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Articles

Induced Mesophases in Binary Mixtures of Lanthanide(III) Dodecanoates

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Mesophase induction was observed in binary mixtures of the liquid-crystalline lanthanum(III) dodecanoate and a nonmesomorphic lanthanide(III) dodecanoate. The compounds have the stoichiometry $La_xLn_{1-x}(C_{11}H_{23}COO)_3$ (where x is the mole fraction of lanthanum, Ln = Nd, Eu, Ho, Tb, and Yb) and were characterized by elemental microanalysis. The thermal behavior was investigated by hot-stage polarized optical microscopy, by differential scanning calorimetry, and by X-ray diffraction at elevated temperatures. The mesophase behavior of the compounds strongly depends on the composition of the mixtures and on the lanthanide ion. For lanthanum−europium dodecanoate mixtures, less than 4 mol % lanthanum(III) dodecanoate is needed to induce mesomorphism, whereas for lanthanum−ytterbium mixtures, the minimum amount of lanthanum(III) dodecanoate increases to 48 mol %.

Introduction

Since metal soaps of lanthanides were synthesized for the first time by Misra et al.[1,2] in the early 1960s, many studies on these compounds have been published.[3−15] Despite these results, it was not until 1998 that Marques et al.[16] discovered the mesophase behavior of cerium(III) alkanoates. They described a pronounced effect of the chain length on the transition temperatures. This effect was later confirmed by our team for lanthanum(III), neodymium(III), cerium(III), and praseodymium(III) carboxylates.[17−20]

Very recently, we found that the size of the trivalent lanthanide ion has a critical effect on the transition temperatures in the sense that a mesophase can only be formed with the lighter lanthanide elements with a large ionic radius [i.e., La(III), Ce(III), Pr(III), and Nd(III)].[21]

Therefore, it was interesting to find out if we could induce mesomorphism in nonmesogenic lanthanide(III) soaps. Until now, information about mesophase induction is scarce. High isotropic pressure has been proved to induce mesomorphism[22] and in particular to induce liquid-crystalline behavior in compounds that do not form liquid-crystalline phases at atmospheric pressure.[23] Levelut et al. published in 1981 the induction of polymorphism in a binary mixture of two liquid crystals.[24] Mirnaya et al. reported on mesophases of binary alkaline salt systems of carboxylic acids,[25] whereas

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Cheda et al. describe binary phase diagrams of lead(II) alkanoates and *n*-alkanoic acids.[26]

Here we describe the synthesis and thermal properties of mixtures of lanthanum(III) dodecanoate with europium(III), neodymium(III), terbium(III), holmium(III), or ytterbium(III) dodecanoate with different compositions.

Experimental Section

CH elemental microanalyses were performed on a CE Instruments EA-1110 elemental analyzer. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC 821e module. Optical textures of the mesophase were observed with an Olympus BX60 polarized optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller. High-temperature X-ray diffractograms were measured on a STOE transmission powder diffractometer system STADI P, with a high-temperature attachment and using monochromatic Cu Kα ($\lambda = 1.54$ Å) radiation.

Reagents and solvents were used as received without further purification. Analytical-grade solvents were used for the synthesis and washing of the soaps. Hydrated lanthanide(III) nitrates were purchased from Aldrich.

The series of $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ (x is the mole fraction of lanthanum in the mixtures) was synthesized by a metathesis reaction between the sodium salt of dodecanoic acid and aqueous solutions prepared from desired amounts of lanthanum(III) and europium(III) nitrate hexahydrate, respectively.[21] The reaction medium is an aqueous ethanol solution (water/ethanol, 1:1). The exact concentrations of the lanthanide solutions were determined by titration with ethylenediaminetetraacetic acid as the complexing agent and a mixed indicator (45 mL of 0.5% sodium alizarine sulfate plus 15 mL of 0.1% methylene blue). After synthesis the soaps were filtered off and washed carefully with water, ethanol, and acetone. The soaps were dried for 24 h in vacuo at 40 °C. The mixtures of lanthanum with the other lanthanides (i.e., neodymium, terbium, holmium, and ytterbium) were prepared in the same way.

The carbon and hydrogen contents of the compounds were determined by CH elemental microanalysis. The analysis results are consistent with an alkanoic acid to lanthanide(III) ratio of 3:1 but also indicate that under the given reaction conditions the compounds cannot be obtained in a total anhydrous form. Most of the soaps are monohydrates, $[La_xLn_{1-x}(C_{11}H_{23}COO)_3]\cdot H_2O$. The degree of hydration does not depend on the drying conditions. However, thermogravimetric study showed that the water molecules are lost before or at the melting point. The amount of water calculated by thermogravimetry is almost the same as that obtained from CH results. Obtained results by CH elemental microanalysis. Exptl for $La_{0.725}Eu_{0.275}(C_{11}H_{23}COO)_3$: C, 57.09; H, 9.70. Calcd (without H_2O): C, 58.40; H, 9.39. Calcd (+ 1 H_2O): C, 57.01; H, 9.44. CH data for all of the compounds are available as Supporting Information.

