

# CUBIC SUSCEPTIBILITY AND HYPERPOLARIZABILITY OF THE LYOTROPIC LIQUID CRYSTAL–VIOLOGEN SYSTEM

A.B. BORDYUH, YU.A. GARBOVSKIY<sup>1</sup>, G.V. KLIMUSHEVA<sup>1</sup>,  
S.A. BUGAYCHUK<sup>1</sup>, T.A. MIRNAYA<sup>2</sup>, G.G. YAREMCHUK<sup>2</sup>,  
A.P. POLISHCHUK

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National Aviation University

(1, Prosp. Komarova, Kyiv 03058, Ukraine),

<sup>1</sup>Institute of Physics, Nat. Acad of Sci. of Ukraine

(46, Prosp. Nauky, Kyiv 03680, Ukraine; e-mail: klimush@iop.kiev.ua),

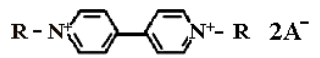
<sup>2</sup>Institute of General and Inorganic Chemistry, Nat. Acad of Sci. of Ukraine

(32/34, Prosp. Palladina, Kyiv 03142, Ukraine)

Nonlinear optical properties of the “lyotropic liquid crystal–viologen” system are investigated. The system shows electrochromism under the action of an external electric field. For the colored samples, the recording of dynamic holographic gratings is obtained, by using the pulse laser method. The main characteristics of a recording on such samples are studied. On their base in view of the electrooptical properties of the system, the mechanism of the recording of gratings is proposed. The recording is realized due to a change in the polarizability of the  $\pi$ -electron system of viologen derivatives under the action of an intense laser radiation. The main nonlinear optical parameters ( $n_2$ ,  $\chi^{(3)}$ ,  $\gamma$ ) of the system under study are determined.

## 2. Materials and Experimental Methods

The lyotropic liquid crystal (LLC) matrix is formed by potassium caprylate with water (the chemical formula is  $C_7H_{15}COOK:H_2O$ ) in 1:1 proportion. As electrochromic admixtures, we chose two viologens, namely: (1) N,N'-diheptyl-4,4'-dipyridilium dibromide ( $HD^{2+}2Br^-$ ) and (2) N,N'-di(2-carboxyethyl)-4,4'-dipyridilium dichloride ( $CED^{2+}2Cl^-$ ) which differ by substitutes near nitrogen atoms and counterions. The common structural formula for both viologens is as follows:



where R is a substitute, A is a counterion. In the case of  $HD^{2+}2Br^-$   $R = C_7H_{15}$ ,  $A^- = Br^-$ , and  $R = (CH_2)_2COOH$ ,  $A^- = Cl^-$  for  $CED^{2+}2Cl^-$ . The content of viologens in the samples is 2% by weight.

The structure of a viologen-doped LLC had been investigated in [6] using a method of small-angle X-ray scattering. Studied LLC-viologen samples have structure of smectic A. Admixture concentrations of 2–4% by weight do not break the LC ordering, and viologen molecules are built into the LLC matrix.

The LLC matrix performs significant functions in the investigated samples: 1) as a consequence of a planar orientation of the LLC, admixture molecules are also plane-oriented; this facilitates the electric field-stipulated adsorption of viologen molecules at the cathode with the further formation of a photosensitive layer of viologen's reduction products; 2) high viscosity and elastic characteristics of LLC promote an increase of the lifetime of colored reduction products and the maintenance of a layer morphology during holographic recording; 3) a heat contact between the viologen layer

## 1. Introduction

It is known that dipyrilidyl quaternary salts (viologens) in solutions [1,2], polymeric matrices [3], liquid crystals [4], and in the crystalline state [5] exhibit various physico-chemical properties such as electro-, thermo-, and photochromism. Complexes based on viologens could be used as redox indicators, light-sensitive systems, electron transfer catalysts, color filters of variable density, etc.

“Lyotropic liquid crystal–viologen” systems show electrochromism under the action of an external electric field. Earlier [4], main electrooptical characteristics of these systems were studied, and peculiarities of the redox reactions of viologens in a liquid crystal matrix were determined.

