UDC 532.783(045)

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MECHANISM OF DIMERIZATION OF VIOLOGENS IN LIQUID CRYSTALLINE MEDIUM

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***Abstract*—*This work presents the analysis of experimental data on optical properties of viologens introduced to the liquid crystalline medium stipulated by the application of increasing voltage values. These data along with quantum mechanical theory allowed to specify the mechanism of dimerization of violoden molecules which leads to the colour change of the liquid crystal-viologen sample. Specifically, the dimerization of viologen molecules in liquid crystalline medium occurs due to interaction between viologen molecules, which were fully reduced under the action a voltage applied, and initial viologen molecules.*

Index Terms—Lyotropic liquid crystals; viologens; optical spectroscopy; absorption; quantum mechanics.

I. INTRODUCTION

It was shown that combining lyotropic liquid crystals (LLC) with electrochromic impurities, namely viologens, allows for creating new class of liquid crystalline materials with regulated optical properties. Physical and chemical properties of such materials were widely investigated in series of works [1]–[3]. Possible practical applications require further investigations concerning intermolecular processes taking place under the action of an electric field and causing colour modifications of interest.

II. ANALYSIS OF INVESTIGATIONS AND PUBLICATIONS

It is known that application of an electric field leads to the reduction of viologen molecules and formation of coloured radical cations and dimers [4], [5]. Spectrometry data for LLC-viologen composites [6] showed that viologens reduce under the action of an electric field in the lyotropic liquid crystalline matrix with formation of blue-coloured radical cations and red-coloured dimers. Their formation is confirmed by the presence of characteristic absorption bands (λ = 395, 605 nm, and λ = 365, 520 nm, respectively) in spectra [6]. Dimerization could be stipulated by two different processes. According to the work [7] dimerization of viologens in water is caused by interaction between two radical cations when their concentration in a sample reaches some critical parameter. In recent works dimerization is associated with interaction between initial viologen molecules and molecules undergone two-electron reduction [8].

Thus, the **aim of the present work** was to combine all the known experimental data concerning formation of viologen dimers in liquid crystalline medium and to specify the mechanism of dimerization.

III. EXPERIMENTAL DATA

Voltamperometry and spectrometry experimental data indicate that in water-containing lyotropic liquid crystalline medium dimerization more likely passes in accordance with the second process. According to the volt-ampere characteristic [6] viologen molecules reduce in LLC matrix in two stages. The first stage (Curve 2, U = 2,5 V) corresponds to the formation of radical-cations, and the second one (Curve 3, U = 3 V) corresponds to the formation of colourless biradicals with plain quinoid structure. The last fact is confirmed by absorption spectrum (Fig. 1) which shows no significant absorbance at voltage value of 3 V. The dimerization process starts after increasing the voltage up to 4 V (Curve 4). Thus, dimerization cannot be caused by radical cation – radical cation interaction since there are no radical cations in the sample at voltage values exceeding 3 V as shown by absorption spectra (Fig. 1). However, initial or non-reduced viologen molecules could still be present in the volume of a sample moving towards electrodes under the action of an increased voltage and interacting with fully reduced molecules to form dimers.

IV. THEORETICAL JUSTIFICATION

For theoretical proof for the dimerization mechanism it is reasonable to turn to the quantum mechanics [9].

In the case of viologen dimerization we talk about the formation of so called physical dimers. Physical dimers form in the case of two equal molecules, which are located closer one to another than to other similar molecules and have specific orientation. At the same time they do not form any chemical bond with each other.

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