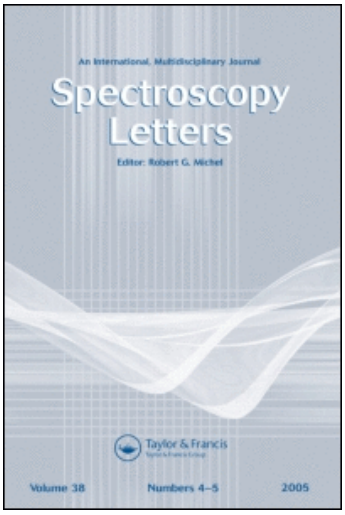

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Acoustic Field Effect on Electrochemiluminescence of Organic Molecules in Solutions

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ACOUSTIC FIELD EFFECT ON ELECTROCHEMILUMINESCENCE OF ORGANIC MOLECULES IN SOLUTIONS.

Key words: Acoustic Field, ECL.

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Electrochemical reactions in solutions causing the production of electrochemiluminescence (ECL) have been studied already for more than ten years[1-4]. In the main the ECL mechanism is established, the main regularities of this interesting phenomenon are determined. The attention is paid to the ECL in connection with the fact that its radiation gives a vast information about the electrochemical reactions in solutions. Moreover on this basis an effective and convenient transformators of the electrical signals into light can be carried out (the quantum efficiency is 20% for some solutions[5]). As a rule the ECL experiments are made under conditions controlled by an ordinary or convective diffusion. In this paper the results of

investigations of the ECL upon condition of great external disturbances of solution which occur due to the application of the ultrasonic fields to the cell are given. To our knowledge such investigations have not been undertaken earlier.

Acoustic vibrations in kilocycle and megacycle ranges are used in the experiments. The oscillator of the bipolar pulses serves as the source of excitation. The ECL was observed on electrodes of different configurations: straight platinum wires, rectangular plates, on couple of electrodes one of which had a helical shape. An acoustic influence on the solution was realized by different means. In one case the vibrations were transferred to the electrodes directly, in the other one to the solution in a cell.

It has been found experimentally that an application of the acoustic vibrations causes the essential variations in different parameters of the ECL solution: the peak power, quantum effeciency, duration of the emission pulse, time of its development and also the redox potentials of the molecules. These variations are revealed in the solutions of 1,5-diphenyl-3-stirylpirasoline, rubrene, 9,10-diphenylanthracene (DPA), 9,10-dimethylanthracene and perylene. N,N-dimethylformamide serves as the solvent, the tetra-n-butylammonium perchlorate as the supporting electrolyte.

In our investigations we did not find out the dependence of the ECL neither on the type of the acoustic currents in the solution and the electrode shapes and media nor the way of an acoustic field application.

The change in the ECL peak power is mainly determined by the voltage on the electrodes, composition of the solution and the intensity of the acoustic vibrations in the cell. In Fig.1 the dependence of the relative ECL peak intensities I/I_o (where I_o is the ECL intensity without acoustic field) in a quasistationary regime in the field on the amplitude of the applied voltage for DPA (a) and for rubrene (b) is given. As it is seen from this figure the switching of an acoustic field decreases intensity of the emission at the threshold

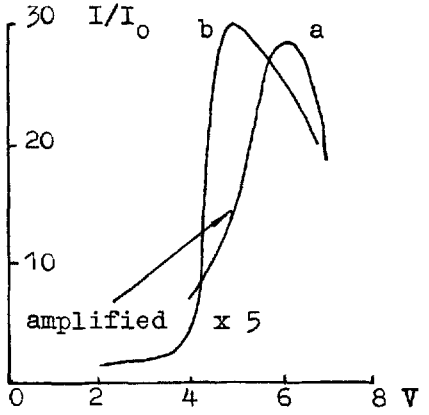

Fig.1. Dependence of the ratio I/I_o on the amplitude of an applied voltage.

potentials (i.e. the potentials corresponding to the ECL appearance), while the growth of the voltage amplitude and the switching of an acoustic field leads to an increase in the ECL intensity.

