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CONDUCTIVITY OF COMPOSITES OF THERMOTROPIC IONIC LIQUID CRYSTALS

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Abstract—This work presents the studies of the transport properties of samples of oriented binary composite of cobalt decanoate with lead decanoate. Found that samples of the mixture at the temperature range of liquid crystal existence are weak electrolytes, which have anisotropy of bulk conductivity caused by the ordering of molecules. The values of mobility and charge concentration were estimated.

Index Terms—Ionic thermotropic liquid crystals; cobalt alkanoate; lead alkanoate; binary mixture; conductivity; anisotropy of conductivity.

I. INTRODUCTION

The research of new perspective materials for engineering and development of data processing and storage devices is one of the important directions of modern science elaboration.

Because of this, in recent years, much attention is paid to the study of composites and multicomponent mixtures of liquid crystals (LC). Mixtures of ionic liquid crystals attract particular interest. Unusual properties of these materials offer new opportunities for a variety of practical applications. Great importance have study the transport properties of these materials.

II. ANALYSIS OF INVESTIGATIONS AND PUBLICATIONS

Metal alkanoates $C_nH_{2n+1}COOM$ form thermotropic ionic liquid crystals (TILC) during their melt. One of the main features of TILC is intrinsic ionic conductivity. Despite this, there are almost no literature data [1]–[3] on the electrical properties of binary mixtures of TILC, charge mobility and charge concentration in such compounds.

Thus, the aim of the present work were:

- investigation of conductivity of binary mixture of cobalt and lead decanoate TILC;
- study of charge carriers mobility in TILC and evaluation of their concentration.

III. METHODS AND OBJECTS OF RESEARCH

The investigation of electric properties was conducted for samples of cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$ ($T_{melt} = 82^\circ C$, $T_{clar} > 300^\circ C$), lead decanoate $(C_9H_{19}COO^-)_2Pb^{2+}$ ($T_{melt} = 87^\circ C$, $T_{clar} = 114^\circ C$) and binary mixture $Pb^{2+}, Co^{2+}[(C_9H_{19}COO^-)_2]$ (90:10 mol. %, $T_{melt} = 83^\circ C$, $T_{clar} = 115^\circ C$).

The bulk electrical conductivity of all samples was determined by oscilloscopic method [4]–[7]. The

triangular voltage signal had peak value of 0,10–0,25 V. The frequency dependence of bulk resistance for all examined samples was investigated in temperature range of LC formation. It was found, that in the frequency range $10^4 < f < 10^6$ Hz measured resistance almost does not depend on frequency. This indicates a uniform volume distribution of the voltage applied to the sample. Low values of alternating voltage applied to the samples made electrochemical processes on electrodes impossible.

Small-angle X-ray studies [8] have shown that LC phase of investigated materials belongs to Smectic A type. The molecules are packed in a bilayers formed by alkyl chains, among which are cation-anion interlayer – cations of cobalt (or lead) and the oxygen atoms of carboxyl groups with negative charge.

The cells with metal electrodes (Ni, Cu) were used for investigation of electrical conductivity of smectic TILC. The samples are characterized by strict homeotropic alignment [8], which allowed to investigate anisotropy of conductivity of TILC. Therefore, the electrodes in cells were placed relatively glass substrates either as a sandwich (Fig. 1a) or planar (Fig. 1b). The cell was filled with material by capillary method during its melting. To prevent the “absorption” of water in the sample cell edges were sealed with glue. In the case of a cell with planar arrangement of electrodes they specified the cell thickness. The thickness of cells with sandwich electrodes was specified by glass spacers. In both cases thickness of the sample was 85 microns.

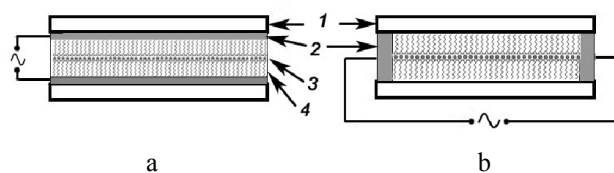


Fig. 1. Types of LC cells for studies of electrical properties: a is the cell with sandwich electrodes; b is the cell with planar arrangement of electrodes: 1 is a glass substrates; 2 is a Ni or Cu electrodes; 3 is a cation-anion interlayer; 4 is a alkyl chains of molecules

To retrieve the mobility of the charge carriers in TILC the method of switching the voltage on the cell [9]–[11] was used. For this purpose, sandwich cell with metal electrodes (Fig. 1a) with sample thickness of 500–900 microns was taken. Because of considerable thickness all tested samples were nonoriented and polydomain.

IV. RESULTS AND DISCUSSION

A Electrical conductivity of binary mixture $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$

Investigation of binary mixtures of metalalkanoates enables creation of mixtures with optimal characteristics. Binary mixture of cobalt decanoate and lead decanoate $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$ 90:10 mol.% was chosen for studies of electric transport properties of binary mixtures. Selected percent of 10 mol.% of lead compound was optimal for the existence homeotropical orientation of the molecules in the liquid crystal cell.

