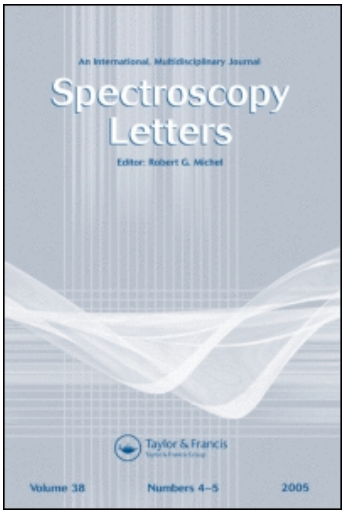

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Electrogenerated Exciting of Luminescence by Direct Current

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ELECTROGENERATED EXCITING OF LUMINESCENCE BY DIRECT CURRENT

Key words: ECL, Double Layer, Cathode's Emission

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INTRODUCTION Electrogenerated chemiluminescence (ECL) phenomenon has been known for more than 10 years and in general the mechanism of processes leading to light emission with the bipolar electrical excitation is clear.

The main reactions leading to ECL has been studied and the quantum yield of a number of systems[1,2,3] has been determined. However, practically the works on study and explanation of ECL observed under the solution electrolysis by d.c. current are not available. It is obvious that the ion-radical recombination possibility is insignificant in this case due to the absence of the opposite sign radical in the vicinity of the electrode. To explain the appearance of light emission a new mechanism is needed.

In this work we have studied the luminescence of anthracene, 9, 10-diphenylanthracene (DPA), rubrene, rhodamine 6G, 1,5-diphenyl-3-styrylpyrazoline (DPSP) in the d.c. current mode.

EXPERIMENT In this experiment a square quartz cell with platinum flat electrodes (5 x 15 mm) was used. Electrode spacing is about 7 mm. The solvents were N,N-dimethylformamide (DMF), acetonitrile (ACN), acetone which were purified according to the known methods[4,5,6]. Solutions were prepared in dry box.

As supporting electrolytes the fresh-calcinated LiCl and tetra-butilammonium perchlorate (TBAP) dried at 75°C were used. The light intensity was registered by memory oscillograph C8-1 with FEU-79 photoelement.

RESULTS All studied dyes giving emission with the bipolar electrical excitation as well as rhodamine 6G have the d.c. current excited luminescence. The thin range of emission appears in the vicinity of the cathode. This luminescence range could not be resolved by the observation through 130^{x} multiplying optical system.

The luminescence spectrum is identical to the emission spectrum obtained with the photoexcitation. The voltage when emission appears depends on the type of electrode, electrolyte and its concentration. The intensity of luminescence is proportional to the elec-

tric current and increase with the voltage (Fig.1) The anthracene luminescence ($1o^{-3}$M) in DMF with LiCL as the supporting electrolyte (5. 10^{-2}M) can be easily observed in the daylight when the voltage is of 10 v. The saturation of the solution by helium and O_2 results in a drastic decrease of the emission intensity. Practically, oxigen quenches luminescence completely and helium by 50 - 60%. When electrolysis of the solution which contains some luminophors (rubrene, DPSP, anthracene) takes place, rubrene fluorescence is first to occur (voltage value is ~1,5v). With the voltage increase the emission spectrum shifts to shorter wavelengths, i.e. in succession DPSP and anthracene fluorescene appears.

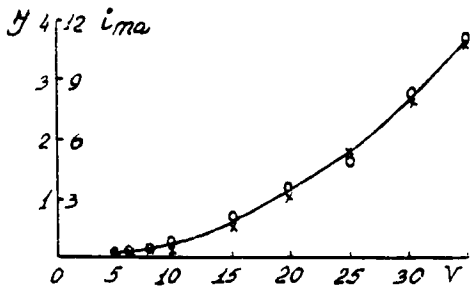

Fig.1 Luminescence intensity (o) and current (x) dependence on electrode voltage in anthracene solution (10^{-3}M) in N,N-dimethylformamide with supporting electrolyte TBAP (5.10^{-2}M).

DISCUSSION The mechanism of luminescence appearance under electrolysis of the solution by d.c. current could not be explained by the models of the ion-radical

annihilation. Emission occurs at the cathode 600-800ms after applying voltage while diffusion processes are not able to transfer cations to the reaction region in such a short period. The applied degassing of the solution excludes the possibility of luminophor chemiluminescence reactions with oxygen. Apparently one could not take seriously the possibility of radiation interaction of dissolved luminophors with impurities as the emission is observed in different solvents and the intensity is practically independent on the purification degree of solvent, electrolyte and fluorescence. The experimental results show that the light intensity increase with the voltage increase, that the intensity depends on the solution conductivity and that the luminescence spectra are typical for the dissolved fluorescent molecules. Experimental characteristics have the same nature as those of electrogenerated chemiluminescence observed in the solid organic phosphors and dielectric liquids. Thus it is quite possible that the fluorescence occuring at the cathode with the solution electrolysis by direct current results from the excitation of luminophor molecules by energetic electrons.

Elementary electrochemical action can be considered as processes caused by a high electrical field strength. These fields result from the forming of do-

uble electric layer at the metal and liquid inter - face and reach the value of $\sim 10^8$ v/cm i.e. values comparable with those of intermolecular field. Thus at the anode the autoionization of the depolarizer molecules which reached the double layer may occur with sufficiently great degree of probability. At the cathode such an electric field strength results in more or less intensive cold emission of electrons from metals. Moreover an excessive energy (~1-2 ev) is gained due to the emitted electron solvation that results in marked decrease of the efficient yield in comparison with that in vacuum and thus favours the cold emission process[7].