The present work considers both the nonlinear optical properties of the system and the holographic recording under the action of a pulse laser radiation on samples of a lyotropic liquid crystal with admixtures of viologens.

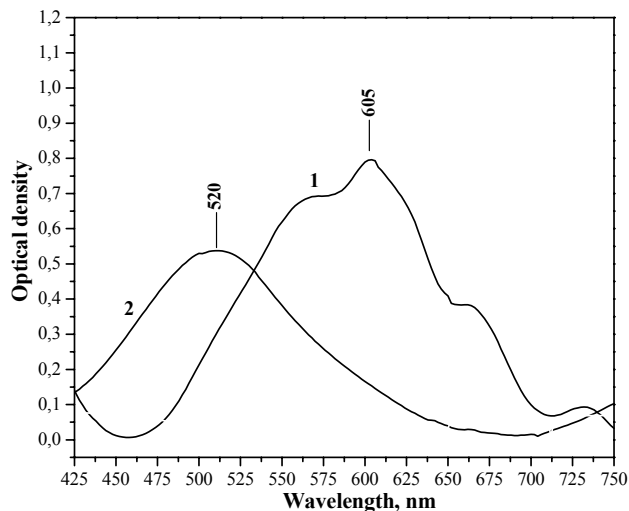


Fig. 1. Absorption spectrum of LLC doped with  $\text{HB}^{2+}2\text{Br}^-$  under the action of the electric field. Curve 1 corresponds to the voltage  $U = 2.5$  V, curve 2 to  $U = 4$  V. Cell thickness is  $20 \mu\text{m}$

and LLC causes the recording of dynamic but not stationary gratings which could appear as a result of the excessive heating and the ablation of a layer substance. The use of LLC is also convenient from a technological point of view – an LC in use does not flow as a liquid because of great viscosity.

For the study of electrooptical and holographic characteristics of samples, we used sandwich cells, whose inner surface was covered with ITO-electrodes. The thickness of the layer in such a cell varied from 15 to  $20 \mu\text{m}$  by teflon gaskets.

For the investigation of nonlinear optical properties of LLC-viologen samples and for the definition of their main holographic characteristics, we used the methods of dynamic holography and those for nonlinear transmission measurement. The two-beam scheme was applied for dynamic gratings recording. We used the second-harmonic radiation of a pulse Q-switched Nd:YAP laser ( $\text{TEM}_{00}$ -mode, wavelength  $\lambda = 539.8$  nm, pulse duration  $\tau = 20$  ns, and the frequency of pulses  $\nu = 3$  Hz).

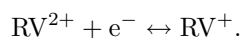
The linearly polarized laser radiation was divided into two beams of the same intensity which were brought then together on the sample with a defined angularity. Varying the contraction angle and the laser beam intensity, it was possible to study the corresponding diffraction efficiency dependences. The incident radiation intensity and the intensity in the first diffracted order were fixed, by using photodiodes. Then the signals were sent to the digital oscillograph.

Recorded gratings were read by a testing nonpolarized radiation of a continuous He-Ne laser (power  $P = 2$  mW,  $\lambda = 630$  nm). Reading the grating allowed us to investigate their relaxation kinetics in a microsecond range.

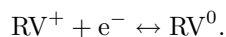
### 3. Results and Discussion

#### 3.1. Electrooptical investigations

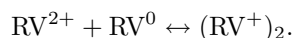
It is known [3] that, under the action of an electric field, two-charged dipyrindyl dication of viologen reduces in two steps with one electron taking part in each stage. At the first stage, radical cations (RC) strongly colored in blue appear to be a product of the one-electron reduction of viologen molecules:



At the second stage, a radical cation catches one more electron and transforms into a biradical which instantly turns into a neutral molecule with a plane quinoid structure [2,5]:



Or, in the other case, molecules reduced to biradicals could interact with initial ones, thus forming dimers and even bigger associates which are characterized by a red coloring [3,7]:



The injection of viologens into LLC media doesn't influence practically their reduction reactions, which is proved by volt-ampere characteristics [4].

