Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Thermal behaviour of lanthanum(III) alkanoates

Liesbet Jongen[a]; Koen Binnemans[a]; Dirk Hinz[b]; Gerd Meyer[b]
[a] Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200 F, B-3001 Leuven, Belgium, [b] Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6 D-50939 Köln, Germany,

To cite this Article Jongen, Liesbet , Binnemans, Koen , Hinz, Dirk and Meyer, Gerd(2001) 'Thermal behaviour of lanthanum(III) alkanoates', Liquid Crystals, 28: 11, 1727 — 1733

To link to this Article: DOI: 10.1080/02678290110078766

URL: http://dx.doi.org/10.1080/02678290110078766

LIQUID CRYSTALS, 2001, VOL. 28, NO. 11, 1727–1733

Thermal behaviour of lanthanum(III) alkanoates

LIESBET JONGEN, KOEN BINNEMANS*
Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200 F,
B-3001 Leuven, Belgium

DIRK HINZ and GERD MEYER
Institut für Anorganische Chemie, Universität zu Köln,
Greinstrasse 6 D-50939 Köln, Germany

(*Received 20 April 2001; accepted 4 June 2001*)

The mesophase behaviour of the lanthanum(III) alkanoates [$La(C_xH_{2x+1}COO)_3$] ($x = 3$–19) has been investigated by hot-stage polarizing optical microscopy, differential scanning calorimetry and high-temperature X-ray diffraction. Lanthanum(III) butyrate monohydrate shows no mesomorphism, whereas for the remaining short chain homologues ($x = 4$–9) a highly viscous mesophase M and a smectic A phase were observed. The longer chain lanthanum(III) soaps ($x = 10$–19) exhibit only a smectic A phase. However, the chain length has a pronounced effect on the transition temperatures. The thermal behaviour of lanthanum(III) alkanoates is compared with that of other lanthanide(III) alkanoates.

1. Introduction

Since Misra *et al.* [1, 2] first synthesized in the early 1960s metal soaps containing elements of the lanthanide series, these compounds have been of great interest due to their catalytic applications, their use as polymer stabilizers, as optical polymer fibres or for scintigraphic applications [3–11]. Given the range of possible applications for this type of compound, it is surprising that the physicochemical properties and especially their thermal behaviour, are so rarely documented. Most of the studies concern lanthanide soaps in solution, and infrared spectroscopic or X-ray diffraction (XRD) studies at room temperature [12–16]. However, Mehrotra *et al.* [17] and Upadhyaya *et al.* [18] reported on the thermal decomposition of lanthanum(III), cerium(III) and terbium(III) soaps.

The mesophase behaviour of cerium(III) alkanoates was discovered by Marques *et al.* in 1998 [19]. They observed a pronounced effect of the chain length on the transition temperatures. This kind of thermal behaviour by lanthanide(III) alkanoates was later confirmed by our group. The mesophase exhibited by lanthanum(III) tetradecanoate and higher homologues was identified as a smectic A phase [20].

It was very surprising to find that only lanthanum(III), cerium(III), praseodymium(III) and neodymium(III) dodecanoate exhibit a mesophase, whereas the other lanthanide(III) dodecanoates (Sm–Lu) are not liquid crystalline [21]. The effect of the chain length on the thermal behaviour has been reported for the cerium(III), praseodymium(III) and neodymium(III) alkanoates [22–24]. The complete homologous series of cerium(III) and praseodymium(III) alkanoates exhibit a mesophase, whereas for neodymium(III) alkanoates a mesophase is present only for the pentadecanoate and the shorter homologues. Here we report on the effect of chain length on the thermal behaviour of lanthanum(III) alkanoates.

2. Experimental

CH elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 821e-module. Optical textures of the mesophase were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller. High temperature X-ray diffractograms were obtained on a STOE Transmission Powder Diffractometer System STADI P, with a high temperature attachment and using monochromatic Cu-K$_\alpha$ ($\lambda = 1.54$ Å) radiation.

FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using KBr pellets. Reagents and solvents were used as received without further purification.

---

*Author for correspondence;
e-mail: Koen.Binnemans@chem.kuleuven.ac.be

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110078766

Analytical grade solvents were used for the recrystallization and washing of the soaps (water content: ethanol $<0.2\%$; 1-pentanol $<0.2\%$; acetone $<0.3\%$). Hydrated lanthanide(III) nitrates were purchased from Aldrich.

