ELECTROOPTICAL AND NONLINEAR OPTICAL PROPERTIES OF LYOTROPIC LIQUID CRYSTALS DOPED WITH ELECTROCHROMIC VIOLOGENS

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This work presents the results of experimental studies of the electrooptical and nonlinear optical properties of lyotropic ionic liquid crystals (LILC) with soluted electrochromic admixtures of viologens. It is established that the Smectic A ordering of the LILC of potassium caprylate is not disrupted by the introduction of viologens. Moreover, LILC-viologen composites obtain electrochromic properties inherent to viologens, which produce colored radical cations and dimers, while reducing. The presence of radical cations and dimers is fixed by the optical absorption spectra. It is found that, under the action of an electric field, the LILC-viologen samples form bilayer structure consisting of a liquid crystal layer and an absorptive layer of viologen redox products (radical cations and dimers). A dynamic grating recording is realized and studied in bilayer LILC-viologen cells. It is determined that the recording takes place in the colored layer of viologen redox products. The possible mechanism of grating recording in LILC-viologen cells is proposed.

1. Introduction

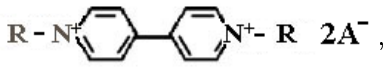
Up to now, the nonlinear optics of liquid crystals (LC) remains quite an underinvestigated area. The discovery of such properties in liquid crystals and their thorough studying leads to new nontraditional applications of LC materials. In works [1–3], it was shown that a good nonlinearity with fast response times was observed for lyotropic LC on the base of metal-alkanoates doped with different dyes and photosensitive admixtures and for thermotropic LC of cobalt alkanoates.

Among the above-mentioned materials, it is worth to note lyotropic ionic liquid crystals (LILC) doped with viologens, which are known due to their electrochromism. Electrochromic properties of viologens appear also in lyotropic LC media, making those materials promising for the further practical application.

In the present article, we give the detailed overview of electrooptical and nonlinear optical properties of the LILC-viologen complex materials and consider a possible mechanism of the optical nonlinearity in such systems.

2. Experimental Methods and Materials

Electrochromic admixtures are represented by two compounds of the viologen class with the common chemical formula:



where **R** is a substitute, and **A** is a counterion.

For the first viologen (N,N'-diheptyl-4,4'-dipyridylium dibromide – $HD^{2+}2Br^{-}$) R = C_7H_{15}, A^{-}= Br^{-}; for the second one (N,N'-di(2-carboxyethyl)-4,4'-dipyridylium dichloride – $CED^{2+}2Cl^{-}$), R=$(CH_2)_2COOH$, A^{-}=Cl^{-}.

Viologens are well soluble in water; therefore, they are also soluble in a lyotropic LC matrix. The lyotropic ionic liquid crystal on the base of potassium caprylate is formed under the mixing with water in the 1:1-proportion. Its chemical formula is $C_7H_{15}COOK{:}H_2O$. For preparing the samples, a powder of potassium caprylate was mixed with viologens (2% by weight) and then with water.

The obtained LILC-viologen system is characterized by the bilayer Smectic A ordering, which is not disrupted by the introduction of viologens [4]. Viologen molecules are harmonically built-in the LILC matrix, so that their long-chained substitutes are situated along alkyl chains of potassium caprylate. Dipyridylium viologen rings are located in the electrostatic interlayer formed by potassium cations, water, and negatively charged oxygen atoms (Fig. 1). X-ray data for crystalline viologens [5] showed that the dipyridylium part of a viologen molecule has a size proportional to that of the electrostatic interlayer in LILC. Arranging the viologen molecules in such a way, the LILC matrix facilitates their transfer along electrostatic layers under the application of an electric field.

For the electrooptical and nonlinear optical investigations of the LILC-viologen samples, we used sand-