Results and Discussion

The thermal behavior of $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ was investigated by DSC, by hot-stage polarized optical microscopy, and by X-ray diffraction at elevated temperatures.

All of the compounds of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ with $x \geq 0.40$ exhibit in the DSC-curve multiple melting phenomena, indicating the presence of a mesophase. This is in contrast with the pure nonmesogenic europium(III) dodecanoate, which shows in the DSC trace only one phase transition, i.e., the melting peak. However, the mesogenic lanthanum(III) dodecanoate exhibits a comparable DSC curve as the compounds of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$. In Figure 1 the DSC trace of $La_{0.55}Eu_{0.45}(C_{11}H_{23}COO)_3$ is shown (first heating and cooling cycle). Both melting and clearing peaks are quite distinct. In the cooling run, a supercooling is observed. This is due to the ionic nature of the compounds.

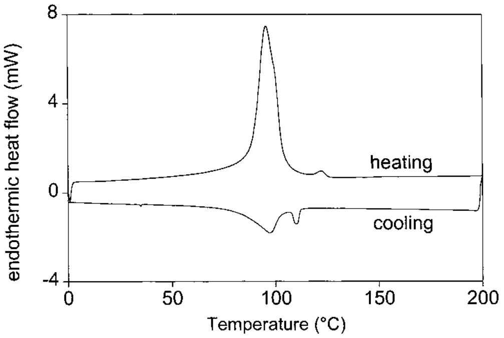

Figure 1. DSC thermogram of $La_{0.55}Eu_{0.45}(C_{11}H_{23}COO)_3$ (first heating−cooling cycle). Endothermic peaks are pointing upward.

The fact that in these compounds both melting and clearing points can be observed means that mesomorphism is induced in a nonmesogenic compound [i.e., europium(III) dodecanoate] by mixing it with the mesogenic lanthanum(III) dodecanoate.

Although the compounds with lower lanthanum(III) content do not exhibit two or more peaks in their DSC traces, we expected a mesophase for several compounds. Indeed, when we plot the melting and clearing temperatures as a function of the lanthanum concentration, we obtain two straight lines which cross each other at a mole fraction of lanthanum of about 0.04. This means that all of the compounds from the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ with $x \geq 0.04$ must be mesomorphic. The fact that we do not see a clearing peak in the DSC trace can be assigned to a very small heat exchange at the phase transition and to overlap between the melting and clearing peaks.

The mesomorphic properties of these compounds have, therefore, been investigated by hot-stage polarized optical microscopy. In this way it was possible to determine the complete phase diagram of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$. The obtained textures had a grainy appearance with white−yellow zones on a dark background. They look very similar to those reported by Marques et al.[16] and to those for lanthanide(III) dodecanoates, which exhibit a SmA phase.[21] Although this is an indication for the mesophase in the mixed compounds, the exact mesophase could only be determined unambiguously by high-temperature X-ray diffraction.

The X-ray diffractogram of $La_{0.60}Eu_{0.40}(C_{11}H_{23}COO)_3$ at room temperature and in the mesophase is given in Figure 2. Up to four peaks were observed in the low-angle region of the X-ray powder diffractogram of the solid mixed lanthanum−europium alkanoates, with the peak at the lowest angle bearing by far the highest intensity. The *d* spacing values are in the ratios $1:{}^1/_2:{}^1/_3 ... {}^1/_n$. These diffraction peaks correspond to the successive (00*l*) reflections and indicate the presence of

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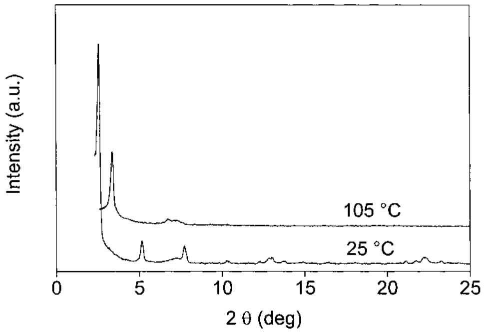

Figure 2. X-ray diffractogram of $La_{0.60}Eu_{0.40}(C_{11}H_{23}COO)_3$ at room temperature and in the mesophase.