3. Results and discussion

3.1. *Synthesis and characterization*

3.1.1. *Lanthanum(III) butyrate*

La(III) butyrate was prepared by reaction between La(III) hydroxide and butyric acid. Pure $La(OH)_3$ was obtained through hydrothermal synthesis. Lanthanum nitrate hexahydrate, $La(NO_3)_3$ $6H_2O$, (1.00 g, 2.30 mmol) and NaOH (3.00 g, 25 mmol) were dissolved in water (15 ml), and the resulting solution was heated in a teflon bomb for 4 days at 220°C. Afterward, the solution was left to slowly cool to room temperature, at a rate of 4°C h^{-1}. Crystalline $La(OH)_3$ was obtained and its purity was checked by X-ray powder diffraction. The pure hydroxide was dissolved in diluted butyric acid (butyric acid/water = 1/1). Crystals were obtained by slow evaporation of the solution in air. The transparent crystals were lath-like and colourless.

3.1.2. *Lanthanum(III) pentanoate*

Pentanoic acid (1.024 g, 10.04 mmol) and triethylamine (1.016 g, 10.04 mmol) were dissolved in toluene (50 ml), and $LaCl_3$ $6H_2O$ (0.60 g, 1.62 mmol) was added. The solution was heated at reflux for 48 h. After leaving the toluene solution to cool to room temperature, water was added to dissolve triethylammonium chloride. The precipitate was filtered and washed with water and ethanol to remove traces of the lanthanum salt, the fatty acid or triethylammonium chloride. Lanthanum(III) pentanoate was dried for 24 h *in vacuo* at 50°C; yield 0.46 g (64%).

3.1.3. *Lanthanum(III) dodecanoate*

Dodecanoic acid (2.75 g, 13.8 mmol) was dissolved in an ethanol/water mixture (1/1) (100 ml), and converted into sodium dodecanoate by adding an equivalent amount of a 0.5M NaOH standard solution (addition via a burette). Lanthanum nitrate hexahydrate (2.00 g, 4.60 mmol) was dissolved in 100 ml of an ethanol/water mixture (1/1). The solution of sodium dodecanoate was added dropwise with stirring to the solution of lanthanum(III) nitrate at ambient temperature. A white precipitate formed immediately. After addition was complete, the solution was stirred for 1 h. The precipitate was then filtered on a Büchner funnel, washed with water (3×100 ml), ethanol (3×50 ml) and acetone (3×50 ml), in order to remove traces of the lanthanum(III) salt and of the dodecanoic acid. The crude lanthanum(III) dodecanoate was dried for 24 h *in vacuo* at 50°C, and recrystallized from a 1-pentanol/ethanol (5/1) mixture. Placing the solution in a refrigerator completed crystallization. The purified soap was filtered, washed with ethanol (25 ml) to remove most of the 1-pentanol, and dried *in vacuo* (10^{-3} mbar) at 50°C for at least 24 h. Lanthanum(III) dodecanoate was obtained as a white powder; yield 2.74 g (82%).

The carbon and hydrogen contents of the lanthanum (III) soaps were determined by CH elemental analysis. The analysis results were consistent with an alkanoic to lanthanum(III) ratio of 3 : 1, but also indicated that the products cannot be obtained in a totally anhydrous form under the given reaction conditions. All the compounds were hemihydrates, $[La(C_xH_{2x+1}COO)_3]$ $1/2H_2O$, except for the lanthanum(III) butyrate ($x = 3$) which was obtained as a monohydrate. The degree of hydratation was independent of the drying conditions. Representative analysis results for one compound are calculated for $[La(C_9H_{19}COO)_3]$ $1/2H_2O$; C 54.46, H 8.84; experimental C 54.30, H 8.74%.

3.2. *Infrared spectroscopy*

Vibrational spectroscopy of long chain carboxylates provides information on the metalion–carboxylate coordination, on the chain conformation and on the packing of the alkyl chain. Infrared spectra in the spectral region 400–4000 cm^{-1} were recorded for all the lanthanum(III) carboxylates. In figure 1 the IR spectrum of lanthanum (III) undecanoate is given.

The symmetric and asymmetric stretching modes for the methyl and methylene groups occur in the 3000–2800 cm^{-1} region. The C=O stretching vibration observed in the alkanoic acid at around 1700 cm^{-1} disappears in the lanthanum(III) alkanoates and is replaced by two new absorption bands. These bands correspond to the symmetric (1410–1420 cm^{-1}) and asymmetric (1520–1550 cm^{-1}) stretching vibrations of the carboxylate ion. According to several authors [19, 25, 26], the interaction between the lanthanum ion and the carboxylate group can be evaluated by

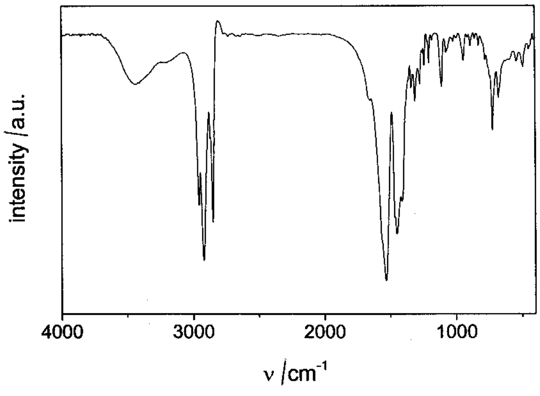

Figure 1. Infrared spectrum of lanthanum(III) undecanoate.

