Sonochemiluminescence of Melatonin quenched by luminol in an aqueous solution

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Melatonin, a hormone of the pineal gland, that plays an important role in energy metabolism and regulation of physiological of the human body, effectively quenches luminol chemiluminescence and sonochemiluminescence in an aqueous solution. The Stern-Volmer quencher rate coefficient has been determined. The detection limit of melatonin in the solution for the effective quenching of luminol sonochemiluminescence is 20 ng/ml.

Keywords: sonochemiluminescence, melatonin, luminol

INTRODUCTION

Melatonin, $C_{13}H_{16}N_2O_2$, is a neuroendocrine hormone synthesized from L-tryptophan via serotonin. Melatonin seems to be almost universal, having been found in every vertebrate so far screened, in unicellular organisms, and in leaves, flowers, fruits and seeds of many plants [1]. Melatonin is involved in circadian rhythm and regulation of diverse body function, including sleep. The circadian rhythm of melatonin concentration is controlled by the biological clock in the suprachiasmatic nucleus and the environmental light signals, therefore, this hormonal information transmits the environmental day and night cycles to the whole body via the circulation of blood [2]. In addition, melatonin is reported to be effective against many diseases such as sleep disorders, cancers, Alzheimer's disease and depressive syndrome. Therefore, melatonin determination is important for the diagnosis of rhythm disorders, for the research f new biologically active substances, and for the estimation of the effect of medicines [3,4].

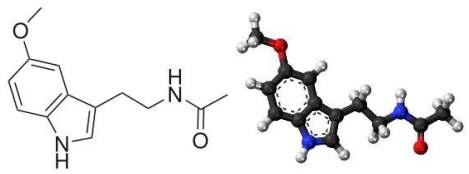

Figure 1. Chemical structure of melatonin (N-acetyl-5-methoxy tryptamine).

Based on the well-known facts of the melatonin's antioxidant effect, particularly on its activity and ability to inhibit OH radicals and hydrogen peroxide [5-8], we aimed to study of determination of melatonin by chemiluminescence (CL), sonochemiluminescence (SCL) and sonoluminescence (SL) in aqueous solution of luminol.

EXPERIMENTAL

The scheme of experimental procedure has been previously described [9]. For sonoluminescence measurements, an ultrasonic disperser from AGE GLASS INCORPORATED (ultrasonic processor, 100W, 6mm titanium probe) was used. The operation frequency was 20kHz. The standard volume of the liquid capacity was 10ml. The ambient temperature of cuvette is monitored by the thermostat and thermocouple. The cuvette was placed in the light tight chamber equipped with photodetector FEU-39.

The SL and SCL measurements were recorded with a spectral resolution of AX=20 nm in the range from 200 to 700 nm of the "Aminco Bohnschap J4-8202" spectrophotometer with photomultiplier "Hamamatsu R4332". Before recording of spectra, the temperature was 10 ± 2^0C and then temperature of all solutions saturated with air and argon. The recording time of the spectrum was about 1 min. Photoluminescence spectra (PL) were recorded on a (Fluorologe 3) spectrofluorometer with a spectral resolution of AX=1. Absorption spectra were recorded on a (Specord UV-VIS) spectrophotometer, 1cm quartz cuvette was used.

RESULTS

In Figure 2 shows the absorption and photoluminescence spectrum of an aqueuos solution of melatonin. The characteristic absorption band of melatonin in the UV region of the spectrum with a maximum at 280 nm makes it possible to determine

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up to 10^{-4} $mol \cdot l^{-1}$ of the hormone. According to the PL spectrum with a maximum in the 370 nm region, lower melatonin concentration in the aqueous solution can be determined. The effect of melatonin on the intensity and spectrum of the multibubble sonoluminescence of water is illustrated in Figure 2. It can be seen from the figure that melatonin effectively suppresses the luminescence band OH radical with a maximum at 310 nm and completely cut off the short-wavelength part of the SL spectrum of water less than 300 nm. Apparent maximum in the presence of melatonin at 370 nm is evidently due to sonophotoluminescence, i.e. cavitation bubbles act as sources of UV radiation, which excites the photoluminescence of melatonin dissolved in water.

