New liquid-crystalline complex $C_{12}DMAO/La^{III}$ with the nematic phase

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The results of the synthesis and characteristics of the new lyotropic lanthanide-containing liquid-crystalline systems possessing the nematic phase based on the zwitterionic surfactant, *N,N*-dimethyldodecylamine oxide (C_{12}DMAO), in the aqueous-decanol environment are presented. The phase diagrams are constructed. The formation of the La—O coordination bonds in the liquid-crystalline complex $C_{12}DMAO/La^{III}$ is confirmed by IR spectroscopy.

Key words: lyotropic liquid crystals, lanthanides, zwitterionic surfactant, nematic phase, IR spectroscopy.

Lyotropic liquid-crystalline systems are of great interest due to the use in various areas of science and technology. Owing to the simple synthesis and the self-organization nature, these systems are applied as flexible templates for the synthesis of diverse nanoobjects with controlled geometry and size and for the creation of ordered and oriented massifs.[1—6] In this respect, nematic liquid crystals (NLC) are most interesting. They are easily oriented by weak external fields due to low viscosity,[7] which makes them attractive for use in various molecular optoelectronic devices. The presence of a metal ion in NLC extends the range of application, imparting and improving the magnetic, electric, and optical properties.[8] From this point of view, lanthanide ions are attractive,[9] because their liquid-crystalline complexes have high magnetic anisotropy and efficient polarized luminescence.[10—12] Among a variety of lyotropic nematic phases, there are no data on the synthesis of lanthanide-containing nematogens. Therefore, the purpose of the present work is to prepare nematic lyotropic liquid-crystalline systems based on lanthanide ions, to study the mesogenic properties, and to establish the character of NLC complex formation.

Experimental

The zwitterionic surfactant (Surf) *N,N*-dimethyldodecylamine oxide, $CH_3(CH_2)_{11}N(O)(CH_3)_2$ (C_{12}DMAO), crystalline hydrate of lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (La^{III}), and decanol were commercial products (Aldrich). Bidistilled water was used for the preparation of the systems.

The lyotropic mesogens were synthesized under mild conditions, and the Surf : La ratio was varied from 1 to 7 moles. The calculated weighed samples of the salt were dissolved in water at 30 °C, and then the surfactant also heated to 30 °C and decanol were introduced into the system. The lyotropic mesophase was formed at 30 °C with stirring in an ultrasonic stirrer. The liquid-crystalline properties of the synthesized systems were studied by polarization optical microscopy (POM) with a NAGEMA-K8 polarization microscope equipped with a Boetius heating stage. The temperature was maintained within ±0.2 K. IR spectra were obtained in an LC film on a Bruker Tensor-27 spectrometer in a frequency range of 4000—400 cm^{-1} and on a Bruker IFS-113v spectrometer in a range of 700—100 cm^{-1}.

Results and Discussion

The phase diagrams of the multicomponent systems are presented in Fig. 1. According to the POM data, the concentration and temperature ranges of existence of the lyotropic systems were determined. Depending on the Surf : La molar ratio, different types of lyotropic LC phases are formed in various concentration ranges: hexagonal, lamellar, and nematic. Unlike the lamellar mesophase formed at all the molar ratios studied, the hexagonal phase is observed in the systems at the ratios Surf : La = 1 : 1 and 4 : 1 in regions with a high content of the complex (50—60 wt.%) and water (35—49 wt.%). The lyotropic

