KERR EFFECT AND DIELECTRIC ANISOTROPY IN SERIES OF RARE-EARTH LC COMPLEXES WITH SYSTEMATICALLY CHANGING COUNTERIONS STRUCTURE

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Abstract

Metallomesogenic lanthanide complexes can be used as a basis for developing of magneto- and electro-optical devices. The magnitude and sign of the dielectric anisotropy both play a leading role in this case. However, any direct measurements of the dielectric anisotropy for the most part of metallomesogenic complexes are highly problematic since they only have a smectic phase, and therefore there is no way to produce macroscopic homogeneous samples. This problem can be solved due to similarity between the mechanism of the dielectric polarization in liquid crystal phase and that of electrical birefringence in the isotropic phase. Thereby, one can estimate the dielectric anisotropy in the liquid crystal phase by studying the electrical birefringence in isotropic melt. We have studied complexes consisting of ions of rare-earth metals such as Dy, Er, Gd, Tb, and of alkylsulfate counterions and Schiff bases as being ligands. The number of methylene groups in aliphatic chains of counterions was varied between 0 and 12. It was found that in the series of the substances under investigation the magnitude as well as the sign of electro- optical effect in the isotropic phase depended on length of the counterions, but not depended on the metal ions used. Thus, dielectric anisotropy of smectic lanthanide complexes can be widely changed by variations of chemical structure of the counterions.

Keywords: metallomesogen; smectic; lanthanides; electrical birefringence; dielectric anisotropy.

Introduction

Electric birefringence is used to study isotropic melts of substances in a thermotropic liquid crystal state. Within the model of Landau–De Gennes phase transitions [1], it was shown that the properties of the isotropic phase such as the Kerr constant and the relaxation time of the Kerr effect are directly related to the optical and dielectric anisotropies and the rotational viscosity of the mesophase in the same substance [2–5]. Consequently, the electric birefringence method can also provide information on the characteristics of the liquid crystal phase. In this work, we use the electric birefringence method to study metallomesogenic lanthanide complexes

[6, 7], whose advantages are the paramagnetic properties [8, 9] and effective luminescence [10, 11]. They are promising for application as liquid crystal materials in electro- and magneto-optical devices. The fundamentally important characteristic for this application is the anisotropy of physical properties, primarily dielectric and magnetic anisotropies, because they determine the possibility of controlling devices where liquid crystal materials are used as active elements. The anisotropy of the physical properties of liquid crystals and the relation of these properties to the molecular structure of these materials can be studied only in the presence of a nematic phase because the homogeneous macroscopic ordering of the optical axis (director) is easily created in a nematic and a liquid single crystal is formed. A macroscopically ordered smectic sample can also be obtained sometimes by cooling a uniformly ordered nematic. However, the synthesis of nematic lantha nide mesogens appeared to be very difficult: the first nematics had narrow intervals of existence of a mesophase and a high clearing temperature at which they were rapidly decomposed [12, 13]. Thermostable nematic lanthanide-containing liquid crystals were obtained only recently [14, 15]. The first studies of the optical [16] and dielectric [17] anisotropies in the nematic and smectic phases were reported. However, the overwhelming majority of lanthanide complexes have only the smectic phase and form multidomain macroscopically disordered structures. For this reason, the direct study of the dielectric anisotropy of such metallomesogens and, therefore, the determination of its relation to the molecular structure are serious problems. We propose a possible solution of these problems based on the study and analysis of the electro-optical properties of an isotropic liquid phase of these materials.

Methods

In this work, we study a number of smectic-A complexes consisting of a lanthanide ion, alkyl sulfate counterions, and ligands with the general formula $Ln(C_nH_{2n+1}SO_4)_2(C_kH_{2k+1}O\text{-}C_6H_3(OH)\text{-}CH{=}N\text{-}C_mH_{2m+1})_3$. Their composition includes lanthanides Ln = Dy, Tb, Gd, and Er and various numbers k, m, and n of CH_2 elements in aliphatic chains. In addition, we studied the $Tb(NO_3)_2(C_kH_{2k+1}O\text{-}C_6H_3(OH)\text{-}CH{=}N\text{-}C_mH_{2m+1})_2$, sample containing a nitrogen acid counterion without aliphatic elements. Electric birefringence in the isotropic phase was measured at a highly sensitive setup by the compensation method involving a modulator of the elliptical polarization of light [4]. We used a pulsed electric field with the strength up to 2.5×10^3 V/cm, a rectangular pulse duration of 10 ms, and a pulse repetition frequency lower than 1 Hz in order to eliminate the negative effect of the electrical conductivity of the samples. Measurements were performed in a small Kerr cell for 15 mg of a material with an optical path length of 2 mm.

Results and Discussion

The Kerr constant K at various temperatures was calculated using the Kerr law $\Delta n_E = KE^2$, where Δn_E is the field-induced birefringence. The Kerr constant K for all samples demonstrates a characteristic temperature dependence (Fig. 1) according to which the inverse Kerr constant varies as $1/K \sim (T - T^*)$, where T* is the temperature of the virtual second-order phase transition [1]. Using these data, we determined the temperature-independent electro-optical constant $K(T - T^*)$ and used it for the comparison of the electro-optical properties of complexes different in composition.

