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CONDUCTIVITY OF THERMOTROPIC IONIC LIQUID CRYSTALS

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Abstract. *The article represents the results of electrical conductivity studies of cobalt decanoate and lead decanoate oriented samples. It was determined that samples are weak electrolytes in the liquid crystal state region. The samples are characterized by great anisotropy of bulk conductivity caused by molecular order.*

Keywords: anisotropy of conductivity; cobalt alkanoate; conductivity; lead alcanoate; thermotropic ionic liquid crystals

1. 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.

Due to recent trends the great attention is paid to studies of untraditional types of liquid crystals (LC). The unconventional properties of these materials open up new possibilities for various practical uses. One of such properties with great practical importance is anisotropy of electrical conductivity.

2. Analysis of research 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 conductivity of oriented liquid crystal phase of TILC. In particular, the temperature dependence of the anisotropy of conductivity and anisotropy value oriented crystal are unknown. Also the impact of near-electrode phenomena on TILC conductivity is unclear.

The aim of the work is:

– investigation of electrical conductivity of TILC of cobalt decanoate and lead decanoate for determining its features;

– detection of the connection between electrical conductivity and structure of LC.

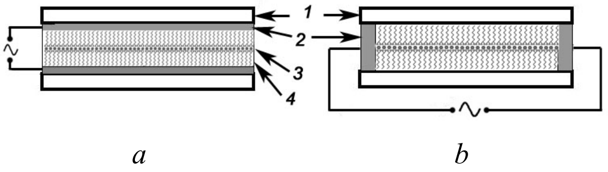
3. Methods and objects of research

The investigation of electric properties was conducted for samples of cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$ (T_{melt}=82^{0}C, T_{clar}>300^{0}C), and lead decanoate $(C_9H_{19}COO^-)_2Pb^{2+}$ (T_{melt}=87^{0}C, T_{clar}=114^{0}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.



a *b*

Fig. 1. Types of LC cells for studies of electrical properties: A) cell with sandwich electrodes, B) cell with planar arrangement of electrodes; *1* – glass substrates, *2* – Ni or Cu electrodes, *3* – cation-anion interlayer, *4* – alkyl chains of molecules.

4. Results and discussion

Electrical conductivity of cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$

Measurements were carried out in the temperature interval 293-395 K for the same sample directions of temperature growth and decrease. It was found, that the conductivity measured along cation-anion layers at the temperature of LC formation (T=355 K) was $\sigma_{||} \approx 4{,}05\times10^{-5} Sm/m$ and exponentially increases with temperature.

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:

$$\frac{\sigma}{T} = \sigma_0 \cdot \exp(-\frac{E_a}{k \cdot T}),$$

where σ – conductivity of TILC, T - temperature, σ_0 – pre-exponential factor, k – Boltzmann constant, E_a – 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 ($q=2$ – 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: $E_{a||}=0{,}12eV$, and $E_{a||}/q=0{,}06J/C$. 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.

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 five orders of magnitude ($\sigma_{\perp} \approx 5{,}24\times10^{-10} Sm/m$, T=355 K).

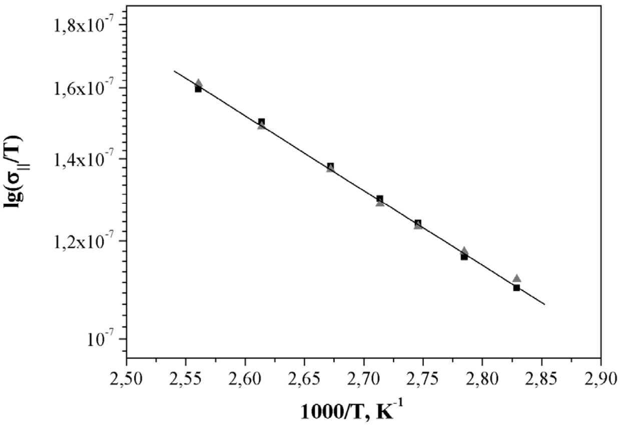


Fig. 2. Logarithmic temperature dependence of the electrical conductivity of cobalt decanoate, measured along the cation-anion layers.