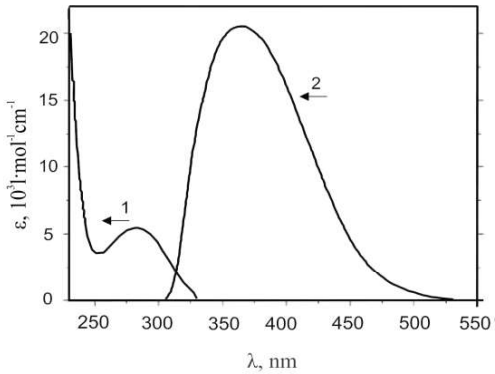

Figure 2. 1-Absorption spectrum of an aqueuos solution of melatonin 2.5·10⁻⁴mol·l⁻⁴. 2-The photoluminescence spectrum of an aqueuos solution of melatonin 2.5·10⁻⁴mol·l⁻¹.λ_{max}=364nm, λ^*=276nm

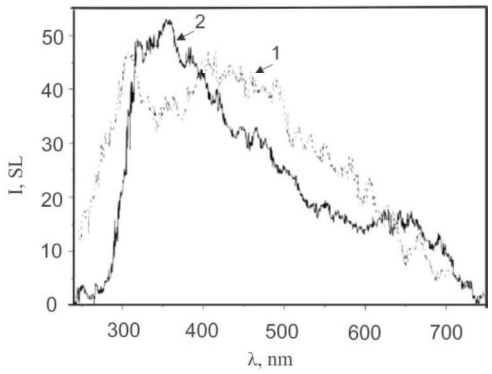

Figure 3. 1-Sonoluminescence spectra of water saturated with argon. 2- Sonoluminescence spectra of an aqueous solution of melatonin 2.5·10⁻⁴mol·l⁻¹

The photoluminescence and chemiluminescence spectra of aqueous solutions of luminol doesn't change when melatonin is added. The quenching obeys the Stern-Volmer equation for the dependence of the luminescence intensity on the concentration of the quencher (Fig. 4). From the Stern-Volmer relationship, we can determine the constant of quencher rate coefficient in the chemiluminescence kinetics.

$$\frac{I_0}{I} = 1 + K_Q \cdot [Q]$$

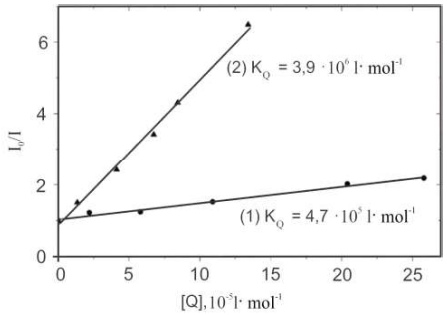

Figure 4. Quenching of CL -1 and SCL, -2 of luminol in water (10^{-4} mol·l^{-4}) with melatonin (Q) in the coordinates of the Stern-Volmer equation.

Where I_0 is the intensity of chemiluminescence without quencher, I is the intensity of chemiluminescence with quencher, K_Q quencher rate coefficient, Q is concentration of the quencher. In the case of chemiluminescence kinetics, quencher rate coefficient was K_Q=4.7·10^5 mol·l^{-1}. Addition of hydrogen peroxide was initiated the chemiluminescence reaction with luminol solution 10^{-4} *mol·l*$^{-4}$ with NaOH 10^{-2}*mol·l*$^{-4}$. The quenching effect of chemiluminescence can be apparently explained by the interaction of hydrogen peroxide with melatonin and inhibition of the oxidation of luminol. In the presence of a more efficient interaction of melatonin with radicals OH-initiators of CL luminol than with hydrogen peroxide [9], it was possible to expect more effective quenching, which was observed in Figure 5, 6. Considering the large size of the molecules of metatonin, their penetration into the cavitation bubbles is uncertain. The quenching reactions of excited products of luminol oxidation probably occur either at the gas-liquid interface, i.e. on the surface of the bubble, or in the volume of the solution.