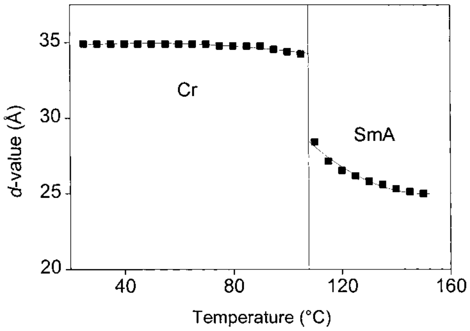

Figure 3. Change of the *d* spacing of $La_{0.95}Eu_{0.05}(C_{11}H_{23}COO)_3$ as a function of the temperature.

a lamellar structure. The polar groups of the lanthanide(III) alkanoates are localized in infinite, parallel, and equidistant planes. These planes are separated from each other by a bilayer of alkyl chains in the all-trans conformation. The interplanar layer spacing *d* corresponds to the distance between two successive layers of lanthanide(III) ions.

It should be noticed that, although the compounds are not anhydrous, the presence of water molecules does not influence the lamellar structure and, therefore, not the mesophase behavior. This is due to the fact that the water molecules are situated in the ionic layer of these compounds.

In the mesophase, the lamellar bilayer structure is retained, but a distinct decrease in the *d* spacing is observed at the solid−mesophase transition (Figure 2). This indicates that the alkyl chains lose their all-trans conformation and that some kind of folding occurs. At the clearing point, all structure is lost, and an ionic melt is formed. The temperature dependence of the *d* spacing in the mesophase (decrease of *d* spacing at increasing temperatures) corresponds to the behavior expected for a smectic A phase (Figure 3).[27]

The whole series of $La_xEu_{1-x}(C_{11}H_{23}COO)_3$, whereby $x \geq 0.04$, exhibits a smectic A phase, although there is a marked influence of the composition of the mixed complexes on the transition temperatures (Figure 4). Both melting and clearing points increase with increasing mole fraction of lanthanum(III). It was possible to fit the data linearly. This resulted in two straight lines with rather good R values (linear regression for the melting point, $y = 80.21 + 29.59x$, $R = 0.991$; linear

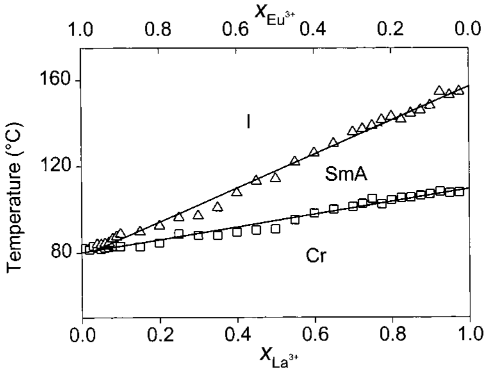

Figure 4. Phase diagram of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ as a function of the lanthanum(III) content. Cr is the crystalline phase, SmA is the smectic A phase, and I is the isotropic liquid.

regression for the clearing point, $y = 78.44 + 79.18x$, $R = 0.997$). The fitted lines cross each other at 3.6 mol % lanthanum(III). So, a very small amount of lanthanum(III) dodecanoate has to be added to induce mesomorphism in the nonmesogenic europium(III) dodecanoate.

The transition temperature for pure lanthanum(III) dodecanoate obtained by this fitting procedure agrees very well with the experimental values reported by Binnemans et al.[21]

This is not the case for the pure europium(III) compound (fitted temperature 80 °C; experimental temperature 90 °C). There are probably special effects at low lanthanum(III) concentrations, so that the transition temperatures do not depend linearly on the composition of the compounds and the fitted and experimental temperatures do not agree.

The results of this experiment confirm the theory about the effect of the ionic radius on the stability of a mesophase.[21] The smaller the lanthanide ion, the more unfavorable the electrostatic interactions between the carboxylate groups become and the easier the layer structure of the lanthanide ions breaks down. This results in lower transition temperatures.

Adding a lanthanide(III) ion with a large ionic radius reduces the unfavorable interactions that much that a mesophase can occur. Whereas the ionic radius of the europium ion is too small to form a stable mesophase, adding small amounts of lanthanum is enough to form a stable smectic A phase. The more stabilizing lanthanum(III) that is added, the more the mesophase will be stabilized and the higher the melting and clearing points will be.

The fact that a stable mesophase can be formed by adding a lanthanide ion with a large ionic radius to one with a small radius was confirmed by studies of mixtures of lanthanum(III) dodecanoate with other lanthanides, i.e., neodymium(III), terbium(III), holmium(III), and ytterbium(III).