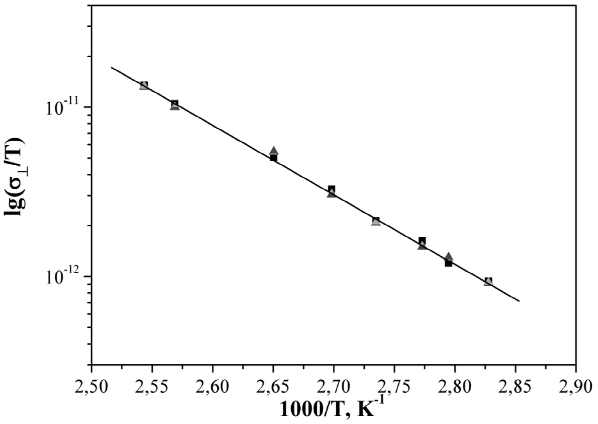


Fig. 3. Logarithmic temperature dependence of the electrical conductivity of cobalt decanoate, measured perpendicular to the cation-anion layers.

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: $E_{a\perp} = 0{,}80 eV$, $E_{a\perp}/q = 0{,}40 J/C$.

Electrical conductivity of lead decanoate $(C_9H_{19}COO^-)_2Pb^{2+}$

In contrast to the cobalt decanoate compound with clear homeotropical alignment of molecules in the liquid crystal cell (sample close to the single-domain LC) the polydomain sample of lead decanoate has quasiplanar alighment of molecules in the cell. Therefore, the studies of electrical conductivity along the cation-anion layers were held using the cell with sandwich electrodes and perpendicular layers - cell with planar electrodes.

The temperature dependences of conductivity for lead decanoate compound are similar to previous case (Fig. 4–5). As for cobalt decanoate, electrical conductivity of the samples of lead decanoate exponentially increases with temperature.

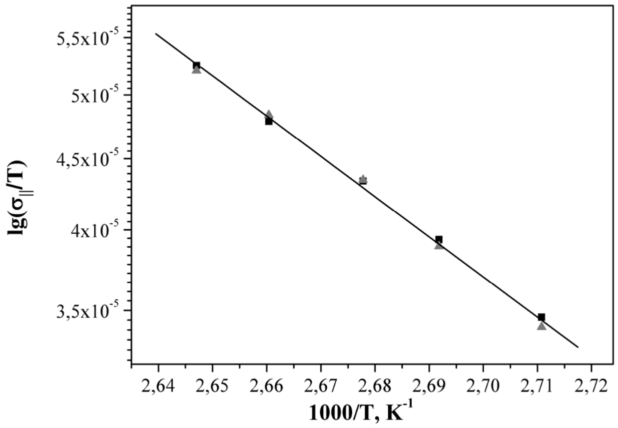


Fig. 4. Logarithmic temperature dependence of the electrical conductivity of lead decanoate, measured along the cation-anion layers

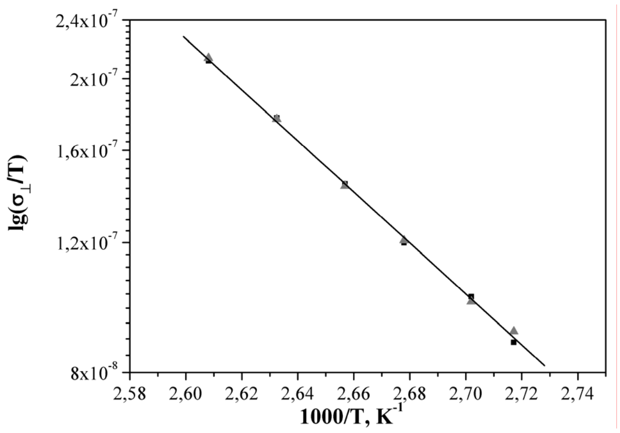


Fig. 5. Logarithmic temperature dependence of the electrical conductivity of lead decanoate, measured perpendicular to the cation-anion layers