The emitted electrons are accelerated by the double layer field and obtain some energy. In solution this energy can be lost due to the interaction of the molecules of solvent, luminophor and electrolyte ions. In particular, the electrons can recombine with the positively charged particles, adhere to the molecules of depolarizer forming the negative ions, participate in the excitation collisions with the molecules of solvent or luminophor. In this case the molecules absorb the energy of free electrons and transit into higher electron vibrational state leading to the fluorescence or dissociation . Under appropriate conditions the electrons can be solvated and in the

solvated state can react with the different reactions. It is difficult to make a quantitative estimation of the electron energy injected from metal into solution. However, knowing the absorption spectra of the investigated luminophors and consequently the quantum energy necessary for their excitation one may consider the presence of the electrons of order of several electron-volts in the vicinity of the cathode. In case there are some different luminophors the first substance to be excited is the one with the lower absorption energy. With the energy increase at the electrodes the electrons will gain higher energy and the emission spectrum of mixture should shift to the blue region. Such dependence is observable from the experiment. When electrolysis of the solution which contains some luminophors (rubrene, DPSP and DPA) takes place, rubrene fluorescence is first to occur. With the voltage increase the emission spectrum shifts to the shorter wavelength, i.e. in succession DPSP and DPA fluorescence appears.

The saturation of solution by oxygen or helium results in the effective free electron capture by the oxygen molecules or a decrease in the electron temperature of the injected electrons as a result of the collisions with the helium molecules, i,e. it results in the emitted intensity decrease. It is evident that

not all electrons from the cathode emission should produce excitation of the electron level of the molecule. For this case the electrons with the energies E_0 which correspond to the lowest excitation potential of the luminophor are needed. Of course, the luminophor excitation can be accomplished under energy transfer from the excited solvent molecules.

If one denotes by D the total probability of all processes leading to light emission the luminescent emission intensity will be proportional to the following expression:

$$J = \mathcal{D} n \int_{E_0}^{\infty} \varepsilon(E)\, dE \,. \qquad (1)$$

where n is the density of electrons in equilibrium, the energy distribution function of the electron outside the double layer. Evidently in the steady state condition:

$$\frac{dn}{dt} = N - \alpha n_0 n - \eta n - \delta n = 0 \qquad (2)$$

where N is the number of electrons exciting in the solution in 1 sec per unit surface of cathode, α is the recombination coefficient of electrons with the positive ions, n_0 is the concentration of positive ions; η is the coefficient of adherence of electrons to the molecules of liquid and luminophor leading to the formation of the negative ions; δ is the coefficient connected with the solvation of electrons.

Hence:

$$n = \frac{N}{\alpha n_0 + \eta + \delta} = \frac{N}{p} \quad . \qquad (3)$$

To determine N we use the equation of Fowler-Nordheim for the current of the autoelectronic emission:

$$N = \frac{J}{\mu x} = \frac{Bx}{\mu} e^{\left(-\frac{A}{E}\right)} \quad . \qquad (4)$$

where μ is the electrical conductivity of the solution; x is the electric strength of double layer; A and B are the constants of the Fowler-Nordheim equation. The thickness of the Helmholtz layer d can be considered as a constant and x can be replaced by U/d where U is the applied voltage. The Maxwell function can be used as the distribution function. Then

$$J = \frac{\mathcal{D} B u e^{\left(-\frac{Ad}{u}\right)}}{\mu d p} \int_{\varepsilon_0}^{\infty} C e^{\left(-\frac{E}{kT}\right)} dE \quad , \qquad (5)$$

i.e.

$$J \sim u e^{\left(-\frac{1}{u}\right)} \quad . \qquad (6)$$

Thus, when the process is controlled by the cold emission of the electrons from the cathode, the dependence of ln (U/J) on 1/U should be a linear one. The values obtained from the experiment are shown dotted in figure 2 and the theoretical curve is given. The satisfactory

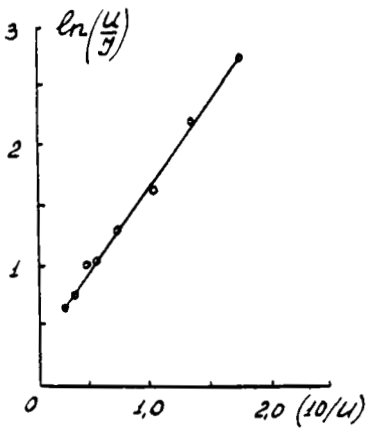

Fig. 2 Dependence of relation $\ln\left(\frac{U}{J}\right)$ on $\frac{10}{U}$ (continuous curve) and experimental value for anthracene solution (10^{-3}M) in N,N-dimethylformamide with supporting electrolyte TBAP(5.10^{-2}M)

agreement of the theoretical and experimental dependences is available.

CONCLUSION The investigation results and also the correspondence of the experimental data to the theoretical calculation speak in favour of the cathode emission mechanism. It seems to us that the appearance of the luminophor emission under the electrolysis by

direct current evidences the exciting in the solution of the free electrons possessing the energy enough for the excitation of the electronic vibrational level of the molecules.

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