For the samples containing an admixture of  $\text{HD}^{2+}2\text{Br}^-$ , the formation of radical cations is observed at the voltage  $U = 2.5$  V. In the absorption spectra, a wide band appears having an optical density maximum at  $\lambda = 605$  nm (Fig. 1, curve 1). At the voltage  $U = 3$  V, two-electron reduction takes place, and the sample becomes colorless. The following increase in the voltage up to  $U = 4$  V causes the initial molecules to come from the deeper layers of the sample and to interact with biradicals forming dimers. The dimers' absorption band has a maximum at the wavelength  $\lambda = 520$  nm (Fig. 1, curve 2).

It is worth noting that, under the action of an electric field, viologen molecules are adsorbed at the cathode, where their following reduction takes place. Thus, the sample becomes two-layered, and an absorptive layer of viologen's reduction products is formed in the near-cathode region. According to our estimations based on

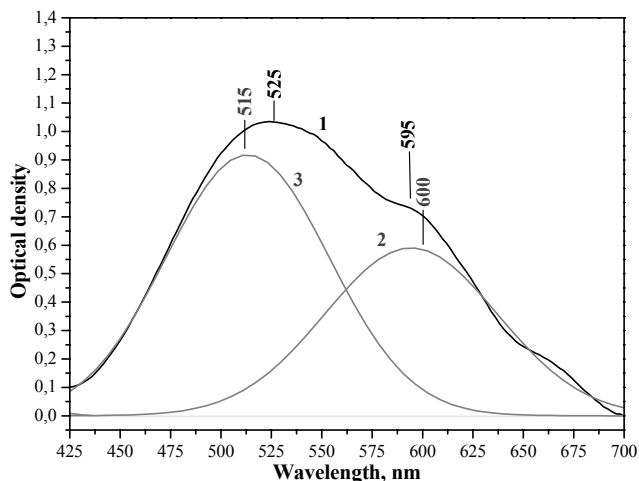


Fig. 2. Absorption spectrum of LLC doped with  $\text{CEB}^{2+}2\text{Cl}^-$  under the action of an electric field. Curve 1 corresponds to the voltage  $U = 3$  V, curves 2 and 3 were obtained as a result of the Gaussian factorization of curve 1. Cell thickness is  $20 \mu\text{m}$

the viologen concentration in the LLC, the thickness of this layer could not exceed  $400 \text{ nm}$ .

Due to the high viscosity of an LLC matrix, colored viologen's reduction products have a longer lifetime as compared with fluid solvents. Both reduction stages are reversible. That is, after switching off an electric field, the samples relax gradually to the initial state. At the repeated switching-on of an electric field, the reduction reactions are observed again.

In the samples containing an admixture of  $\text{CED}^{2+}2\text{Cl}^-$ , the running of reduction reactions does not allow us to distinguish both stages. This can be related to the presence of functional carboxyl  $\text{COOH}$ -groups in viologen molecules. These groups participate in the formation of intramolecular hydrogen bonds, which, in its turn, influences the velocity of reactions. After applying the voltage  $U = 3$  V, the sample is colored in violet. A wide band with two maxima at  $\lambda = 525 \text{ nm}$  and  $\lambda = 595 \text{ nm}$  (Fig. 2, curve 1) appears in the absorption spectra. Factorizing the spectrum into Gaussian components, it is possible to distinguish two separate absorption bands which obviously characterize radical cations ( $\lambda = 600 \text{ nm}$ , Fig. 2, curve 2) and dimers ( $\lambda = 515 \text{ nm}$ , Fig. 2, curve 3). The lifetime and the reversibility in such samples are comparable with similar characteristics of the  $\text{HD}^{2+}2\text{Br}^-$  samples.

