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MECHANISM OF DIMERIZATION OF VIOLOGENS IN LIQUID CRYSTALLINE MEDIUM

This work presents the analysis of experimental data on electrooptical properties of viologens incorporated into the liquid crystalline medium. These data along with theoretical considerations allow specifying the mechanism, which leads to the double color change in the liquid crystal – viologen samples stipulated by the application of increasing voltage values. Specifically, it is proved that the first color change takes place due to the one-electron reduction of viologen molecules, and the second color change is caused by the dimerization between viologen molecules, which were fully reduced under the action of a voltage applied, and initial viologen molecules.

K e y w o r d s: lyotropic liquid crystals, viologens, optical spectroscopy, absorption, dimerization.

1. Introduction

Works devoted to the investigation of chemical and physical properties of nonconventional classes of liquid crystals (LC) significantly extend the range of fundamental knowledge on these materials, which include organosilicon compounds [1, 2], Schiff base metal complexes [3, 4], and ionic thermotropic and lyotropic liquid crystals of metal alkanoates. While thermotropic liquid crystals, when being in the mesophase or glassed mesophase [5, 6], have significant optical absorption in the visible region, metal alkanoates that form the lyotropic liquid crystalline phase generally do not absorb. To provide liquid crystalline materials with desired optical properties, one needs to combine lyotropic ionic liquid crystals (LILC) and different impurities, namely polymethine dyes [7], viologens, *etc.* Particularly, the introduction of photo- and electrochromic impurities such as viologens allows creating materials with optical properties that could be regulated, by using the ultraviolet irradiation or application of an external electric field. Structural and electrooptical peculiarities of such materials were previously investigated in a number of works [8–10]. Possible practical applications require a further specification of intermolecular processes taking place under the action of an electric field and causing color modifications of interest.

The present work discloses the possible mechanism of reduction and dimerization of viologen molecules introduced into a lyotropic ionic liquid crystalline medium under the action of an electric field.

2. Experimental Methods and Materials

The lyotropic ionic liquid crystalline phase was formed by mixing a powder of a potassium caprylate ($C_7H_{15}COO^-K^+$) with water in the 1 : 1 weight proportion at room temperature. LILC samples were doped by N,N′-diheptyl-4,4′-dipyridilium dibromide ($HD^{2+}2Br^-$) viologen with the general structural formula shown in Fig. 1. The viologen content in LILC samples amounts to 2% by weight.

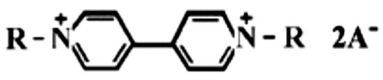

Fig. 1. General structural formula of $HD^{2+}2Br^-$ viologen. *R* is a substitute (C_7H_{15}), *A* is a counterion (Br^-)