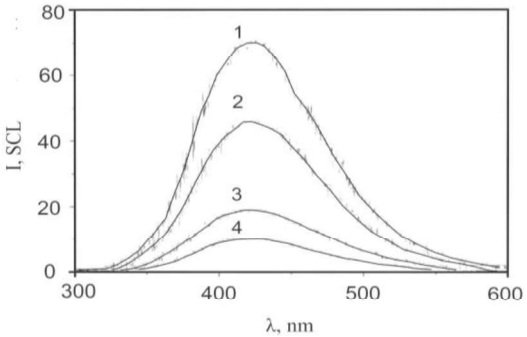

Figure 5. Chemiluminescence spectrum of 10^{-4}mol·l^{-4} luminol solution containing with varied concentration of melatonin: 1-

0 mol·l-1, 2- 1.35·10-5 mol · l−1, 3- 6.73·10-5mol·l-1, 4- 13.4·10-5mol·l-1. All solutions contain 10-2mol·l-1 NaOH.

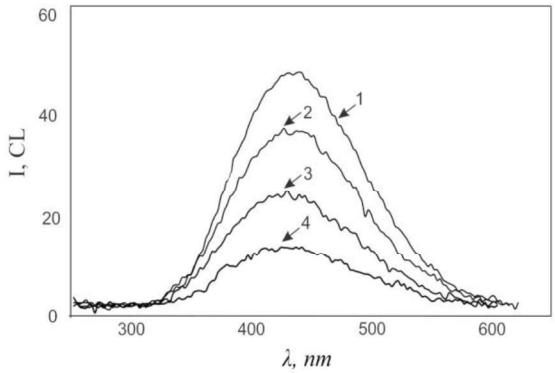

Figure 6. Sonochemiluminescence spectrum of 10-4mol·l-4 luminol solution containing with varied concentration of melatonin: 1- 0 mol·l-1, 2- 1.35·10-5 mol·l-1, 3- 6.73·10-5mol·l-1, 4- 13.4·10-5 mol·l-1. All solutions contain 10-2 mol·l-1 NaOH.

CONCLUSION

According to the Stern-Volmer relatioship, we calculated the value of the quencher rate coefficient in the case of sonochemiluminescence kinetics. It obeys the rule of quenching in SCL, which is equal to K_Q=3.9·10^6 $mol \cdot l^{-1}$ (for the compare of quencher rate coefficient, it was the greater than the chemiluminescence kinetics), which makes it possible to determine up to 20 ng/ml (~8·10^{-8} $mol \cdot l^{-1}$) of melatonin in an aqueous solution. Therefore, the quenching of sonochemiluminescence of luminol is a highly sensitive method for determining the melatonin in aqueous solution.

REFERENCES

[1] Bespyatikh A.U., Brodski V.Y., Burlakova O.V et al. Melatonin: Theory and Praticies. M.:Medpractica-M., 2009. P99.

[2] Karasek M., Winczyk K. Melatonin in humans //J. of Physiology and Pharmacology. 2006. V. 57, p. 19-39.

[3] Poeggeler B., Balzer I., Harderland R., Lerchl A. Pineal hormone melatonin oscillates also in the dinoflagellate Gonyaulax polyedra // Naturwissenschaften.1991. V. 78. P. 268-269.

[4] Balzer I., Hardeland R. Melatonin in algae and higher plants - possible new roles as a phytohormone and antioxidant //Botanica Acta. 1996. V. 109. P. 180-183.

[5] Tan D.X., Manchester L.C., Reiter R.J., Qi W.B. Karbownik M., Calvo VR. Significance of melatonin in antioxidative defense system: reactions and products //Biol. Signals Receptors. 2000. V. 9. 137-159.

[6] Matuszak K., Reszka K.J., Chignell C.F. Reaction of melatonin and related indoles with hydroxyl radicals: EPR and spin trapping investigation //Free Radical Biology and Medicine. 1997. V. 23. P. 367-372.

[7] Poeggeler B., Thuermann S., Dore A., Schoenke M., Burkhardt S., Hardeland R. Melatonin's unique scavenging properties - roles of its functional substituents as revealed by a comparison with its structural analogues // J. of Pineal Research. 2002. V. 33. P. 20-30.

[8] Sharipov G.L., Abdrakhmanov A.M., Gainetdinov R.KH., Sonochemiluminescence of H_2SO_4 and SO_2 solution. J. of Chem. 2003. V.9. P.1863-1865.

[9] Vladimorov U.A., Proskurnina E.V., Chemiluminescence of cell and free rsdicals, J. of Biol. Chem. 2009. V.49. P.341-388.