### 3.2. Holographic recording of dynamic gratings

In the interference field of two laser beams crossing on the sample, a modulation of the complex refractive index

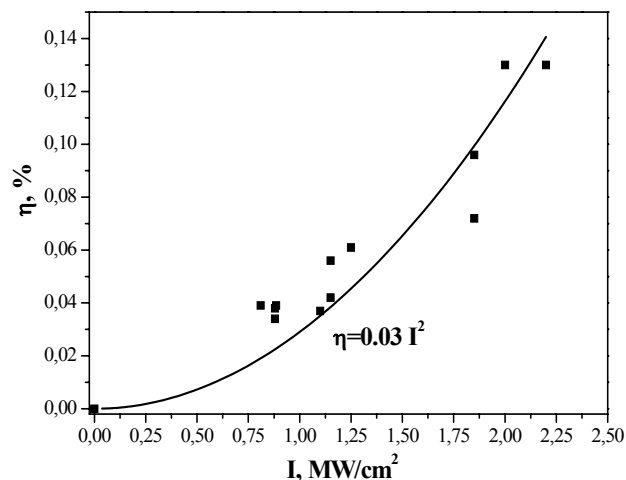


Fig. 3. Diffraction efficiency ( $\eta$ ) versus the laser radiation intensity ( $I$ ) for the colored samples of  $\text{LLC-HB}^{2+}2\text{Br}^-$  ( $U = 4$  V). The grating period  $\Lambda = 20 \mu\text{m}$ , the optical density  $D = 0.46$  (when  $I = 0.38 \text{ MW/cm}^2$ ), the cell thickness  $d = 20 \mu\text{m}$

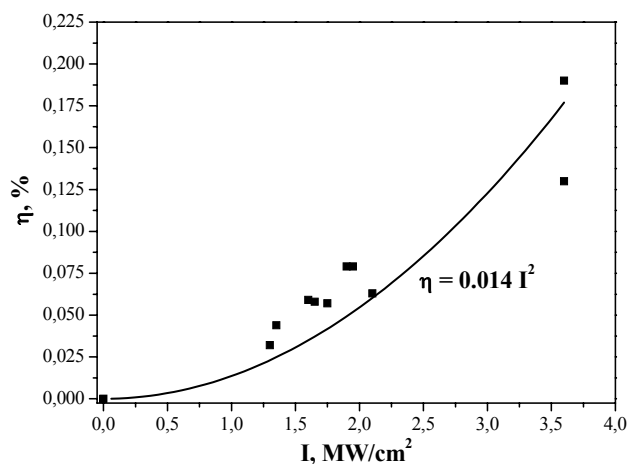


Fig. 4. Diffraction efficiency ( $\eta$ ) versus the laser radiation intensity ( $I$ ) for the colored samples of  $\text{LLC-CEB}^{2+}2\text{Cl}^-$  ( $U = 2$  V). The grating period  $\Lambda = 20 \mu\text{m}$ , the optical density  $D = 0.45$  (when  $I = 0.38 \text{ MW/cm}^2$ ), the cell thickness  $d = 20 \mu\text{m}$

takes place, i.e. we observe the recording of a diffraction grating. One laser pulse is enough for the recording. Usually, we see few diffraction orders in a self-diffraction regime. The value of the Cook-Klein parameter ( $Q < 0.1$ ) indicates that the recorded gratings are thin.

It was established that a diffraction efficiency measured in the self-diffraction regime depends in the second order on the intensity of a recording laser radiation (Figs. 3 and 4). Such a dependence indicates a cubic optical nonlinearity of the investigated samples.