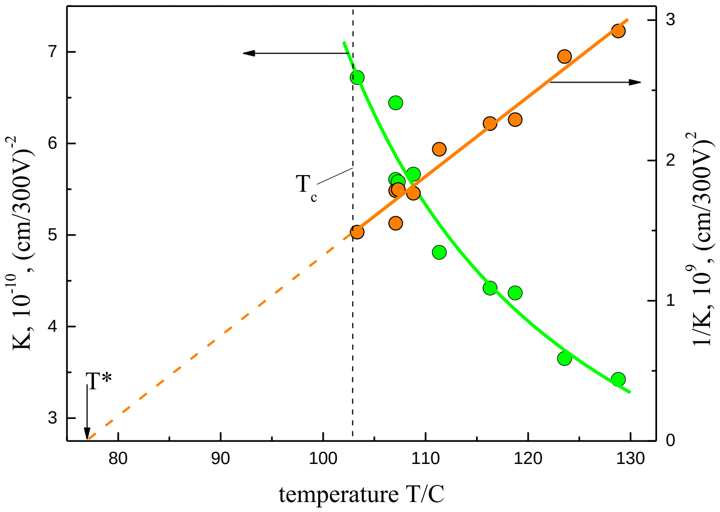

Figure 1. Temperature dependences of the Kerr constant K and inverse quantity 1/K for the $Tb(C_2H_5SO_4)_2(C_{12}H_{25}O–C_6H_3(OH)–CH{=}N–C_{17}H_{35})_3$ complex. The temperature T_c of the smectic-A–isotropic phase transition and the temperature T* of a virtual second-order phase transition are indicated.

As is seen in Fig. 2, K(T–T*) strongly depends on the number of aliphatic units n in alkyl sulfate counterions. At large n values, the sign of the Kerr effect is negative and the shortening of a counterion reduces the negative effect. Near n=7, where the electrooptical effect nearly vanishes, the sign of the constant K changes to positive. These changes occur independently of the nature of the rare-earth metal and the length of aliphatic ligand chains. The only metallomesogen with shortest nitrogen-acid counterions NO_3 without methylene groups also has these properties. It is noteworthy that the number of CH_2 units in counterions varied significantly by a factor of 12 (n=0, 2, 8, or 12). Relative changes in the length of aliphatic ligand chains are small (k=12 or 14, m=16, 17, or 18). Long aliphatic ligand chains are also involved in the formation of the spatial geometry of a complex and should affect the electro-optical properties. The variation of the length of ligands was very limited because of the choice of the optimal structure of ligands for the formation of a stable liquid crystal phase.

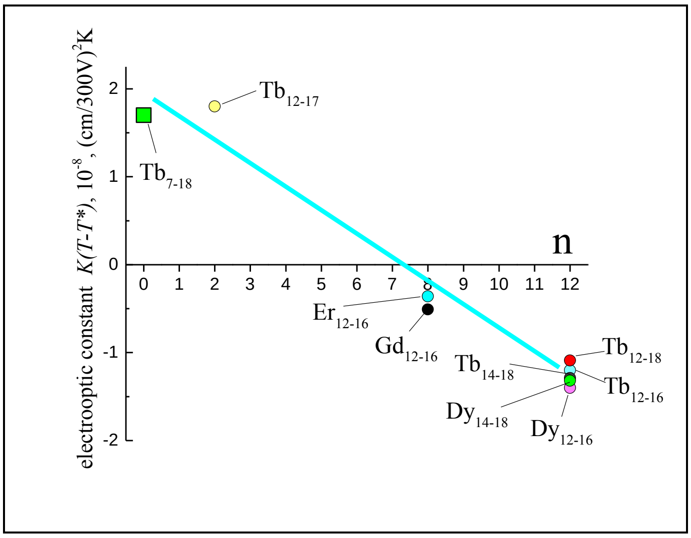

Figure 2. Electro-optical constant versus the number n of methylene groups CH_2 in the aliphatic chain of counterions. The composition of each complex is indicated near the points in the form $Ln_{k–m}$, where Ln is the lanthanide ion and k and m are the numbers of methylene groups in ligands.

The resulting dependence (see Fig. 2) can be interpreted as follows. Using the Landau–De Gennes theory, Chandrasekhar [18, Chap. 2] proposed the following expression for the Kerr constant K in the isotropic phase of liquid crystals whose molecular structure has the axial symmetry of the optical and dielectric properties:

$$K = \frac{\Delta n_E}{E^2} = \frac{2\pi N_A^2\, b(n^2+2)^2 F h^2}{27 n V a(\mathrm{T}-\mathrm{T}^*)}\left[\alpha + \frac{F\mu^2}{2k\mathrm{T}}\left(3\cos^2\gamma - 1\right)\right] \qquad (1)$$

