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STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF COMPLEX COMPOUNDS

Structure and Intermolecular Interactions in Ionic Liquid Crystals Doped with Electrochromic Viologen

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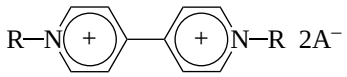
Abstract—The results of an investigation of structural and electrooptical properties of potassium caprylate lyotropic liquid crystals (LCs) doped with electrochromic viologen are presented. The samples are colored when an electric field is applied. The color deepens with the voltage applied, and relevant features appear in electronic absorption spectra. Two stages may be recognized in the processes that occur in a sample in the field. The first stage (at 2–2.5 V) involves the formation of radical cations (RCs) from viologen molecules, which makes the samples blue (two absorption bands appear at wavelengths of 395 and 610 nm in optical spectra). At the second stage (at 3.5–4 V), the radical cations are dimerized, and the sample becomes red (the spectra show bands in the region of 365 and 520 nm). Absorption in a lyotropic LC increases with the viologen concentration increasing from 1 to 2 to 4%. Small-angle X-ray scattering was measured on unoriented samples of pure potassium caprylate with thicknesses ranging from 30 μm to 1 mm. In all samples, a smectic order was observed in lyotropic ionic LC (LILC). From the X-ray scattering data, the bilayer thickness and the smectic correlation length were computed. It was inferred that viologen molecules, when present in low concentrations (1–4%), are organically incorporated into the matrix without spoiling the layer order intrinsic to the matrix.

Liquid crystals (LCs) are of both scientific and applied interest thanks to their wide electrooptical applications. LCs are nonlinear-optical media for data visualization, processing, and storage systems. One route to design novel photorefractive materials is to dope LC matrices with electro- and photochromic dopants. Quaternary bipyridylium salts (their trivial name is viologens) can serve as such dopants. Their important feature is the ability to enter reversible redox reactions with the formation of radical cations (RCs) that deeply color LCs [1].

The goal of this work was to study the electrooptical and structural properties of viologen-doped lyotropic ionic liquid crystals (LILCs) and to elucidate which processes occur inside a sample in an external electric field. Intrinsic ion conductivity and high viscosities are characteristic of LILCs [2]. High viscosities are essential for the reason that RCs have longer lifetimes in viscous media.

EXPERIMENTAL

The test samples were LILCs of potassium caprylate with water ($C_7H_{15}COOK–H_2O$) with a weight ratio of 1 : 1 doped with 2 wt % diheptylviologen and having the formula



where R = C_7H_{15}, and A = Br^-.

Electronic spectra in the visible were studied on a spectrometer equipped with an MDR-6 monochromator. Sandwich cells with their inner surfaces coated with ITO electrodes were used in electrooptical measurements. The layer thickness (≈30 μm) of such cells was adjusted using Teflon liners. The measurements were performed at room temperature (T = 293 K).

Electrochemical investigations were carried out using cyclic voltammetry on a PI-50-1.1 potentiostat equipped with a PR-8 programmer. Current–potential curves were recorded on a PDP self-recording potentiometer. The potential scan rate was 20 mV/s. The electrochemical cell used was composed of two glass plates coated with a thin, transparent, conducting titania layer (δ = 20 μm). The reference electrode used was a platinum wire.

The structure of the undoped LILC and viologen-doped LILCs was investigated using small-angle X-ray scattering. The experiment was carried out on a small-