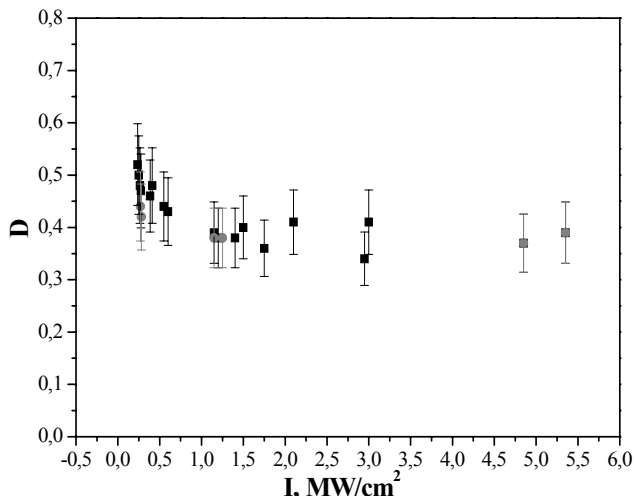


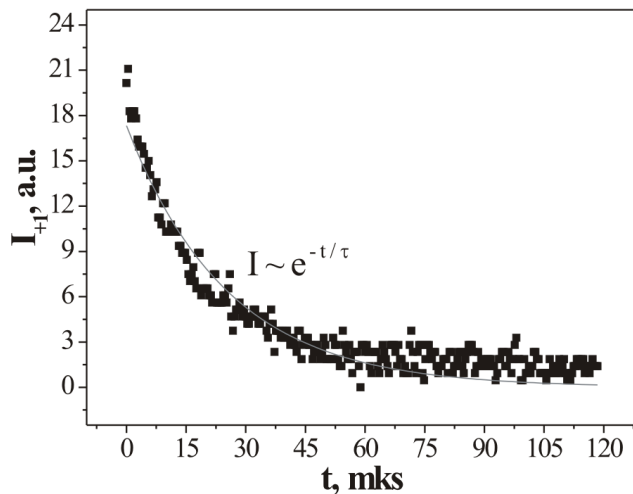
Fig. 5. Optical density ( $D$ ) versus the laser radiation intensity ( $I$ ) for LLC-viologen samples. ■ correspond to the measurement from  $I_{\min}$  to  $I_{\max}$ , □ – from  $I_{\max}$  to  $I_{\min}$

The study of the samples' optical density dependence on the intensity (Fig. 5) showed that the nonlinear absorption is negligible in the given range of intensities. Thus, the recorded gratings are mainly phase ones.

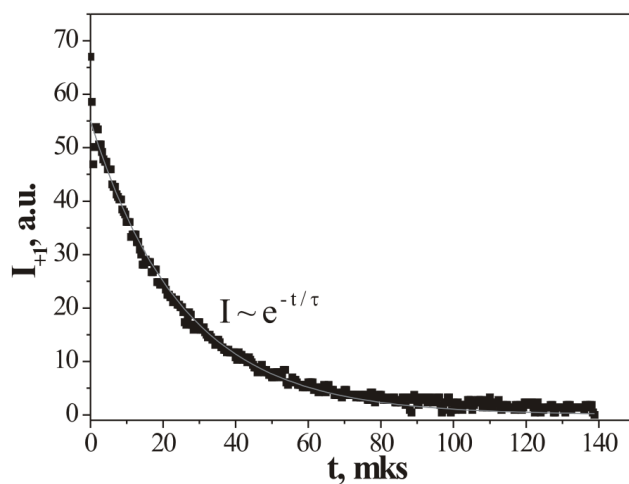
Studying the erasing kinetics of recorded gratings shows the existence of the exponential temporal dependence of the intensity in the first diffracted order (Fig. 6). The decay constant  $\tau$  for the grating period  $\Lambda = 15 \mu\text{m}$  is  $25 \mu\text{s}$ . Such a dependence is typical of thermal gratings. But, if we compare the diffraction efficiency of a thermal grating  $\eta_T$  with the diffraction efficiency in the self-diffraction regime  $\eta$  (Fig. 3, 4), it is seen that  $\eta_T \ll \eta$  ( $\eta/\eta_T > 100$ ). This proves that the investigated gratings in the self-diffraction regime are not thermal. The cause of small thermal gratings is the formation of two-layered cells under the action of an external electric field. In [8], it was shown that, at the holographic recording in bilayer cells, the diffraction efficiency of thermal gratings formed as a result of the laser radiation absorption by a photosensitive layer is by a few orders less than the diffraction efficiency of non-thermal gratings in the self-diffraction regime.

