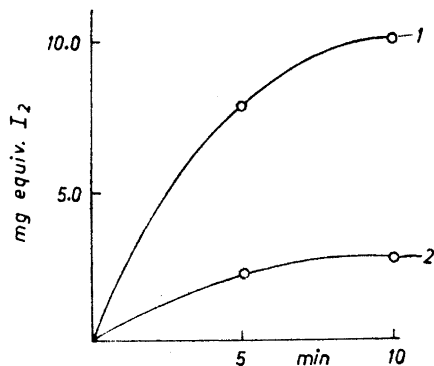


Fig. 3. 1) Control without butanol addition, 2) addition of 1% *n*-butanol.

occurring oxidation reactions still take place and that cavitation occurs in the presence of this alcohol, since substances with a high vapour pressure such as ether *etc.* completely extinguish the light given by luminol. Due to the addition of alcohol, however, radical changes have taken place in the system. The hypothesis that alcohols should act as acceptors for oxidizing agents is not well-founded because no liberation of iodine from KI was observed in a 1% butanol solution. Since the changes caused by alcohol cannot be due to the ability of the substances to compete for oxygen with nitrogen, nor to the destruction of cavitation because of the vapour pressure, it seems reasonable to suppose that the substances which lower the surface tension decrease the energetic state of cavitation, so that for merely energetic reasons some reactions do not take place. As to the mechanism of the decrease of the energy level at least two possible ways had to be observed.

In the first case the mechanism of the lowering of the energy level is assumed to be connected with the mechanism of cavity formation. According to Lindström³ cavitation is preceded by the nucleation process during which separate gas bubbles dissolved in the liquid combine, and a germ consisting of six gas molecules is built up. Through the formation of this germ, or box, the great cohesive forces in water are overcome and cavitation is initiated. Earlier we assumed it hardly likely that surface active substances should accumulate on the inside surface of the cavitation bubble because of its short duration, but if the nucleation process precedes cavitation it may be assumed that during this lag period surface active substances are mobilized in the vicinity of the box. On this account it can perhaps be understood why there is a difference in regard to inhibition between dissociated and undissociated fatty acids. The dissociated carboxyl group is surrounded by such a large amount of water molecules that, contrary to the undissociated group, its

mobility is hampered. From this the observed difference between neutralized and unneutralized valeric acid arises, *i. e.* the former is able to inhibit nitrogen fixation by only 30 or 40 % whereas the latter inhibits it completely.

Lindström assumes further that the chemical reactions in cavitation are due to the fact that the water surface around a gas bubble is negatively charged, the surface charge acquiring rather high values (0.08 e.s.u./cm²). When the surface of the cavity is formed the surface charge must be established by transport of electricity, by which process the gas molecules in the cavity will be ionized. In such a case it is evident that if surface active substances have been accumulated in the surface of the gas bubble the surface charge per cm² should be lower than in a solution without surface active substances for the very reason that the number of water molecules per cm² of the surface of the bubble has decreased.

In this case the explanation of the changes in the chemical activity of cavitation is assumed to be connected with the drastic changes in the physical structure of water caused by addition of different alcohols.

According to Bernal and Fowler⁴ water may be regarded as a partially broken down ice structure, tridymite-like, with each oxygen atom surrounded tetrahedrally by four other oxygen atoms, the structure being held together by hydrogen bonds. When a molecule of solute is introduced into the water structure a cavity can first be formed in this by taking away a given number of water molecules. Hereby a number of hydrogen bonds have to be broken proportional to the size of the molecule. This breaking of hydrogen bonds is reflected in changes in compressibility, viscosity and surface tension. A decrease in compressibility means a closer packing of the water molecules with increased cohesive forces. It could therefore be assumed that the formation of cavity is prevented because of the depolymerization of the association of water.

It should, however, be observed that no inhibition of nitrogen fixation was observed in a solution in which a depolymerization of water had been produced by sodium chloride. It is therefore suggested that changes in the physical structure of water is not responsible for changes in the chemical activity of the cavitation.

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