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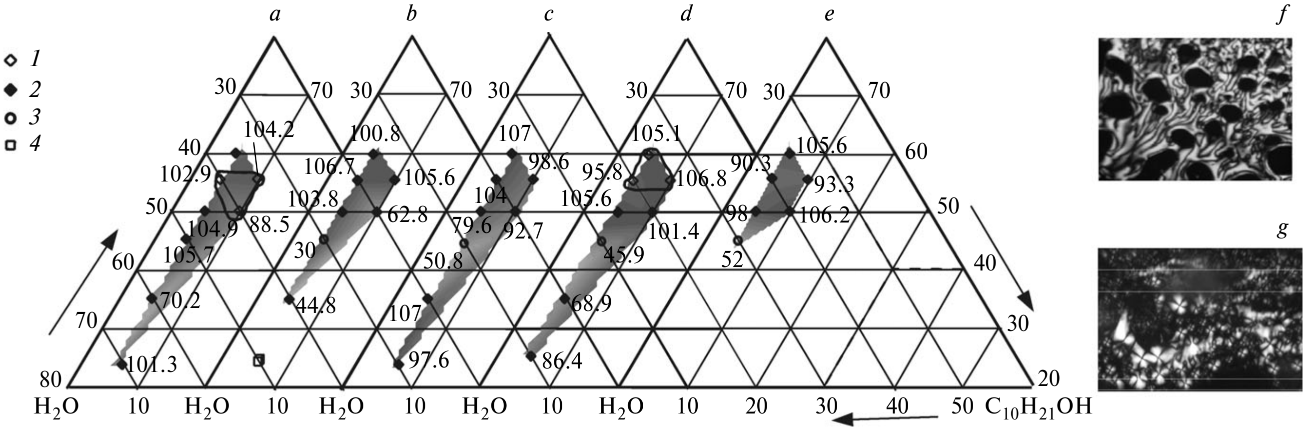

Fig. 1. Phase diagrams of the multicomponent systems at the ratio $C_{12}DMAO : La^{III}$ = 1 : 1 (*a*), 2 : 1 (*b*), 3 : 1 (*c*), 4 : 1 (*d*), and 7 : 1 (*e*). The types of lyotropic liquid-crystalline phases are hexagonal (*1*), lamellar (*2*), nematic (*3*), and liquid crystals (*4*). The temperatures of phase transitions to the isotropic liquid are given in Centigrade (°C). The Schlieren texture of the lyotropic nematic mesophase (*f*) and the texture of the lyotropic lamellar mesophase (*g*) (polarization microscope, ×96).

nematic mesophase is formed at the following concentrations of the components: 45 wt.% $C_{12}DMAO : La^{III}$, 50 wt.% H_2O, and 5 wt.% $C_{10}H_{21}OH$. The Schlieren texture characteristic of the nematic phase was observed in the polarized light (see Fig. 1). An analysis of the phase composition of the NLC systems obtained showed that these phases were formed at the molar ratio Surf : La = = 2 : 1, 3 : 1, 4 : 1, and 7 : 1. Unlike the high-temperature metal-containing thermotropic nematics, the lyotropic nematic phases under study exist already at temperatures above 5 °C (Table 1). The temperature of phase transition to the isotropic liquid increases with an increase in the Surf content in the system. The temperature of the phase transition nematic (*N*) → isotropic liquid (*I*) upon several heating and cooling cycles remained unchanged, which indicated the stability of the system.

IR spectroscopy was used to obtain information about the structure of the complex generated upon the formation of the lyotropic nematic mesophase and to reveal molecular structural changes that occurred during this process.