### 3.3. Mechanism of holographic recording: cubic nonlinear susceptibility and second-order hyperpolarizability

Organics, whose molecules contain delocalized  $\pi$ -electrons, could show the effect of nonlinear polarization in the intense laser radiation field, when the polarization



a



b

Fig. 6. Erasing kinetics of gratings in the microsecond range for LLC-HB $^{2+}$ 2Br $^{-}$  (a) and LLC-CEB $^{2+}$ 2Cl $^{-}$  (b) samples. The relaxation constant  $\tau = 25 \mu\text{s}$  for the grating period  $\Lambda = 15 \mu\text{m}$

$P$  (dipole moment per unit volume) depends nonlinearly on the external electric field strength  $E$  [9–24]. Taking the structural formulas of a viologen dication, a radical cation, and a dimer into account, it is clear that the delocalization length for  $\pi$ -electrons increases in this row from the first to the last one. In fact a viologen dication consists of two aromatic rings with two nitrogen heteroatoms, both of them carrying a positive charge. The positive charge of heteroatoms usually decreases the polarizability of a  $\pi$ -electron cloud [21]. A radical cation carries only one positive charge, the delocalization length of its  $\pi$ -electron cloud becomes greater as compared with that of a viologen dication. The number of delocalized

$\pi$ -electrons in dimers is even greater. As a result, the polarization of dimers in the intense laser radiation field will be the greatest.

The LLC–viologen system can be considered as a cubic nonlinear optical medium. For such a medium, the refractive index depends linearly on the laser radiation intensity  $I$ :

$$n(I) = n_0 + \Delta n(I) = n_0 + \frac{\chi^{(3)}}{\varepsilon_0 c (n_0)^2} I = n_0 + n_2 I,$$

$$n_2 = \frac{\chi^{(3)}}{\varepsilon_0 c (n_0)^2}, \quad I = \frac{\varepsilon_0 c \sqrt{\frac{\varepsilon}{\mu}} E^2}{2}, \quad (1)$$

where  $n_0$  is the average refractive index,  $n_2$  is the nonlinear refraction coefficient,  $\chi^{(3)}$  is the cubic nonlinear susceptibility,  $\varepsilon_0$  is the electric constant,  $\varepsilon$  is the permittivity, and  $\mu$  is the magnetic permittivity.

The coefficient of nonlinear refraction  $n_2$  (or the corresponding value of cubic nonlinear susceptibility) is an important characteristic of a cubic optical nonlinearity of the medium. Having found experimentally the value of  $n_2$  (and, also  $\chi^{(3)}$ ), it is possible to evaluate the hyperpolarizability  $\gamma$ , if the local field factor  $L$  is known:

$$\gamma = \frac{\chi^{(3)}}{N L^4}. \quad (2)$$

Let the spatially modulated laser radiation (as a result of the interference of two coherent laser beams) fall onto the investigated medium:

$$I = (I_1 + I_2) \left(1 + m \cos\left(\frac{2\pi}{\Lambda} x\right)\right), \quad m = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}, \quad (3)$$

where  $I_1$  and  $I_2$  are the laser beams intensities which interfere on the investigated sample,  $m$  – the modulation depth,  $\Lambda$  – the interference pattern spacing, and  $x$  – the direction of intensity modulation. Due to the nonlinear optical response of the medium (1), the spatial periodic intensity distribution (3) causes the appearance of a refractive index grating, where writing laser beams diffract (self-diffraction regime). For a thin grating,

the diffraction efficiency  $\eta$  is defined by the following expression [25]:

$$\eta = T \left( J_1 \left( \frac{2\pi d n_2 m I}{\lambda} \right) \right)^2 \approx T \left( \frac{\pi d n_2 m (I_1 + I_2)}{\lambda} \right)^2, \quad (4)$$

where  $T$  is transmission,  $J_1$  is the first-order Bessel function,  $d$  is the depth, where the nonlinear phase incursion takes place (usually, it is the thickness of a sample), and  $\lambda$  is the laser radiation wavelength. The nonlinear refraction coefficient is determined from expression (4) as

