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Liquid crystal formation in mixtures of metal alkanoates: gadolinium-containing binary systems

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Mesophase formation is reported in ionic liquid crystal mixtures of lead decanoate with gadolinium alkanoates. The negative effect of Gd salts on mesophase thermal stability increased in the order stearate < undecanoate < 2-ethylhexanoate, with gadolinium-containing mesophase persisting on introduction of the non-mesogenic Gd salts up to 40 %, 12 % and 5 %, respectively. In a ternary system, the mesophase range of ~20°C, starting below 80°C, could be obtained at ~25 % gadolinium salt concentration.

Рассмотрено образование мезофазы в смесях ионных жидких кристаллов деканоата свинца и алканоатов гадолиния. Влияние солей Gd на снижение термостабильности мезофазы возрастало в ряду стеарат < ундеканоат < 2-этилгексаноат с сохранением мезофазы при введении этих немезогенных солей гадолиния до концентраций 40 %, 12 % и 5 %, соответственно. В тройной системе возможно достижение интервала мезофазы ~20°C, начиная от температур ниже 80°C, при содержании солей гадолиния ~25 %.

Recently an increased interest has been noted in condensed phases formed by metal alkanoates. These substances can form both thermotropic and lyotropic mesophases, Langmuir-Blodgett (LB) films, isotropic and mesomorphic glasses, which can be used as materials for non-linear optics, media for stabilization of nanoparticles, etc. [1–3].

Systematic studies of thermotropic liquid crystals formed by metal alkanoates and their binary mixtures were carried out by Mirnaya e.a. [4–8] and Binnemans e.a. [1, 9–11]. In these works, the effects of uni-, bi- and trivalent metal ions, as well as shorter and longer alkyl chains, upon mesophase formation have been thoroughly studied. A special interest was noted for alkanoates of rare-earth (RE) metals, where the combination of optico-luminescent and magnetic properties of *f*-elements with liquid crystalline supramolecular ordering can allow creation of functional materials with unique physical properties [6, 9, 12].

Studies of mesomorphic properties of lanthanide alkanoates have been reviewed in [1]. The characteristic liquid crystalline ordering is of smectic-A (SmA) type. The major factors affecting the mesomorphic properties are the RE ion size and the alkyl chain length. The liquid crystal formation is suppressed with heavier RE ions; thus, in the dodecanoate series, only La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} salts appear to be mesomorphic [9]. No data have been found for gadolinium salts, which, according to general considerations, are not expected to form mesophases as individual compounds.

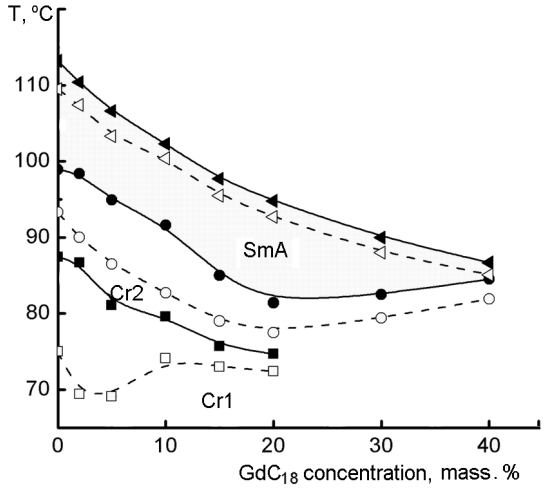

Fig. 1. Phase transition temperatures in PbC_{10}+GdC_{18} binary system. I — isotropic phase, SmA — smectic-A, Cr2 and Cr1 — solid crystal phases. Solid lines – heating; dashed lines — cooling.

