Sonoluminescence of aqueous solutions of sulfuric acid and sulfur dioxide

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Sonoluminescence (SL) of aqueous solutions of sulfuric acid and sulfur dioxide enhances with an increase in their concentration and reaches a maximum at 16 and 0.05 mol L^{-1}, respectively. The further increase in the concentration of these substances decreases the SL intensity. The SL spectra of the solutions have a broad maximum at 450 nm. Excited SO_2 molecules formed in sulfuric acid due to sonolysis are luminescence emitters. The proposed mechanism of bright SL in these systems is based on the energy transfer from the electron-excited sonolysis products to the SO_2 molecules in cavitation bubbles.

Key words: sonoluminescence, aqueous solutions, sulfuric acid, sulfur dioxide.

Sonoluminescence (SL) is a weak glow accompanying ultrasonic cavitation in liquids. Sonoluminescence emitters are localized in cavitation cavities rather than in the liquid bulk.[1] The SL intensity and spectra depend on the physicochemical properties of sonicated liquids. In addition, SL is affected by dissolved gases and substances with a high saturated vapor pressure capable of penetrating in the cavitation cavity. They either enhance or quench luminescence.[1—3]

Luminescence of liquids in the ultrasonic field can be explained in the framework of two types of models, thermal and electric. According to the thermal model, quasi-adiabatic compression of the cavitation cavity results in heating of its content. In this case, SL is caused by the equilibrium thermal radiation[4] or deactivation of excited molecules formed in cavitation cavities by inelastic collisions of particles with an enhanced kinetic energy.[3] The electric model related SL to the electric disruption in the cavitation cavity upon its compression or cleavage.[1]

The mechanism of SL can be revealed and methods for the enhancement of its intensity can be found by the study of SL of aqueous solutions of different substances and comparison of the obtained results with the data on sonoluminescence of water. In this work, we studied SL of aqueous solutions containing H_2SO_4 and SO_2.

Experimental

Doubly distilled water was used in all experiments. Sulfuric acid (special-purity grade) was distilled until no absorption was detected in a cell (l = 1 cm) in the UV region >200 nm. Sulfur dioxide was synthesized by the reaction of sulfuric acid with sodium thiosulfate according to a standard procedure.[5] Solutions of sulfur dioxide were prepared by gas bubbling through water. The concentration of SO_2 was determined from the absorption intensity at λ = 276 nm (ε = 500 L mol^{-1} cm^{-1}).[6]

Absorption spectra were recorded on a Specord UV-VIS spectrophotometer. Sonolysis of solutions was carried out in a stainless steel reactor, whose temperature was maintained constant, equipped from the bottom with a quartz window (inner diameter of the reactor 20 mm, height 75 mm). In all experiments, the volume of the sonicated liquid was 10 mL. An Ace Glass ultrasonic disperser (working frequency 20 kHz, maximum electric power 100 W) equipped with an acoustic power sensor was used for sonication. In all experiments, solutions were sonicated with an acoustic power of 30 W using a rod-type titanium acoustic horn of the disperser (diameter of the radiating surface 6 mm). The temperature of 20±2 °C was maintained in the reactor.

Sonoluminescence spectra were recorded on an Aminco-Bowman spectrofluorimeter (Hamamatsu 1P28 multiplier, spectral width of monochromator slits 20 nm). The total SL intensity in the 200—650 nm interval was detected without spectral deconvolution using a previously[7] described technique (for studying chemiluminescence) equipped with a FEU-140 multiplier as a photodetector.

Results and Discussion

The SL spectra of water saturated with air or argon and of aqueous solutions of SO_2 and sulfuric acid are presented in Fig. 1. Saturation of water with argon increases the SL intensity in the whole spectral region, which corresponds to the published data.[1,2,8] Our experiments showed that the SL intensity of argon-saturated water is eightfold (according to the data,[8] 3—12-fold) higher than that of air-saturated water. The addition of SO_2 or H_2SO_4 to water (as in the case of saturation of water with argon) increases considerably the SL intensity. The resulting plots of the total SL intensity of aqueous solutions of H_2SO_4

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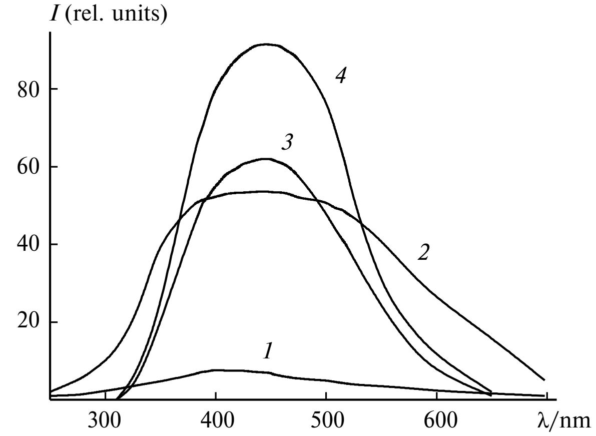