The comparative analysis of the absorption spectra of the individual surfactant and the liquid-crystalline system $C_{12}DMAO : La^{III}/H_2O/C_{10}H_{21}OH$ (Fig. 2) showed the appearance of a broad shoulder in the region of OH stretching vibrations (3600—3000 cm^{-1}) caused by the presence of hydrogen bonds in the LC system. The intense absorption bands at 2955, 2923, and 2854 cm^{-1} attributed to stretching vibrations of the CH_3 and CH_2 groups undergo no changes, because they are not involved in the complex formation. The shape of the spectrum of $C_{12}DMAO$ at 2300—2750, 1550—1800, and 950—970 cm^{-1} allows one to judge[13,14] about the protonated or deprotonated form of the Surf molecule. The absence of absorption in this region and the weak band at 1699 cm^{-1} indicate that the amine oxide is in the deprotonated form. In the LC system an absorption band appears at 2395 cm^{-1}, and the shift of the absorption band of *N*,*N*-dimethyldodecylamine oxide characteristic of $\nu(N \to O)$ from 964 to 927 cm^{-1} in the complex confirms the protonated form of the amine oxide. This possibly indicates that the OH group of the Surf forms a hydrogen bond ($—N^+ \to O^-...HO—La <$) upon the formation of a complex with the La^{III} ion in an aqeuous-decanol medium. The comparative analysis of the spectra of the LC system and $La(NO_3)_3 \cdot 6H_2O$ salt showed that the $O—NO_2^-$ antisymmetric vibrations are observed at 1646 and 1647 cm^{-1}, respectively. In the spectrum of the LC system $C_{12}DMAO : La^{III}/H_2O/C_{10}H_{21}OH$, the bands at 1464 and 1054 cm^{-1} indicate the vibrations of the bound nitro group. In frequency regions of 1410—1340 and 860—800 cm^{-1} absorption bands at 1382 and 824 cm^{-1} were detected, which can be interpreted as characteristic vibrations of the free NO_3 ion.[15,16] Therefore, two types of nitrate ions exist in the system upon the formation of a metal complex: the free NO_3^- anion and the NO_3^- associated anion bound to the lanthanum ion through the bidentate mode. The studies in the low-frequency region 600—150 cm^{-1} were performed to establish the character of changing the coordination unit of the lanthanum ion

Table 1. Types* and temperatures of phase transitions at various Surf : La molar ratios

Molar ratio Surf : La	Types and temperatures of phase transitions
2 : 1	$Cr \xrightarrow{5\ °C} N \xrightarrow{28\ °C} NI \xrightarrow{30\ °C} I$
3 : 1	$Cr \xrightarrow{5\ °C} N \xrightarrow{48.6\ °C} NI \xrightarrow{50.8\ °C} I$
4 : 1	$Cr \xrightarrow{5\ °C} N \xrightarrow{43.8\ °C} NI \xrightarrow{45.9\ °C} I$
7 : 1	$Cr \xrightarrow{5\ °C} N \xrightarrow{50\ °C} NI \xrightarrow{52\ °C} I$

* *Cr* is the crystalline mesophase, *N* is the nematic mesophase, *I* is the isotropic liquid, and *NI* is the two-phase system.

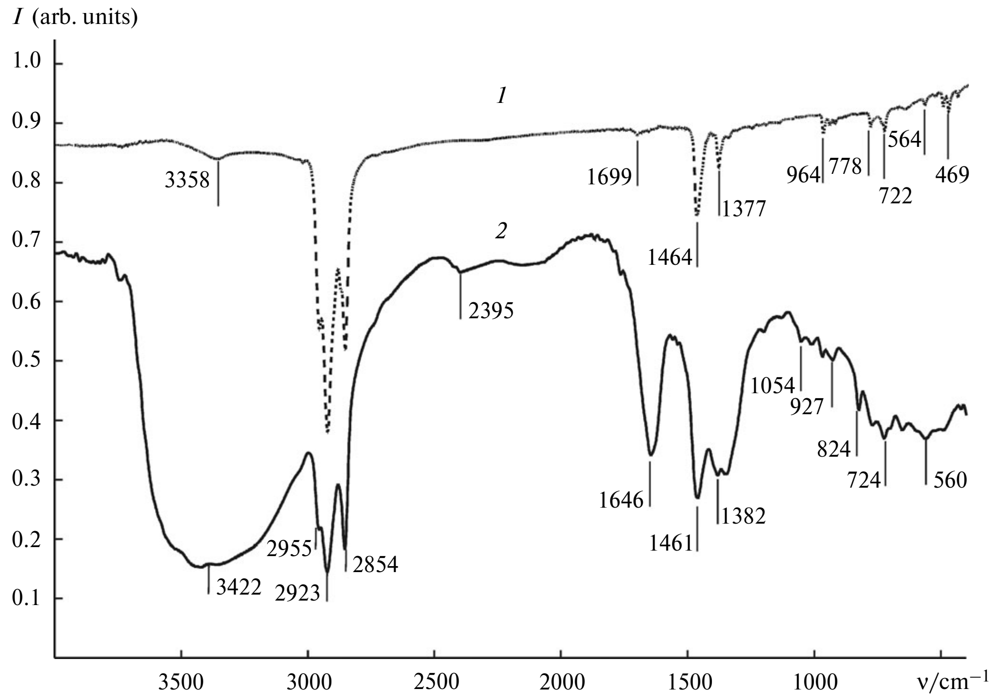

Fig. 2. IR spectra of C_{12}DMAO (*1*) and C_{12}DMAO : $La^{III}/H_2O/C_{10}H_{21}OH$ (ratio Surf : La = 3 : 1) (*2*).