The ratio I/I_0 depends on the concentration of the electrolyte and the substance (Fig.2). For example, the concentration growth of the substance from 10^{-3}M to 10^{-2}M results in the intensity increase by 5 times for the DPA solution. By changing the electrolyte concentration from 5.10^{-3}M to 10^{-1}M the ratio I/I_0 rises approximately 4 times.

The ultrasonic effect is followed by an increase of the absolute value of the measured redox potentials (for

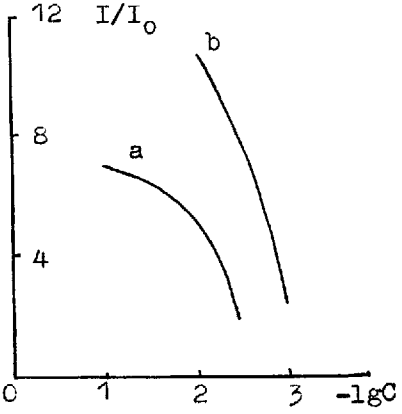

Fig.2. Dependence of the ratio I/I_0 on the concentration of the electrolyte (a) and the substance (b).

example, the oxidation potential $E_{(R/R^+)}$ is changed by 400 mV, and the reduction potential $E_{(R/R^-)}$ by 50 mV in perylene solution).

To the best of our knowledge an ultrasonic influence on the solution can be accompanied by a number of physicochemical phenomena[6,9]. We suggest that the essential influence on the ECL is mainly connected with the mixing effect of an acoustic field. This mixing is more intensive than the mechanical mixing particularly near the electrodes. The current passed through the electrochemical cell increases under the influence of the acoustic field. This indicates the increase of the neutral molecule flow to the electrode and consequently increase in the production of the cation and anion radicals at the electrode. The growth of the ion-radical number gives rise to a lengthening of the ECL light pulse (sometimes the duration can increase by 4 - 5 times). Moreover an acoustic mixing contributes favourably to the removal of the irreversible reaction products from the vicinity of the electrode.

The intensive solution mixing affects the recharge time of the double layer which determines the delay of the ECL pulse rising with respect to the moment of polarity change in the initiating exciting electric pulse as in the case of acousto-optic modulation[10].

It should be noted that the strong vortex flows must result in an increase of the ion-radical recombination coefficient in comparison with its diffusion value. The influence of ultrasonic field on the redox potentials changes the energetics of ECL reactions; a similar effect on dye laser cavity has been recently suggested in the literature[11]. It is known[12] the course of the reaction is determined by its free enthalpy

$$-\Delta H^{o} = E_{(R/R^{+})} - E_{(R/R^{-})} - T\Delta S^{o}$$

where $E_{(R/R+)}$ and $E_{(R/R^{-})}$ are the oxidation and reduction potentials, $T\Delta S^{o}$ is the entropy factor.

Thus the increase of the absolute magnitudes of $E_{(R/R^{+})}$ and $E_{(R/R^{-})}$ values causes an increase in the system enthalpy. The increase of this value might turn out to be enough for converting an energy deficient reaction into a sufficient one. Probably such a situation takes place, for example, in rubrene where the emission intensity considerably exceeds the ECL of the nonradiated solution but the emission intensity of DPA under irradiation tends to the peak intensity of the first pulse of the ECL.

Certainly all of the above phenomena contribute to the changing of the ECL under the acoustic influence. Further experiments and calculations let us estimate the contribution of each phenomenon. The results of the

experiments suggest that the application af the acoustic field provides valuable information about the electrochemical reactions in the solutions. These results testify that the acoustic field influences appreciably on the electrochemical reactions in solutions. It is noteworthy to emphasize that this permits to lead the reactions which do not take place under usual conditions of experiment.

We consider the investigation of ECL to be the most important under high intensities of the acoustic field where the ECL may exhibit new features.

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