Fig. 1. Sonoluminescence spectra of water saturated with air (*1*) or argon (*2*), an aqueous solution of SO_2 (0.1 mol L^{-1}) saturated with air (*3*), and an aqueous solution of sulfuric acid (18 mol L^{-1}) saturated with air (*4*) (*3* and *4*, the ordinate is threefold decreased).

and SO_2 *vs.* concentration of these components introduced separately are presented in Fig. 2. It can be seen that at $[H_2SO_4] = 16$ mol L^{-1} the SL intensity is maximum and 70-fold exceeds the SL intensity of water. In the case of sulfur dioxide, the maximum luminescence intensity is achieved at $[SO_2] = 0.05$ mol L^{-1}, being 55-fold higher than the SL intensity of water. In the region of high H_2SO_4 and SO_2 concentrations, the SL intensity is saturated and then somewhat decreases.

These results can be explained in the framework of the thermal SL model.[3] In the cavitation cavity heated due to compression, the kinetic energy of molecules is converted into the electron excitation energy due to inelastic collisions of the first order, generating excited states of water $\tilde{A}(^1B_1)$, $\tilde{B}(^1A_1)$, and $\tilde{C}(^1B_1)$ with the energies 7.5, 8.3, and 9.9 eV, respectively. Up to 90% of excited water molecules in the $\tilde{B}(^1A_1)$ state dissociate to form the excited hydroxyl radical emitting at 280—340 nm.

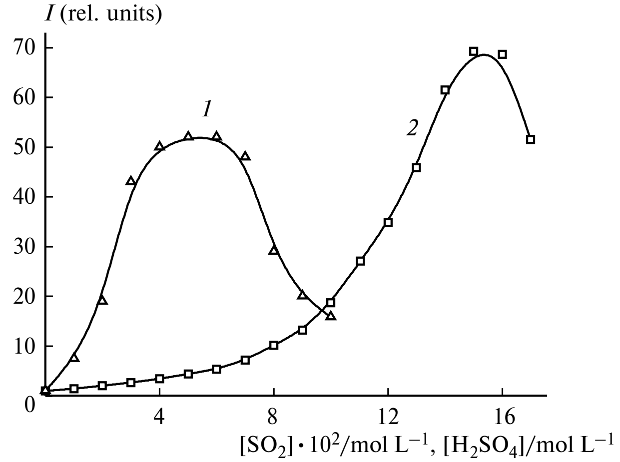

Fig. 2. Plots of the sonoluminescence intensity (*I*) of aqueous solutions of SO_2 (*1*) and H_2SO_4 (*2*) *vs.* their concentration.

$$H_2O^*(\tilde{B}) \longrightarrow H + OH^*(^2\Sigma^+) \longrightarrow H + OH(X) + h\nu$$

The $\tilde{C}\rightarrow\tilde{A}$ transitions of the excited water molecules are accompanied by light emission in the 380—600 nm interval with a broad maximum at ~425 nm.

The exciplexes $H_2O^*\cdot M$ or excited $[H...OH...M]^*$ complexes formed due to triple collisions when the energy of colliding particles is sufficiently high can be a luminescence source in the region <300 nm

$$H_2O^* + 2\,M \longrightarrow H_2O^*\cdot M + M \longrightarrow H_2O + 2\,M + h\nu,$$

$$H + OH(OH)^* + M \longrightarrow [H...OH...M]^* \longrightarrow H_2O + M + h\nu,$$

where M is a water molecule or an inert gas atom.

Quenching of the excited molecules by water molecules in the ground state exerts a noticeable effect on the SL intensity.

The thermal conductivity of a vapor-gas mixture in the cavitation cavity plays a substantial role in this SL mechanism.[1,3] First, a decrease in the thermal conductivity results in higher long-term temperatures appeared inside the cavity due to compression. This increases the number of molecules excited due to inelastic collisions. Second, the cavity expansion is accompanied by temperature equalization inside the cavity and at the interface from which the vapor is evaporated inside the cavity. The rate of temperature equalization depends on the thermal capacity of the vapor-gas mixture in the cavity, and its decrease leads to a decrease in the temperature at the interface. As a result, the vapor pressure in the cavity reduces, and the quenching efficiency decreases.