Research of electrical conductivity of binary mixture was conducted in the temperature range 295–400 K. It was found, that the conductivity measured along cation-anion layers at the temperature of LC formation ($T = 356$ K) was $\sigma_{\parallel} \approx 1,08 \times 10^{-4}$ Sm/m and exponentially increases with temperature (Fig. 2.).

At the temperature dependence of particular sample (and in all other samples) the hysteresis phenomenon wasn't observed. That indicates the absence of irreversible electrochemical processes and the stability of the structure of the sample during the study.

The experimental points are well described by Arrhenius exponential dependence:

$$\frac{\sigma}{T} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right),$$

where σ is the conductivity of TILC; T is the temperature; σ_0 is the pre-exponential factor; k is a Boltzmann constant; E_a is the activation energy of conductivity. This dependence is linear in coordinates $\ln(\sigma/T)$ versus $10^3/T$ (Fig. 2). The activation energy E_a can be determined by the slope of the linear dependence. Value E_a/q ($q = 2$ is ion charge) characterizes energy barrier per unit ion charge ($q = 1$), which it have to overcome in order to start moving. For the reduced dependence: $E_{a\parallel} = 0,43\text{eV}$, and $E_{a\parallel}/q = 0,21\text{J/C}$. It should be noted that for the same sample measurement accuracy of activation energy was higher than the

accuracy of the conductivity measurement, since the error of the geometric factor of the cell is added to the error of conductivity measurement.

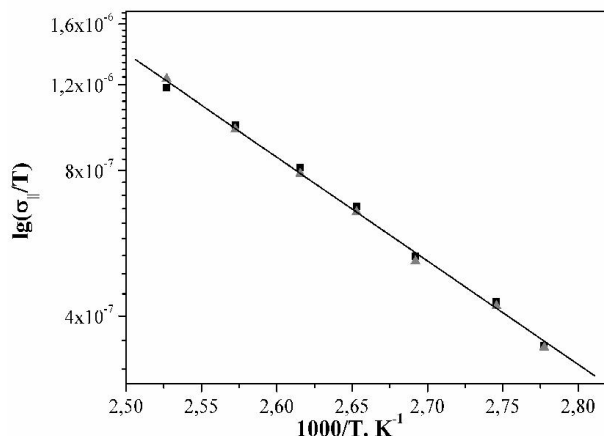


Fig. 2. Logarithmic temperature dependence of the electrical conductivity of binary mixture $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$, measured along the cation-anion layers

The same studies were held using cell with sandwich electrodes to determine anisotropy of electrical conductivity (measurements were performed perpendicular to the cation-anion layers). In this case electrical conductivity also exponentially increases with temperature. But the value of conductivity decreased by four orders of magnitude ($\sigma_{\perp} \approx 1,05 \times 10^{-8}$ Sm/m, $T = 356$ K).

The corresponding temperature dependence of conductivity measured perpendicular to the layers is shown in logarithmic coordinates in Fig. 3. The activation energy of electrical conductivity and the value of the energy barrier significantly increased: $E_{a\perp} = 0,82\text{eV}$, $E_{a\perp}/q = 0,41\text{J/C}$.

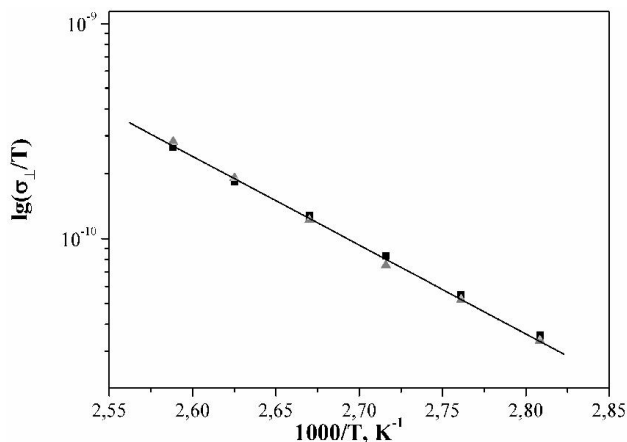


Fig. 3. Logarithmic temperature dependence of the electrical conductivity of binary mixture $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$, measured perpendicular to the cation-anion layers

Obtained values of electrical conductivity measured along and perpendicular to the smectic layers indicate the existence of anisotropy of conductivity with corresponding value $\sigma_{\parallel} / \sigma_{\perp} = 10^4$. In comparison to individual compound of cobalt decanoate, obtained results show that adding impurities of lead has led to the increase of conductivity along the smectic layers about 2 times, and perpendicular to it – 20 times [8].

Thus, studies have shown that all oriented samples of TILC binary mixture were characterized by anisotropy of conductivity. Along with correlation between the values of conductivity along and perpendicular to the smectic layers, the correlation between the corresponding values of activation energy and the energy barrier is observed. The higher the conductivity σ , the less energy characteristics E and E/q . This dependence means that along with the anisotropy of conductivity the anisotropy of activation energy and energy barrier is also observed.