$$|n_2| = \frac{\lambda}{\pi d m (I_1 + I_2)} \sqrt{\frac{\eta}{T}}. \quad (5)$$

By the obtained value of  $n_2$ , the nonlinear susceptibility  $\chi^{(3)}$  can be determined according to expression (1), and the second-order hyperpolarizability follows from expression (2). For the evaluation of the order of  $\gamma$ , it is possible to use the Lorenz factor of the local field

$$L = \frac{n^2 + 2}{3}. \quad (6)$$

Using the obtained experimental dependences ( $\eta \sim I^2$ ) and expressions (2), (1), (5), and (11), it is possible to find the nonlinear optical parameters ( $n_2$ ,  $\chi^{(3)}$ ,  $\gamma$ ) of the investigated samples. The quantities determined in such a way (in the CI and esu systems) and formulas describing the transition between the systems are given in the Table.

The large values of nonlinear susceptibility ( $\chi^{(3)} \sim 10^{-8}$  esu) and hyperpolarizability ( $\gamma \sim 10^{-28}$  esu) of viologen radical cations and dimers are worth noting. According to the literature data, the close values among organics are peculiar to retinal ( $\gamma \sim 10^{-31}$ – $10^{-29}$  esu [9]) and polythiophen ( $\chi^{(3)} \sim 10^{-8}$  esu [10, 11]) derivatives, azo dyes ( $\chi^{(3)} \sim 10^{-8}$  esu [12]), compounds on the basis of phthalocyanine dyes ( $\chi^{(3)} \sim 10^{-8}$  esu [13–16]), stilbasolium derivatives ( $\gamma \sim 10^{-31}$  esu [17]), squaryl ( $\chi^{(3)} \sim 10^{-8}$ – $10^{-6}$  esu [18]) and cyanine ( $\gamma \sim 10^{-28}$  esu [19]) dyes provided that the frequency of an exciting laser radiation coincides with (or is close to) the

**Table**

Nonlinear optical media	$n_2, \text{cm}^2 \cdot \text{W}^{-1}$	$\chi^{(3)}, \text{m}^2 \cdot \text{V}^{-2}$	$\chi^{(3)}, \text{esu}$	$\gamma, \text{m}^5 \cdot \text{V}^{-2}$	$\gamma, \text{esu}$
$(\text{RV}^+)_2\text{Cl}^-$	$1.8 \times 10^{-10}$	$1.1 \times 10^{-16}$	$0.8 \times 10^{-8}$	$1.7 \times 10^{-42}$	$1.2 \times 10^{-28}$
$\text{RV}^+\text{Br}^-$	$1.3 \times 10^{-10}$	$0.8 \times 10^{-16}$	$0.6 \times 10^{-8}$	$0.8 \times 10^{-42}$	$0.6 \times 10^{-28}$
$(\text{RV}^+)_2\text{Br}^-$	$3 \times 10^{-10}$	$1.8 \times 10^{-16}$	$1.3 \times 10^{-8}$	$3.7 \times 10^{-42}$	$2.7 \times 10^{-28}$

$$\chi^{(3)}(\text{esu}) = \frac{9}{4\pi} 10^8 \chi^{(3)}(\text{CI})$$

corresponding resonance frequency of the molecule's optical transition. If the frequency of an exciting laser radiation belongs to a nonresonant optical region, the typical hyperpolarizability values of organics are 2–8 orders less ( $\gamma \sim 10^{-36}$ – $10^{-31}$  esu [20–24]) than those in the case of the resonant excitation.

Large values of the second-order hyperpolarizability can be caused by an extension of the delocalization lengths of  $\pi$ -electrons of viologen's reduction products as compared with those of the initial molecules. This assumption agrees with the experiment, since viologen dications show no nonlinear optical response, while the recording of dynamic gratings is observed on radical-cations.