Since the thermal conductivity of gases decreases in the series air—argon—sulfur dioxide,[9] the SL intensity should increase in this series, which is observed experimentally. According to our data, the SL intensity of an aqueous solution of SO_2 at concentrations >0.02 mol L^{-1} is higher than that of water saturated with argon. When argon is passed through a saturated solution of sulfur dioxide (0.14 mol L^{-1}), the SO_2 concentration decreases. The SL intensity first increases and then decreases, which is in agreement with the obtained plot of the SL intensity of a solution of SO_2 *vs.* its concentration (see Fig. 2).

The increase in the SL intensity in solutions of sulfuric acid is likely caused mainly by the appearance of SO_2 due to reactions of excited H_2SO_4 molecules similarly to the reactions accompanying the radiolysis of sulfuric acid.[10] It has been shown[11] that the sonolysis of sulfuric acid affords SO_2 and sulfur. During sonolysis, as during radiolysis, H_2SO_4 is decomposed noticeably at concentrations >9 mol L^{-1} when nondissociated H_2SO_4 molecules begin to predominate in a solution.[10,12] At lower concentrations, the fraction of sulfuric acid molecules penetrating in the cavitation cavity is insignificant.

In addition, the enhancement of the SL intensity with an increase in the H_2SO_4 concentration, especially in the interval from 0 to 9 mol L^{-1}, can be explained by an increase in the solution density resulting in an increase in the amount of the absorbed acoustic energy. It is known,[1] for example, that the addition of metal salts in high concentrations (1—2 mol L^{-1}) to water enhances the luminescence continuum of the H_2O^* molecules.

When concentrated sulfuric acid is saturated with argon for 60 min, the SL intensity increases tenfold, and the luminescence spectrum remains unchanged (under our experimental conditions, the total SL intensity of argon-saturated sulfuric acid is 700-fold higher than that of air-saturated water). This fact can be explained by a decrease in the thermal conductivity of the vapor-gas mixture in the cavitation cavities and an enhancement of the sonolysis efficiency of the acid with SO_2 formation.

It is seen from the data in Fig. 1 that the SO_2 or H_2SO_4 additives increase the intensity and also narrow the SL band. The observed narrowing can be attributed to the appearance of the prevailing emitter at 450 nm, because the greater width of the SL spectrum of water is a result of the superposition of luminescence from several emitters. In addition, the SL spectrum changes due to the light absorption in the UV region by sulfur dioxide. The comparison of the SL and photoluminescence spectra of SO_2 in the gas phase at a low pressure[13] suggests that one of the main SL emitters are the triplet-excited SO_2 molecules ($\tilde{a}(^3B_1)$, 3.194 eV), whose quantum yield of photoluminescence is close to unity and exceeds the luminescence quantum yields of the H_2O^* molecules.[13] The larger width of the band in the SL spectrum compared to the band of SO_2 photoluminescence detected at a low pressure in the gas phase is likely related to broadening due to the high pressure in the cavitation cavities and the contribution from other emitters.

The data obtained allow us to propose the following mechanism of sonolysis in the $H_2O—SO_2$ and $H_2O—H_2SO_4$ systems resulting in the formation of the excited $^3SO_2$ molecules. The compression of the cavitation cavity results in heating of its content (steam, air, H_2SO_4 or SO_2 molecules). Collisions of the first order lead to the direct excitation of the SO_2 molecules, which penetrate in the cavity from the liquid

$$SO_2 —))) SO_2^* \longrightarrow SO_2 + h\nu,$$

λ = 350—500 nm.

Excitation is also possible due to the energy transfer from the excited water and sulfuric acid molecules or hydroxyl radicals

$$H_2O^* (OH^* \text{ or } H_2SO_4^*) + SO_2 \longrightarrow$$
$$\longrightarrow H_2O (OH \text{ or } H_2SO_4) + SO_2^*.$$

This mechanism is favored by the increase in the SL intensity already at low sulfur dioxide concentrations when the SO_2 content in the cavitation cavity is low and cannot exert a noticeable effect on the thermal conductivity and direct excitation is insignificant. Since the $^3SO_2$ luminescence state lies lower than the excited states of the H_2O or H_2SO_4 molecules, the SO_2 luminescence is not quenched by the solvent molecules, which also favors, probably, an increase in the SL intensity of SO_2 and H_2SO_4 solutions over the SL intensity of water. The intensity decrease observed at a high SO_2 content can be explained by self-quenching

$$SO_2^* + SO_2 \longrightarrow SO_2 + SO_2 + \Delta,$$

where Δ is the "dispersion" energy (energy of the excited state converted into the thermal energy).

It is difficult to explain these results in the framework of the electric SL model, because an increase in the concentration of an electrolyte solution increases its electric conductivity and decreases the electrokinetic potential and, correspondingly, the noncompensated charge on the walls of the cavitation cavity.[3] Therefore, the SL intensity should decrease with an increase in the concentration of solutions.

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