The electrical conductivity measured along cation-anion layers is equal $\sigma_{||} \approx 4{,}93 \times 10^{-4} Sm/m$ at the temperature of the formation of LC (T=360 K). And measured perpendicular layers - $\sigma_{\perp} \approx 3.69 \times 10^{-6} Sm/m$ at the same temperature region. Values of activation energy and of the energy barrier are the following: $E_{a||} = 0{,}57 eV$, $E_{a||}/q = 0{,}29 J/C$ – along layers (Fig. 4), $E_{a\perp} = 0{,}69 eV$, $E_{a\perp}/q = 0{,}35 J/C$ – perpendicular layers (Fig. 5).

Obtained values of electrical conductivity measured along and perpendicular to the smectic layers indicate the existence of anisotropy of conductivity, but its value $\sigma_{||}/\sigma_{\perp} = 10^2$ is three orders of magnitude smaller than the anisotropy of the conductivity of cobalt compound ($\sigma_{||}/\sigma_{\perp} = 10^5$). This is because the sample of lead decanoate is polydomain with mostly planar alignment of molecules in the cell, i.e. the alignment of molecules are not strictly planar. However, the conductivity of lead compound was greater than cobalt. In particular, its value along layers approximately ten times more ($\sigma_{||} \approx 4{,}05 \times 10^{-5} Sm/m$ - cobalt decanoate sample, $\sigma_{||} \approx 4{,}93 \times 10^{-4} Sm/m$ - lead decanoate sample). The reason is the viscosity of substances, which for cobalt compound was significantly greater [12, 13].

Thus, studies have shown that all the oriented samples of TILC 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.

Interconnection of the electrical properties of TILC with the structure

Layered structure of TILC [8] causes the occurring of significant differences between the transport of main charge carriers in the oriented LC compared with not oriented and isotropic melt. Charge transfer occurs along the direction of vector of applied electric field. The value of conductivity depends little on the direction of the field in the case of nonoriented LC and does not depend for isotropic melt. At the same time there is a large anisotropy of conductivity for oriented LC, i.e. the conductivity along the smectic layers 2–5 orders of magnitude higher than the conductivity perpendicular to the layers $\sigma_{||} >> \sigma_{\perp}$.

Anisotropy of conductivity can be explained qualitatively using Stokes model for the movement of charged spherical particles of radius r in a homogeneous medium with viscosity η [14, 15]. According to this model, the mobility μ of charged spherical particles is inversely proportional to the value of viscosity $\mu \sim 1/\eta$. For oriented smectic mesophase viscosity along the layers is always less than the viscosity in the direction perpendicular to the smectic layers. Due to this, layers of molecules in the smectic phase sufficiently freely move relative to each other. Since conductivity is inversely proportional to viscosity, then the most efficient charge transfer direction is the direction with the lowest viscosity, i.e. charge transport in TILC takes place in the direction along the smectic layers.

5. Conclusions

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

Established, that TILC of cobalt decanoate and lead decanoate are weak electrolytes in the temperature range of LC existence. They are characterized by a large anisotropy of bulk conductivity caused by the ordering of molecules.

Found the large anisotropy of bulk conductivity ($\sigma_{II}/\sigma_{\perp} \approx 10^5$) during the measurement parallel and perpendicular to the cation-anion layers with homeotropic orientation of molecules. The presence of anisotropy 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.

References

[1] *Ubbelohde A.R.* The Molten State of Matter / A.R. Ubbelohde., 1978. – 454 p. – (John Wiley)..

[2] *Delimarsky Yu.K.* Chemistry of ionic melts / Yu.K. Delimarsky // K.: "Naukova dumka". – 1980. – 103 p. (in Russian).

[3] *Ubbelohde A.R.* Liquid Crystals in Molten Salt Systems / A.R. Ubbelohde, H.J. Michels, J.J. Duruz // Nature. – 1970. – Vol.228. – P. 50-52.

[4] *Twarowski A.J., Albrecht A.C.* Depletion layer studies in organic films: Low frequency capacitance measurements in polycrystalline tetracene / A.J. Twarowski, A.C. Albrecht // The J. of Chem. Phys. – 1979. – Vol.70, № 5. – P. 2255–2261.

[5] *Koval'chuk A.V.* Low and infralow-frequency dielectric spectroscopy of the liquid crystals – solid substrate interface. Sliding layers / A.V. Koval'chuk // Ukr. J. of Phys. – 1996. – Vol.41. – P. 991–998.

[6] *Koval'chuk A.V.* Relaxation processes and charge transport across liquid crystal – electrode interface / A.V. Koval'chuk // J. of Phys: Condensed Matter. – 2001. – Vol.13. – P. 10333–10345.

[7] *Koval'chuk A.V.* Mechanism of charge exchange at a liquid crystals – electrode interface / A.V. Koval'chuk // JETP Lett. – 2000. – Vol. 72. – P. 542–546.

[8] *Gridyakina O.V.* Optical, nonlinear optical and electric properties of ionic thermotropic liquid crystals and layered glasses of cobalt alkanoates: PhD manuscript: 01.04.15 / O.V. Gridyakina– Kiev, 2012. – 129 p. (in Ukrainian).

[9] *Gryshchenko N.I., Kuryk M.V., Rogoza A.V.* Mobility and concentration of charge carriers in cholesteric liquid crystals / N.I. Gryshchenko, M.V. Kuryk, A.V. Rogoza // Ukr. Phys. J. – 1985. – V. 30, №10. – P. 1497-1499. (in Ukrainian).

[10] *Belotsky E.D., Byvalkevich M.A., Gryshchenko N.I.* Mobility of charge carriers in nematic liquid crystals / E.D. Belotsky, M.A. Byvalkevich, N.I. Gryshchenko // Solid-state physics. – 1990. – V. 32, №4. – P. 961 – 965. (in Russian).

[11] *Gritsenko N.I., Rogoza A.V., Gruzinko V.V.* Conductivity and mobility of charge carriers in liquid crystals / N.I. Gritsenko, A.V. Rogoza, V.V. Gruzinko // Ukr. Phys. J. – 1987. – V. 32, № 6. – P. 880–885. (in Ukrainian).

[12] *Mirnaya T.A.* Liquid crystal state of saline melts with organic ions / T.A. Mirnaya // Uspehi himii. – 1989. – V.58, № 9. – P. 1429–1450. (in Russian)

[13] *Adeosun S.O.* Properties of molten carboxylates. Part 8. A.c. impedance of mesophases of some even chain length lead (II) n-alkanoates / S.O. Adeosun, S.J. Sime // J. Chem. Faraday Trans. I. – 1979. – Vol.75. – P.953-961.

[14] *Vedenov A.A.* Chemistry of solutions / A.A. Vedenov. – M.: Science, 1984. – 112 p. (in Russian).

[15] *Delimarsky Yu.K.* Electrochemistry of ionic melts / Yu.K. Delimarsky // M.: "Metalurgiya". – 1978. – 248 p. (in Russian).

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О.В Грідякіна. Електропровідність термотропних іонних рідких кристалів

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У роботі наведено результати досліджень електричних характеристик термотропних іонних рідких кристалів деканоату кобальту та деканату свинцю. Показано наявність анізотропії провідності. Встановлено зв’язок транспорту заряду з двошаровим пакуванням молекул (катіон-аніонний прошарок між шарами алканоатних ланцюгів), властивим смектичній А фазі.

Ключові слова: алканоат кобальту; алканоат свинцю; анізотропія електропровідності; електропровідність; термотропні іонні рідкі кристали

А.В. Гридякина. Электропроводность термотропных ионных жидких кристаллов

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В работе приведены результаты исследований электрических характеристик термотропных ионных жидких кристаллов деканоата кобальта и деканата свинца. Показано, наличие анизотропии проводимости. Установлена связь транспорта заряда с двухслойной упаковкой молекул (катион-анионная прослойка между слоями алканоатних цепей), присущей смектической А фазе.

Ключевые слова: алканоат кобальта; алканоат свинца; анизотропия электропроводности; термотропные ионные жидкие кристаллы; электропроводность

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