Although neodymium(III) dodecanoate forms a liquid crystal phase (Cr·91·SmA·117·I), the stability range of the mesophase is much lower as for the lanthanum(III) dodecanoate. However, adding small amounts of lanthanum(III) dodecanoate causes a lower stability of the mesophase. Also for higher lanthanum(III) content, the stability of the mesophase is lower than can be expected from the *additivity law*, that is, $T_{cl} = T_1 + x(T_2 - T_1)$.[28] T_{cl} is the clearing point of the binary mixture,

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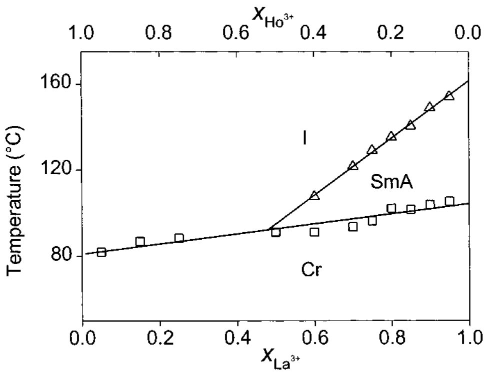

Figure 5. Phase diagram of the series $La_xHo_{1-x}(C_{11}H_{23}COO)_3$ as a function of the lanthanum(III) content. Cr is the crystalline phase, SmA is the smectic A phase, and I is the isotropic liquid.

T_1 and T_2 are the clearing points of both components of the mixtures, and x_2 is the mole percent of the second component. This is in contrast to the observations of Mirnaya et al., who describe binary mixtures of ionic mesogenic systems.[25] It was found that for binary systems with symmetrically charged cations the clearing point exhibits a positive or S-shaped deviation from additivity for small ionic mesogens. The fact that our compounds have lower clearing points than expected can be assigned to the long alkyl chains in the mixed lanthanum(III)−neodymium(III) dodecanoates. In lanthanide(III) alkanoates phase transitions are a competition between electrostatic interactions and melting of the alkyl chain.[21]

Additionally, phase diagrams of $La_xTb_{1-x}(C_{11}H_{23}COO)_3$, $La_xHo_{1-x}(C_{11}H_{23}COO)_3$, and $La_xYb_{1-x}(C_{11}H_{23}COO)_3$ have been investigated. It can clearly be seen that mesomorphism is induced by mixing the nonmesogenic compounds terbium(III), holmium(III), and ytterbium(III) dodecanoate with the mesogenic lanthanum(III) dodecanoate, but the amount of lanthanum(III) dodecanoate necessary for inducing mesomorphism is much higher than that for the lanthanum−europium mixtures.

All of the data can be fitted easily, so we were able to deduce the lanthanum(III) content, whereby the mixed lanthanum−lanthanide complexes form mesophases. In this way we were able to determine the minimum lanthanum(III) content which is necessary to induce mesomorphism. Whereas for lanthanum−europium mixtures not more than 4 mol % lanthanum(III) was needed, the minimum lanthanum(III) content increases to 42% for lanthanum−terbium, 47% for lanthanum−holmium, and 48% for lanthanum−ytterbium mixtures. In Figure 5 the phase diagram of lanthanum−holmium is given.

So there is a marked influence of the lanthanide ion on the stability of the induced mesophase. This shows again the relation between the formation of a mesophase and the ionic radius of the lanthanide ions which was found for the lanthanide(III) dodecanoates.[21]

The transition temperatures and enthalpies of all of the compounds described in this work and the phase diagrams of the lanthanum−neodymium, lanthanum−terbium, and lanthanum−ytterbium mixtures are available as Supporting Information.

Conclusion

In this paper, we described the induction of a mesophase by mixing of a nonmesogenic lanthanide(III) dodecanoate with the mesogenic lanthanum(III) dodecanoate. Mesophase induction strongly depends on the ionic radius of the lanthanide ion. This can be explained by taking in account unfavorable electrostatic interactions between the carboxylate groups. So, mesomorphism is observed at very low lanthanum concentrations for the mixtures of lanthanum(III) dodecanoate with europium, but for the heavier lanthanides (i.e., terbium, holmium, and ytterbium), much more lanthanum is needed ($x = 0.42$, 0.47, and 0.48, respectively).

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Supporting Information Available: Tables of chemical analysis results of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$, $La_xNd_{1-x}(C_{11}H_{23}COO)_3$, $La_xTb_{1-x}(C_{11}H_{23}COO)_3$, $La_xHo_{1-x}(C_{11}H_{23}COO)_3$, and $La_xYb_{1-x}(C_{11}H_{23}COO)_3$. Tables of transition temperatures of the series $La_xEu_{1-x}(C_{11}H_{23}COO)_3$, $La_xNd_{1-x}(C_{11}H_{23}COO)_3$, $La_xTb_{1-x}(C_{11}H_{23}COO)_3$, $La_xHo_{1-x}(C_{11}H_{23}COO)_3$, and $La_xYb_{1-x}(C_{11}H_{23}COO)_3$. Phase diagrams of $La_xEu_{1-x}(C_{11}H_{23}COO)_3$ ($0 \le x \le 0.1$), $La_xNd_{1-x}(C_{11}H_{23}COO)_3$, $La_xTb_{1-x}(C_{11}H_{23}COO)_3$, $La_xHo_{1-x}(C_{11}H_{23}COO)_3$, and $La_xYb_{1-x}(C_{11}H_{23}COO)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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