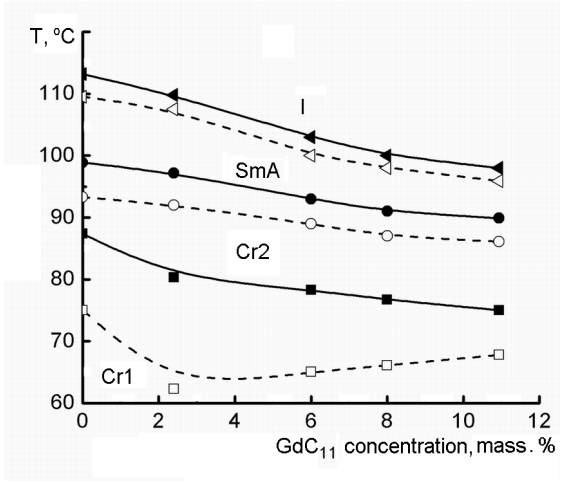

Fig. 2. Phase transition temperatures in PbC_{10}+GdC_{11} binary system. Notation symbols are similar to Fig. 1.

Gadolinium is a very interesting element from the viewpoint of possible applications due to its intrinsic magnetic moment, large neutron capture cross-section, and luminescent properties. The use of gadolinium alkanoates in liquid organic scintillators for neutron detection has been reported [13]. Even more promising can be gadolinium-containing anisotropic media; thus, gadolinium stearate LB films were considered as two-dimensional magnetics [14]. It has been also known that mesomorphic properties of RE alkanoates can be enhanced by using binary systems of "mesogen — non-mesogen" type [11].

The aim of the present work was to outline the way for preparation of gadolinium-containing mesophases with sufficiently broad temperature ranges and high concentration of gadolinium in metal alkanoate mixtures. We used lead decanoate as a basic (matrix) compound of these mixtures, due to its broad mesomorphic range, relatively low temperature of liquid crystal — isotropic transition, and good solvent properties with respect to many mesogens and non-mesogens of different chemical classes [15]. Also, binary systems of metal alkanoates of different valence (in our case, Pb^{2+} and Gd^{3+}) could be expected to show a tendency to glass formation [16], which could result in preparation of RE-containing anisotropic organic glasses.

In our experiments, temperatures and enthalpies of phase transitions were determined using a Mettler TA 3000 thermoanalytical system under argon flow both on heating and cooling, with temperature scanning rate of 2 K/min.

The lead decanoate (PbC_{10}) sample was the same as used in our previous work [15]; its measured phase transitions were Cr1 → 87.4°C → Cr2 → 98.9°C → SmA → 113.2°C → I, which was in good agreement with the literature data [17, 18].

Gadolinium stearate (GdC_{18}) was synthesized from freshly prepared amorphous gadolinium hydroxide in isopropanol/toluene solvent. The temperature was increased from 75°C to 105–110°C, and octadecanoic acid was added dropwise, with the reaction water continuously removed. Gadolinium 2-ethyl hexanoate ($GdC_{6(2)}$) was synthesized in a similar way, using ethylhexanoic acid.

Gadolinium undecanoate (GdC_{11}) was obtained from freshly prepared sodium undecanoate and water-free gadolinium chloride in toluene at room temperature under argon flow.

All the esters obtained were purified by recrystallization from hexane; the measured melting temperatures were, respectively, 89.5°C (GdC_{18}), 148.7°C ($GdC_{6(2)}$), and 119.7°C (GdC_{11}). As it could be expected, no mesophase formation was noted.

The phase diagram of the binary system PbC_{10}+GdC_{18} is shown in Fig. 1. The liquid crystal phase persisted up to ~40 % GdC_{18}. Up to ~20 %, gadolinium stearate did not cause narrowing of the mesophase temperature range; all phase transition temperatures were monotonously decreasing. The strongest suppression of the Cr2 → SmA and SmA → I transition temperatures (~15 K)

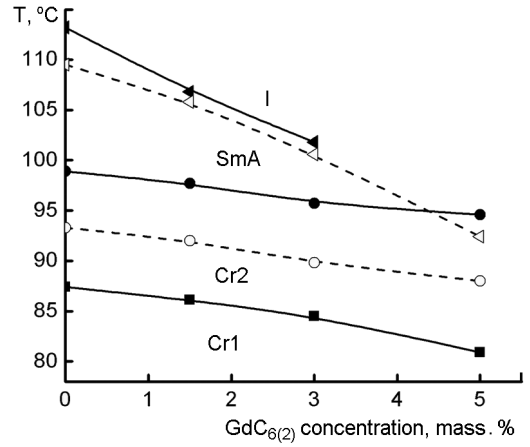

Fig. 3. Phase transition temperatures in PbC_{10}+$GdC_{6(2)}$ binary system. Notation symbols are similar to Fig. 1.