(Fig. 3). The bands at 541 cm^{-1} in the LC complex and at 552 cm^{-1} in $La(NO_3)_3 \cdot 6H_2O$ are characteristic of librational vibrations of water of crystallization. In the spectrum of $La(NO_3)_3 \cdot 6H_2O$, the absorption bands at 319 and 220 cm^{-1} are due to vibrations of the La—O bond.[17] In the LC system C_{12}DMAO : $La^{III}/H_2O/C_{10}H_{21}OH$, the band shift to 307 cm^{-1} is observed, and the absorption band at 220 cm^{-1} is retained, but its intensity changes slightly. The appearance of a new band at 239 cm^{-1} indicates the coordination of the oxygen atom of the amine oxide by the lanthanum ion.

Thus, the regions of self-organization of the nematic lanthanum-containing lyotropic systems were established: the concentration limits, temperatures of phase transitions, and types of mesophases were determined. The structure of the LC complex C_{12}DMAO : $La^{III}/H_2O/C_{10}H_{21}OH$ was determined by IR spectroscopy. The structure is formed by intermolecular hydrogen interactions of the coordinating ions with the oxygen atoms of the molecules of the zwitterionic surfactant, and the coordination sphere contains water and the nitro group bound in a bidentate mode.

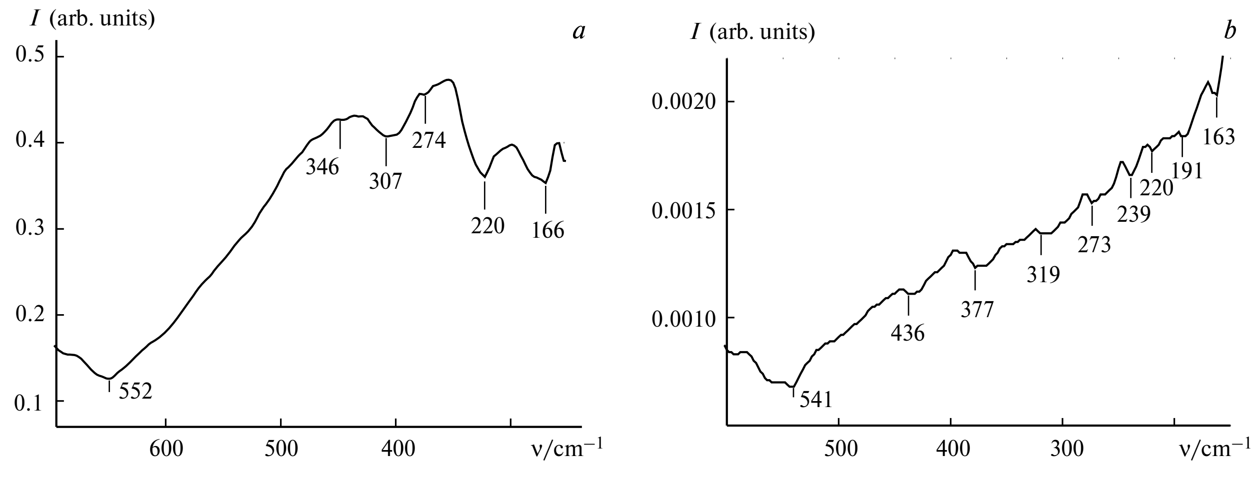

Fig. 3. IR spectra of the $La(NO_3)_3 \cdot 6H_2O$ salt (*a*) and the C_{12}DMAO : $La^{III}/H_2O/C_{10}H_{21}OH$ system (*b*) in the low-frequency region.

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