It is known that the hyperpolarizability  $\gamma$  depends nonlinearly on the effective delocalization length  $L$  of  $\pi$ -electrons in the following way [26,27]:

$$\gamma \sim L^m \quad (7)$$

where  $m = 4.2 - 5$ .

Using the results of X-ray investigations of viologen crystals [28], it is possible to evaluate the maximal delocalization length  $L_{\max}$  for the initial dication, radical cation, and dimer:  $L_{\max}$  for a dication will be less than the length of the long axis of a pyridine ring,  $L_{\max}$  for a dimer will be of the same order as the long axis length of two pyridine rings, and  $L_{\max}$  for a radical cation can be estimated from the inequality

$$L_{\max}(\text{dication}) < L_{\max}(\text{radical cation}) < L_{\max}(\text{dimer}).$$

From the literature data [28], we obtain the following values of  $L_{\max}$ :

$$L_{\max}(\text{dication}) < 2.7 \text{ \AA}, \quad L_{\max}(\text{radical cation}) \approx 3.5 \text{ \AA}, \\ L_{\max}(\text{dimer}) \approx 6.9 \text{ \AA}.$$

According to expression (7), the bigger value of  $L_{\max}$  corresponds to the bigger value of  $\gamma$ , which is in accordance with experimental evaluations of  $\gamma$  (Table).

One more factor which facilitates the increase in the hyperpolarizability is an excitation close to a resonance. The laser exciting radiation wavelength is 539.8 nm, the absorption maxima for radical cations and dimers lie at 605 and 510 nm, respectively. So the effect of resonant amplification of the hyperpolarizability will be bigger for a dimer as compared with a radical cation. This fact is also in agreement with a larger experimental value for the dimer's hyperpolarizability than that for a radical cation (Table).

So, at the excitation by a radiation with the wavelength  $\lambda = 539.8$  nm, viologens are characterized by a considerable phase nonlinear optical (cubic) response.

## 4. Conclusions

1. In this work, the nonlinear optical properties of the system "lyotropic liquid crystal-viologen" are investigated. For the first time for such systems, the holographic recording of gratings by nanosecond pulses is studied. It is established that, for the investigated samples under the action of laser radiation, there is a change in the refractive index  $\Delta n$ . This change is proportional to the laser radiation intensity  $I$ .

2. Based on the obtained holographic characteristics of the investigated samples, the mechanism of the optical nonlinearity in such systems related to the nonlinear (cubic) polarization of the  $\pi$ -electron system of viologen derivatives is proposed.

3. From the experimental data for the systems under study, we have obtained the basic nonlinear optical parameters such as the cubic nonlinear optical susceptibility ( $\chi^{(3)}$ ) and the second-order hyperpolarizability ( $\gamma$ ). The determined values of  $\chi^{(3)}$  and  $\gamma$  are close by the order to the results obtained for organics with  $\pi$ -electron systems, when the excitation takes place in the absorbance region.

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ТА ГІПЕРПОЛЯРИЗОВАНІСТЬ СИСТЕМИ  
ЛІОТРОПНИЙ РІДИННИЙ КРИСТАЛ–ВІОЛОГЕН

*А.Б. Бордог, Ю.А. Гарбовський, Г.В. Клімушева,  
С.А. Бугайчук, Т.А. Мирна, Г.Г. Ярмчук, А.П. Поліщук*

## Резюме

Досліджено нелінійні оптичні властивості системи ліотропний рідинний кристал–віологен, яка завдяки домішці віологену проявляє електрохромізм під дією зовнішнього електричного поля. На забарвлених зразках було отримано запис динамічних голографічних ґраток за допомогою імпульсної лазерної методики. Досліджено основні характеристики голографічного запису на цих зразках. На їх основі та на основі електрооптичних властивостей системи було запропоновано механізм запису ґраток. Запис відбувається завдяки зміні поляризованості  $\pi$ -електронної системи похідних віологену під впливом потужного лазерного випромінювання. Визначено основні нелінійні оптичні параметри ( $n_2$ ,  $\chi^{(3)}$ ,  $\gamma$ ) досліджуваної системи.