B Mobility and concentration of charge carriers

Defined values of charge carriers mobility in LC μ for individual compounds $(C_9H_{19}COO^-)_2Co^{2+}$, $(C_9H_{19}COO^-)_2Pb^{2+}$ are about the same $\mu \approx 2 \cdot 10^{-7} m^2/V \cdot s$. Unfortunately, it is not possible to measure the mobility of the charge carriers for mixture of these substances, because of fast exfoliation of sample after polarizing voltage application. This method also failed to conduct a study of the temperature dependence of the mobility of charge carriers in the individual compounds of cobalt and lead decanoates. In a constant electric field during prolonged heating required for the implementation of the experiment, irreversible processes occur in samples that led to their destruction.

Obviously, owing to melting of metal alkanoates salts, under formation of the LC, there two types of ions appear - carboxylate anions and metal cations. Carboxylate anions have large molecular size compared with metal cations and they primarily determine the value of the period of LC layered structure (Smectic A). Because of the large size their mobility should be much lower than the mobility of metal cations. So, it can be assumed that the main charge carriers in LC are metal cations (Co^{2+} and Pb^{2+}). This confirm to the conclusions of [12], which states that the charge transfer is performed mainly by metal cations in isotropic carboxylate melts.

The value of concentration of charge carriers n in TILC can be founded from conductivity and mobility:

$$n = \sigma / q\mu,$$

where $q = 2$ is the charge of metal cations. Since the measurements of charge mobility were held using nonoriented polydomain samples of TILC and conductivity was measured for oriented samples, electrical conductivity of nonoriented sample was determined as a linear combination of values σ_{\parallel} and σ_{\perp} :

$$\sigma = \alpha\sigma_{\parallel} + \beta\sigma_{\perp},$$

where α, β are coefficients that depend on the specific type of TILC orientation. For nonoriented sample expression for σ can be represented as:

$$\sigma = \frac{2\sigma_{\parallel} + \sigma_{\perp}}{3}.$$

As can be seen from Table, the conductivity of nonoriented samples is close to the conductivity obtained for TILC samples when measured along the cation-anion layers at a temperature $T = 380$ K [8].

Electrical characteristics of nonoriented TILC (380 K)

	$\mu, m^2/V \cdot s$	$\sigma, Sm/m$	n, m^{-3}
Co^{2+}	2×10^{-7}	$3,67 \times 10^{-5}$	$5,73 \times 10^{-20}$
Pb^{2+}	2×10^{-7}	$1,33 \times 10^{-2}$	$2,08 \times 10^{-23}$

CONCLUSIONS

1. A detailed complex research of the electrical properties of smectic A phase of binary mixture of cobalt decanoate and lead decanoate were conducted. According to a study results the values of the basic electrical characteristics such as conductivity and activation energy were determined.

2. Established, that observed TILC samples are weak electrolytes in the temperature range of LC existence. They are characterized by a large anisotropy of bulk conductivity caused by the smectic ordering of molecules.

3. During the measurement of conductivity parallel and perpendicular to the cation-anion layers the large anisotropy of bulk conductivity was found the ($\sigma_{\parallel} / \sigma_{\perp} \approx 10^4$). Observed anisotropy of electric conductivity confirms the two-layer model of molecules packing in LC and indicates that the charge transport, with metal cations as the main carriers, occurs along the cation-anion layer.

4. Using switching voltage method the values of charge carriers mobility ($\mu = 2 \cdot 10^{-7} m^2/V \cdot s$) and concentration ($n \sim 10^{20}$) were obtained in TILC polydomein samples for the first time.

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О. В. Грідякіна. Електропровідність сумішей термотропних іонних рідких кристалів

Проведено дослідження транспортних властивостей орієнтованих зразків бінарної суміші деканоату кобальту зі свинцем. Виявлено, що зразки суміші в області існування рідкокристалічного стану є слабкими електролітами, для яких характерна анізотропія об'ємної провідності, зумовлена впорядкованістю молекул. Проведено оцінку рухливості та концентрації заряду у зразках деканоату кобальту та деканоатусвинцю.

Ключові слова: іонні термотропні рідкі кристали; бінарні суміші; електропровідність; анізотропія провідності; рухливість заряду; концентрація заряду.

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А. В. Грідякина. Электропроводность смесей термотропных ионных жидких кристаллов

Проведено исследование транспортных свойств ориентированных образцов бинарной смеси деканоата кобальта со свинцом. Обнаружено, что образцы смеси в области существования жидкокристаллического состояния являются слабыми электролитами, для которых характерна анизотропия объемной проводимости, обусловленная упорядоченностью молекул. Проведена оценка подвижности и концентрации заряда в образцах деканоата кобальта и деканоата свинца.

Ключевые слова: ионные термотропные жидкие кристаллы; бинарные смеси; электропроводность; анизотропия проводимости; подвижность заряда; концентрация заряда.

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