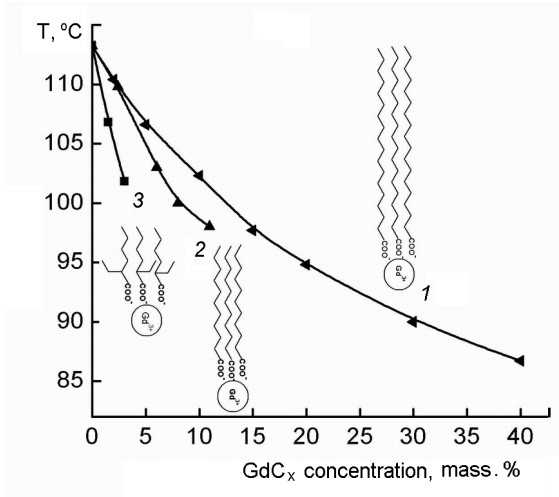

Fig. 4. Isotropic transition temperatures in binary systems based on lead decanoate as function of gadolinium alkanoate concentration: *1* — GdC_{18}, *2* — GdC_{11}, *3* — $GdC_{6(2)}$.

was noted for 20 % of GdC_{18} in lead decanoate. With gadolinium undecanoate, the general picture was similar (Fig. 2), though the mesophase range became noticeably narrower at ~12 %, where the widening calorimetric peaks became smeared.

Unlike GdC_{18} and GdC_{11}, the short-chained and branched gadolinium 2-ethylhexanoate showed much worse solubility in the PbC_{10} mesophase — up to < 5 % (Fig. 3). This could be expected, since gadolinium 2-ethylhexanoate molecules, due to their shape, could not be incorporated into smectic layers of the matrix without disrupting of the alkyl chains packing.

With longer alkyl chains, the depression rate of the liquid crystal – isotropic transition temperature T_i is decreasing. For initial segments of plots in Fig. 4, where the dependence of T_i on concentration c is linear, the values of dT_i/dc for GdC_{18}, GdC_{11} and $GdC_{6(2)}$ are 1.0 K/%, 1.6 K/% and 3.6 K/%, respectively. For the $Cr2 \rightarrow SmA$ transition, the values of dT_c/dc are lower and close for all three gadolinium alkanoates (~0.9 K/%).

Further broadening of the mesophase range and its shift to lower temperatures can be achieved by using ternary mixtures, e.g., $PbC_{10} + GdC_{18} + GdC_{11}$. Addition of 5 % GdC_{11} to the PbC_{10}+GdC_{18} mixture with 20 % GdC_{18} (Fig. 1) lowers T_i by 4.3°C (from 94.9 to 90.6°C), and T_s — by 5.6°C (from 81.4 to 75.8°C), broadening the mesophase range by 1.3°C.

Thus, we have demonstrated a possibility to obtain sufficiently stable gadolinium-containing mesophases by incorporating gadolinium alkanoates into mixtures based on lead decanoate. For such systems, the effect of alkyl chain on the maximum content of gadolinium ions in the mesophase and on its thermal stability have been determined, and ways for improvement of mesomorphic characteristics are outlined.

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Утворення рідких кристалів у сумішах алканоатів металів: бінарні системи, що містять гадоліній

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Розглянуто утворення мезофази у сумішах іонних рідких кристалів деканоату свинцю та алканоатів гадолінію. Негативний вплив солей Gd на термостабільність мезофази зростав у послідовності стеарат < ундеканоат < 2-этилгексаноат зі збереженням мезофази для концентрацій немезогенної солі гадолінію до, відповідно, 40 %, 12 % та 5 %. У потрійній системі можливо досягнення інтервалу мезофази ~20°C, починаючи від температур нижче 80°C, зі вмістом солей гадолінію ~25 %.