Here, N_A is the Avogadro number; k is the Boltzmann constant; V is the molar volume; *a* is the coefficient in the expansion of the free energy of the melt in a series in the orientational order parameter S; n is the refractive index; b and α are the anisotropy parameters of the optical and electrical polarizabilities, respectively; F and h are the multipliers of the internal field; and μ and γ are the dipole moment and its angle, respectively. The magnitude and sign of K obviously depend crucially on the parameters μ and γ in square brackets in Eq. (1) because the anisotropy parameter α is always positive for liquid crystal molecules. The electro-optical constants of the complexes are large, characteristic of polar liquid crystals [19, 20]. This indicates the presence of a large dipole moment μ, and a change in the angle of inclination of this dipole moment to the longitudinal geometric axis of the complex leads to variations of the electro-optical constant at the variation of the composition. Expression (1) allows the computer simulation of the effect of the angle of inclination of a static dipole within a range of 0°to 90°on the dependence *K(T)* with the parameters of well-studied pentylcyanobiphenyl [21]. According to Eq. (1) and Fig. 3, when 0°<γ<55°, the expression in square brackets is positive and $K>0$. If 90°>γ>55°, the expression in square brackets becomes negative and, correspondingly, $K<0$.

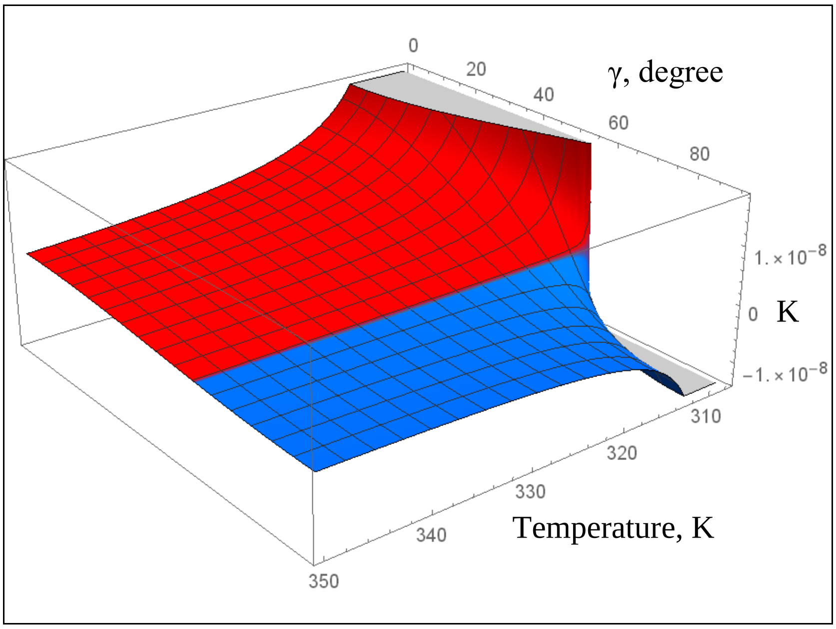

Figure 3. Temperature dependence of the Kerr constant K at different angles of inclination γ of the static dipole moment to the longitudinal axis of the molecule as calculated by Eq. (1) with the parameters of pentylcyanobiphenyl. Red indicates the area where K is positive, blue - where K is negative.

The dipole moment of the mesogenic complex is due to the system of coordination bonds inside a coordination sphere whose elements are a rare-earth ion, two alkyl sulfate counterions, and three ligands. The variation of the length of counterions leads to a change in the spatial geometry of the sphere and, thereby, the angle of the dipole moment. Even small deviations of the angle from the critical value γ≈55 are enough to ensure the experimentally observed changes in the sign and magnitude of K.

For our purposes, it is important that the direction of the dipole moment similarly affects the dielectric anisotropy of the liquid crystal phase. The dielectric anisotropy parameter Δε is the difference between the relative permittivities along and across the director of the liquid crystal. The Maier–Meier theory [22], which describes the dielectric properties of a uniformly oriented liquid crystal, gives the following relation between the dielectric anisotropy and molecular parameters:

$$\Delta\varepsilon = \frac{4\pi\rho}{M} N_A hF\left[\alpha + \frac{F\mu^2}{2kT}\left(3\cos^2\gamma - 1\right)\right]S \qquad (2)$$

The expressions in square brackets in Eqs. (1) and (2) are identical because the same orientational mechanism is present both in the dielectric polarization of the mesophase and in the electro-optical effect in the isotropic melt. Previous experimental works [4, 23] confirm this conclusion. The comparative analysis of the mechanisms of dipole orientation depending on the temperature and frequency of the electric field was performed by the dielectric spectroscopy and electric birefringence methods in a sinusoidal field for H-44 and H-21 calamitic nematics, whose molecules have different angles of inclination γ of dipoles. It was shown that $\Delta\varepsilon$ and K at low frequencies are positive for H-44 ($\gamma = 47°$) and negative for H-21 ($\gamma = 59°$).

To summarize, it has been shown that mesogenic lanthanide complexes with Schiff bases and with the necessary signs and magnitudes of the electro-optical effect, as well as the signs and magnitudes of the dielectric anisotropy of the liquid crystal phase, can be obtained by varying the length of counterions.

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Conflicts of Interest: The authors declare no conflict of interest.

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