In recent times electrochemiluminescent (ECL) compositions have attracted considerable attention as the basis for fabrication of optoelectronic systems [1, 2]. Therefore, it is of practical importance to study mechanisms for the appearance of excited states of efficient ECL compositions; one such efficient ECL system is a solution of pyrazoline derivatives in dimethylformamide with LiCl as the electrolyte [3, 4].

Light bursts from these solutions consist of two brightness waves and an afterpulse (a third brightness wave). It has been hypothesized that the mechanism responsible for the first brightness wave and the afterpulse involves molecules which have been raised to the excited triplet [4] and singlet [5] states as a result of electron injection from the electrode to the ion-radicals. However, this hypothesis rests on very limited experimental evidence [6] and on a method [6] which, as we shall show, does not apply to the solution described above. Therefore, it cannot be assumed that the origin of the brightness waves is known; a solution of this problem requires further investigation.

This paper considers the nature of the first and second brightness waves and the afterpulse in ECL. It is shown that LiCl is not neutral in the range of excitation potentials encountered in the course of operation and that it may play a role in the excitation of activator molecules.

Reactor preparation and the excitation and recording of ECL were conducted as described previously [3]. The pin-shaped working electrode was placed inside an auxiliary electrode of spiral shape made of platinum wire having a diameter of 0.5 mm. The voltage applied to the electrode consisted of alternating positive and negative pulses having durations of 0.5 and 0.1 sec.

First Brightness Wave. In [4, 5], LiCl was assumed to be an inert electrolyte over the range of excitation voltages; this made it possible to use Feldberg's method to determine the mechanisms responsible for the formation of the first and second brightness waves. The ECL from 1.5 diphenyl-3-styril-pyrazoline-2 (DPhSP) was not independent of the excitation voltage (see Fig. 1). Oxidation polarograms were obtained on platinum disk electrodes rotating at 860 rpm and reduction polarograms on mercury droplet electrodes; these were measured with an LP-7 device (from the Czechoslovakian SSR). The ratio of the areas of the disk and the auxiliary electrodes was 1:100.

![Fig. 1. Polarograms of DPhSP (5·10⁻³ mole/liter) with background electrolyte of tetrabutylammonia (5·10⁻³ mole/liter) (1), LiCl (5·10⁻² mole/liter) (2), and perchlorate of tetrabutylammonia (5·10⁻¹ mole/liter) (3). The solvent is dimethylformamide.](image-url)
Fig. 2. Diagram showing the formation of the excited molecules responsible for each of the brightness waves (a) (A are the electron acceptors) and the brightness waves (b) of DPhCP (10^{-2} mole/liter) with LiCl electrolyte (1-3) and with perchlorate of tetrabutylammonia (4) (5·10^{-2} mole/liter) with $t_{\text{int}} = 0$ (1, 4) 8 sec (2), and 10 sec (3). The time in milliseconds is plotted along the abscissa.

Fig. 3. Brightness waves of DPhSP (5·10^{-2} mole/liter) with the following electrolytes: a) LiCl, $C_e = 5·10^{-2}$ mole/liter; b) LiCl, $C_e = 10^{-2}$ mole/liter; $V^-- = 3$ (1, 4), 4 (2, 1', 3'), and 5 V (3, 2'); $V^+ = 3$ (1-3, 1', 3'), 4 (4, 4'), and 5 V (5).

Fig. 4. The brightness waves of DPhSP excited by a sinusoidal voltage. $V = 5$ V (a, and 3'), 6 V (2'), and 7 V (1'); $f = 0.35$ Hz (1), 0.23 Hz (2 and b), and 0.16 Hz (3).

Oxidation of Cl^- begins at 1.2 V relative to a water-saturated calomel electrode (rel. s.c.e.). The oxidation potential of a DPhSP half-cell is also equal to 1.2 V rel. s.c.e. When ECL is excited by the application of a potential large enough to saturate the current on the polarogram of DPhSP ($V > 1.4$ V rel. s.c.e.), cation-radicals of the activator are formed, but chloride anions are also oxidized (1). Atomic chlorine transforms into molecular chlorine at a specific reaction rate (2).

$$\text{Cl}^- \rightarrow e \rightarrow \text{Cl}, \quad (1)$$
$$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2. \quad (2)$$

Both Cl and Cl_2 have electron-acceptor properties similar to those of the cation-radical activator $R^+$. During the negative portion of the applied voltage cycle, the following reactions can occur at the surface of the electrode in addition to the recombination of the ion-radical activator: