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Electrophysical Properties of Coordination Compounds Based on Cobalt(II) and Manganese(II) Chlorides and ε-Caprolactam

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Abstract—The metal complex systems based on Co(II) and Mn(II) chlorides and ε-caprolactam were studied. Temperatures of the phase transition, activation energy of the electrical conductivity, and mobility of the charge carriers in the compounds obtained were determined.

In [1–3], we found that a series of coordination compounds of transition metal [Co(II), Mn(II), Cu(II), and V(III)] chlorides cross-link polymers containing electron-donor groups. Up to now, aromatic diisocyanates and related urethane-forming systems were the main objects of the study of interaction with metal complexes.

The initial components forming metal-complex modifying systems can be subdivided in two types. In the first group, 3*d* metal chlorides with variable metal oxidation state [Cu(II), Fe(III), V(III), and Cr(III)] are used as coordinating centers, and *N*,*N*'-diethylhydroxylamine and polyoxyethylene glycol, as ligands. Interaction is accompanied by redox process, and yields polynuclear complexes in which 3*d* metal ions exist in two oxidation states. The resulting reactive system cross-links polyurethane matrix, enhances its physicomechanical properties, and substantially (by a factor of 10^4–10^5) increases the electrical conductivity. It was shown that the cross-linking effect in the urethane-forming system occurs at a low content of metal chloride (0.1–1%).

In the second case, 3*d* metal chlorides in the lower oxidation state [Co(II) and Mn(II)] and monoethanolamine (MEA) were the initial components for obtaining a metal-complex modifier. It was found that the reaction of $CoCl_2$ with MEA is completed by formation of a mixture of mono-, bi-, and polynuclear tetrahedral cobalt complexes in which the metal ions keep their oxidation state and are bound with each other by chloride bridges.

The ability of metal ions to coordinate the urethane amide group and thus to cross-link macromolecules was used in synthesis and studying modifying systems based on Co(II) and Mn(II) chloride complexes with ε-caprolactam.

It was found that on addition of a $CoCl_2$ ($MnCl_2$)–MEA mixture the ε-caprolactam melt becomes turbid, and its viscosity increases. Thermooptical study on a polarization microscope with a thermal stage showed that the resulting turbid melt is a smectic liquid crystal phase, which is readily identified through characteristic “schlieren” textures. These results were confirmed by DSC (Fig. 1).

The intrinsic viscosity was measured for the initial ε-caprolactam and products of the final stage of its reaction with $MnCl_2$–MEA and $CoCl_2$–MeA. For caprolactam, the intrinsic viscosity is close to zero, while for coordinated ε-caprolactam it is 0.027 dl g^{-1}. Such a small increase in the intrinsic viscosity in-

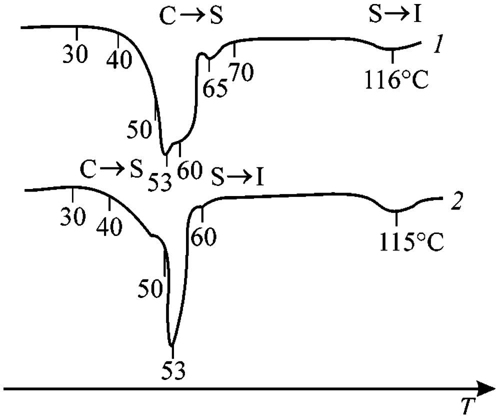

Fig. 1. DSC curves for the (*1*) $CoCl_2$–MEA–ε-caprolactam and (*2*) $MnCl_2$–MEA–ε-caprolactam systems. Heating rate 8 deg min^{-1}. (*T*) Temperature. Phase state of the substance: (C) crystalline, (S) smectic liquid crystal, and (I) isotropic liquid.

dicates that ε-caprolactam does not polymerize under reaction conditions.

The change of the chemical composition of ε-caprolactam caused by interaction with the metal-complex system was controlled by IR spectra. The most characteristic absorption band for ε-caprolactam caused by stretching vibrations of the amide carbonyl group lies at 1672 cm^{-1}. After interaction with the metal-complex system it shifts to 1678 cm^{-1} and noticeably broadens. Such changes are characteristic for coordinated carbonyl group and suggest that ε-caprolactam forms coordination bonds with metal complexes in the $CoCl_2$–MEA system.

To study features of mesomorphic phase formed, we measured the temperature dependences of electrical conductivity in the systems $CoCl_2$–MEA–ε-caprolactam and $MnCl_2$–MEA–ε-caprolactam. These dependences are shown in Fig. 2 in semilogarithmic coordinates. Three sections of the curves are observed. They can correspond to the crystalline state (C), mesomorphic state of the smectic type (S), and state of isotropic liquid (I).

At phase transitions S → I (at heating) and I → S (at cooling), the electrical conductivity changes by more than an order of magnitude. At C → S phase transition, no jump of the electrical conductivity is observed; however, the break appears in the $\ln\sigma–1/T$ curve, caused by the change of the activation energy. The position of this break in the temperature curve approximately corresponds to the C → S phase transition temperature in the DSC curve. Since it is known that the temperature dependence of the electrical conductivity for organic semiconductors is well fitted by the Arrhenius equation, we used the equation

$$\sigma = \sigma_0 \exp[-E_a/kT] \qquad (1)$$

to determine the activation energies E_a of the electrical conductivity. The activation energies, phase transition temperatures, and conductivities are listed in the table.

The shape of DSC dependences and the values of E_a obtained in our work are similar to published data for other systems [4–6]. However, we can note certain features characteristic for the systems studied: the activation energies of high-frequency and dc electrical conductivity for the isotropic phase are practically the same; the temperature range of the mesophase existence is fairly broad; the electrical conductivity is several orders of magnitude larger than that described in the literature (up to 10^{-3} Ω^{-1} cm^{-1} in the I phase); the pronounced temperature hysteresis occurs, i.e. at sample cooling the temperature interval of the existence of the mesophase is fairly narrow.

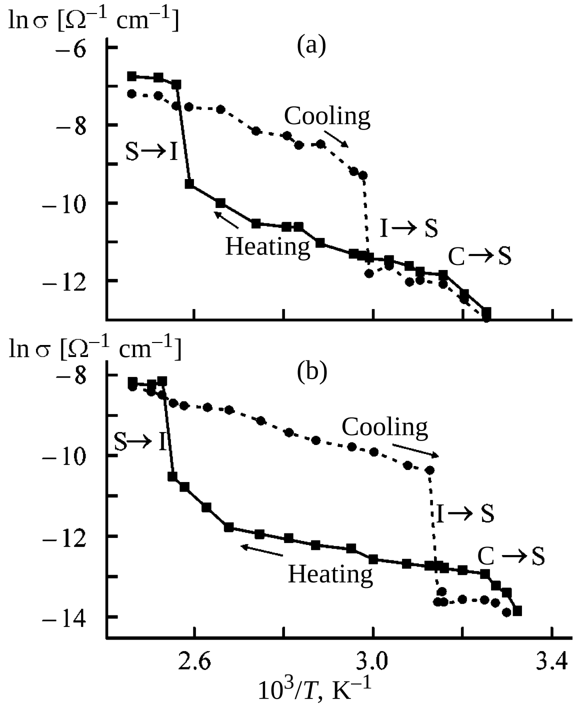

Fig. 2. Temperature dependence of the electrical conductivity σ for the (a) $CoCl_2$–MEA–ε-caprolactam and (b) $MnCl_2$–MEA–ε-caprolactam systems.

The DSC curves are shown in Fig. 1. For both systems the melting point varies within the range 50–60°C. The DSC curves were measured up to the corresponding S → I transitions. The temperature of the transition into the isotropic liquid was determined from both the corresponding jumps in the curves of temperature dependence of the electrical conductivity and the DSC curves. It is 116–120°C and 115–119°C for the $CoCl_2$–MEA–ε-caprolactam and $MnCl_2$–MEA–ε-caprolactam systems, respectively.

Phase transfer temperatures *T*, activation energies E_a, and electrical conductivity σ for systems MCl_2–MEA–ε-caprolactam; M = Co, Mn

Parameter	Co	Mn
T, °C: C → S	55	57
S → I	116	115
I → S	65	45
E_a, eV: for C	1.06	1.29
for S	0.43	0.14
for I	0.38	0.24
σ I/σ S	15	23
Δσ, Ω cm^{-1}	8.35×10^{-7}– 1.00×10^{-3}	1.21×10^{-6}– 2.75×10^{-4}

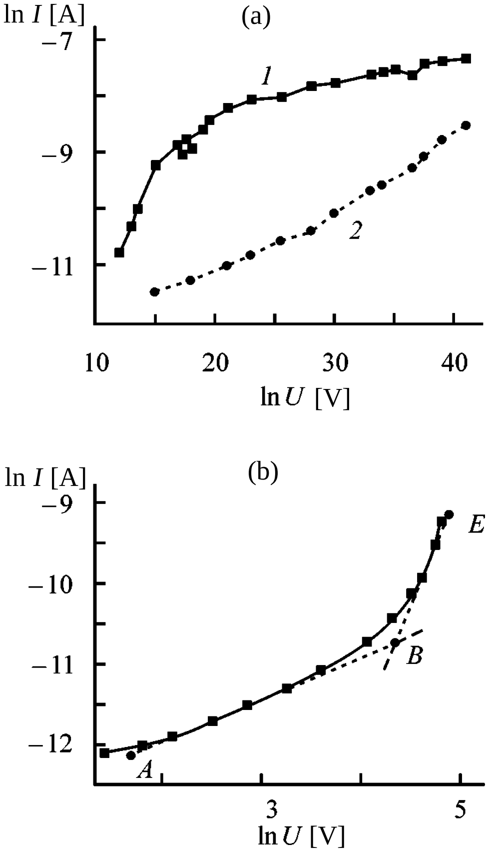

Fig. 3. Volt-ampere characteristics of the (a) $MnCl_2$–MEA–ε-caprolactam and (b) $CoCl_2$–MEA–ε-caprolactam systems. (*I*) Current and (*U*) voltage. Sample: (*1*) initial and (*2*) after electrochemical purification.

The volt–ampere characteristics (VAC) measured for freshly prepared samples are linear at a low field intensity. At fields $E > 4 \times 10^3$ V cm^{-1} they become sublinear up to saturation. Moreover, the current decreases with time. Such a phenomenon is known for liquid crystals and the other systems with the ionic conductance and is due to the electrochemical purification to remove extrinsic ions. After standing for 30 min in the maximal electric field of 2×10^4 V cm^{-1}, the current through the sample decreases and becomes independent of time. Probably, after the electrochemical purification to remove extrinsic ions, the volt–ampere characteristic of samples is mainly caused by the electronic component of the current. The volt–ampere characteristics for $MnCl_2$–MEA–ε-caprolactam and $CoCl_2$–MEA–ε-caprolactam systems are shown in Figs. 3a and 3b, respectively. For the system with $CoCl_2$, both ohmic and nonohmic sections are described by the Child–Langmuir law. Such a behavior of VAC is caused by the following two effects. At a relatively high current density corresponding to the strong electric field, the concentration of current carriers moving in the gap between the electrodes is fairly large, and these carriers form a space charge. The next reason of the VAC nonlinearity is the existence of traps such as impurities, defects of crystal packing, dislocations, and other lattice defects. These defects give rise to additional localized levels in the band gap [7].

At low voltages, injection of current carriers from the electrode is negligible, and the current obeys the Ohm law (section *AB*). In the absence of traps, the current is restricted by the space charge at the voltage corresponding to point *B*. In this point, the concentration of free carriers injected from the electrode begins to prevail over the thermally equilibrium concentration of carriers. After this point, VAC obeys the Child–Langmuir law and follows the *BE* line, and the current *I* (A cm^{-2}) is determined by the equation

$$I \cong 10^{-13}\frac{\mu\varepsilon U}{d^3}, \qquad (2)$$

where *U* is applied voltage (V), μ is the carrier mobility (cm^2 V^{-1} s^{-1}), ε is the dielectric constant, and *d* is the distance between the electrodes (cm).

The current stops to be ohmic beginning from the definite voltage U_{tr} (point *B*) at which the currents start to be limited by the space charge. After determining U_{tr} from the experimental VAC curve for the substance studied ($CoCl_2$–MEA–ε-caprolactam system) and its substitution in Eq. (2), we obtain a formula for determination of the carrier mobility μ:

$$\mu = 10^{13} Id^3/(\varepsilon U^2)$$

All liquid crystal compounds are characterized by anisotropy of dielectric parameters. In this case, the average dielectric constant equal to 41 was used for the $CoCl_2$–MEA–ε-caprolactam system.

After substitution of U_{tr} = 73 V from the VAC curve for the $CoCl_2$–MEA–ε-caprolactam system in Eq. (3), we calculated the mobility of charge carriers: $\mu = 7 \times 10^{-4}$ cm^2 V^{-1} s^{-1}, which corresponds to the electronic mobility characteristic typical of organic semiconductors in the case of hopping (electronic) conductance.

The volt–ampere characteristic for the $MnCl_2$–MEA–ε-caprolactam system after the electrochemical purification is ohmic; transition to the quadratic section at field intensities up to 2×10^4 V cm^{-1} was not observed.

EXPERIMENTAL

The crystal hydrate $MnCl_2 \cdot 4H_2O$ was dried to $MnCl_2 \cdot 3H_2O$ at 106°C, and $CoCl_2 \cdot 6H_2O$ was dried at 60°C in a thermal box. Monoethanolamine was purified by vacuum distillation. Chemically pure grade ε-caprolactam was prepared by recrystallization of commercial grade ε-caprolactam from ethyl acetate. The reaction of $CoCl_2$ and $MnCl_2$ with MEA was performed with vigorous agitation and heat removal. The molar ratios $MnCl_2$: MEA and $CoCl_2$: MEA was 1 : 10 and 1 : 3.6, respectively. The resulting complex was introduced directly into the ε-caprolactam melt at the molar ratio [$MnCl_2$] and [$CoCl_2$] : [ε-caprolactam] = 1 : 9. The reaction mass was agitated at 90°C for 30 min. Catalytic amounts of acetonitrile and 2,4-toluylene diisocyanate were also introduced into the reaction mass.

The IR spectra were registered on a Perkin–Elmer 16PC FT-IR spectrometer with precise fixation of the light radiation (±1%). The thickness of the spectrometric cell was 0.022 cm. Thermograms were obtained on a DSM-2M differential scanning microcalorimeter (rate of heating to 200°C 8 deg min^{-1}). The intrinsic viscosity was determined on a Ubbelohde viscometer at 20°C. Phase transitions were registered with a Polam P-211 polarization microscope equipped with a thermal stage.

The study of electrophysical characteristics was reduced to measurement of the temperature dependences of the dc electrical conductivity within the 290 – 420 K range by the standard method. Platinum electrodes with optimal size were introduced into the vessel with the sample studied. To avoid field end effects, the fixed distance between the electrodes was substantially smaller than their linear sizes. The temperature was controlled through the change of the voltage on a thermostat heater and monitored with a Chromel–Alumel thermocouple (connected with a V7-21 voltmeter) placed directly in the vessel with the sample. The electrical resistance of the latter was measured with a E6-13A teraohmmeter with an error of 2.5%.

The charge carrier mobility was determined through recording volt–ampere characteristics at 290 K. The sample was installed into a specially fabricated cell of the “sandwich” type: two flat glass plates with the applied transparent conducting layer of SnO_2 were separated by a mica layer with a small window in which the sample was placed. The thickness of the gap between the glass plates was equal to the thickness of the mica layer, which in our case was 4×10^{-5} m. The voltage on the sample (40 V) was fed from a stabilized V5-9 source. The current was recorded on a V7-21 universal voltmeter. The electric field intensity was varied up to 2×10^3 V cm^{-1}.

CONCLUSIONS

(1) Data on electrical conductivity and conductivity activation energy show that the compounds obtained by the reaction between $MnCl_2$ (or $CoCl_2$), monoethanolamine, and ε-caprolactam and existing in the crystalline, liquid-crystalline, and isotropic state are organic semiconductors.

(2) Phase transitions crystal–liquid crystal and liquid crystal–isotropic liquid appear in the temperature dependence of the electrical conductivity as a break or sharp jump (at the liquid crystal–isotropic liquid transition). The pronounced temperature hysteresis in the heating–cooling cycle is observed.

(3) The electrical conductance of freshly prepared samples has a mixed ionic-electronic character. After the electrochemical purification, volt–ampere characteristics of the systems studied are characteristic for organic semiconductors with hopping electronic conductance.

(4) The transition from ohmic to quadratic (the Child–Langmuir dependence) section in the volt–ampere curves of the $CoCl_2$–MEA–ε-caprolactam system is observed. The mobility of charge carriers was calculated from the inflection point.

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