considering the splitting of the two carboxylate bands, $\Delta\nu = \nu_{asymm} - \nu_{symm}$, being 120–130 cm^{-1} in our complexes. This splitting is lower than the carboxylate stretching vibrations in alkali soaps ($\Delta\nu = 138$ cm^{-1}) [21], but indicates that the lanthanum(III)–carboxylate bond is largely ionic. From the observed splitting we conclude that the lanthanum(III)–carboxylate interaction must be bidentate chelating. However, we do not think this approach is very suitable for lanthanide(III) alkanoates. The splitting of the asymmetric and symmetric stretching vibration of the carboxylate anion does not depend on the chain length, nor on the lanthanide ion [21, 22]. We were able to determine the single crystal structure of lanthanum(III) butyrate monohydrate [27]. It was found that there are several types of lanthanum(III)–carboxylate coordination (i.e. bridging bidentate, chelating bidentate and bridging tridentate), although the splitting of these bands is the same (125 cm^{-1}) as for the longer lanthanum(III) soaps. This indicates that more than one type of carboxylate coordination is present in these compounds.

Further structural information can be obtained from the number of CH_2 wagging progression bands in the 1350–1150 cm^{-1} region. There exists an experimental relationship between the number of wagging bands and the alkyl chain length, if the alkyl chain is in all-*trans* conformation [23]. For an even number of carbon atoms in the alkyl chain, the number of IR bands is $n/2$ (n being the total number of carbon atoms in the chain). For an odd number of carbon atoms, the number of IR bands is equal to $(n+1)/2$. This relation can easily be seen in all the IR spectra of the lanthanum(III) alkanoates.

3.3. *Thermal behaviour*

The thermal behaviour of lanthanum(III) alkanoates was investigated by DSC, hot-stage polarizing optical microscopy (POM) and high-temperature X-ray diffraction (XRD). The DSC traces of the homologous series $[La(C_xH_{2x+1}COO)_3]$ ($x = 4$–19) show several transitions. The shorter members ($x = 4$–9) exhibit three phase transitions, suggesting that several mesophases are present. Lanthanum(III) dodecanoate and the higher homologues show only two peaks in their DSC curves. In figure 2 the DSC trace of $[La(C_{12}H_{25}COO)_3]$ is given (first heating–cooling cycle). The first peak can be assigned to the crystal to mesophase transition, while the second peak is associated with the mesophase to isotropic transition. On cooling, a slight supercooling is observed for the clearing point. This is often observed for ionic metallomesogens [28].

The mesophase behaviour was also investigated by hot-stage POM. Most of the compounds soften before they exhibit birefringence at the melting point. Except for lanthanum(III) butyrate monohydrate which does not exhibit any mesomorphism, all the compounds of the series $[La(C_xH_{2x+1}COO)_3]$ ($x = 4$–19) are liquid crystalline (see the table). The shorter ones (lanthanum(III) pentanoate to decanoate) show two mesophases. The first mesophase, labelled as M, has a very high viscosity and the texture contains star-like regions on a black background. The high temperature mesophase (i.e. the only mesophase in the lanthanum(III) undecanoate–eicosanoate series) is less viscous and has a texture similar to the one reported by Marques *et al.* for cerium(III) alkanoates [19]. Specifically the texture has a grainy appearance, with a white–yellow zone on a dark background.

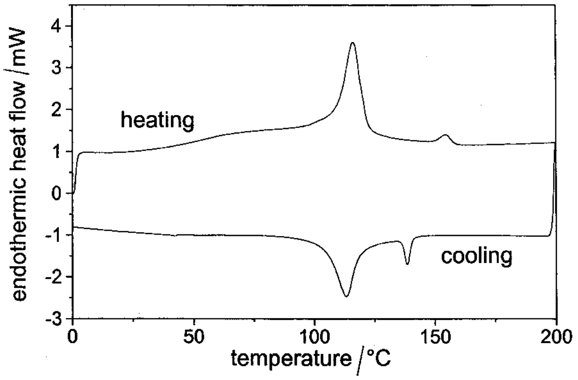

Figure 2. DSC curve of lanthanum(III) tridecanoate (1st heating–cooling cycle). Endothermic peaks are upwards.

The identity of the mesophase could only be determined unambiguously by high temperature XRD. In figure 3 the diffractogram of $[La(C_{11}H_{23}COO)_3]$ is given at room temperature and in the mesophase. At room temperature up to four peaks are observed in the low angle region of the X-ray powder diffractogram of the solid lanthanum(III) dodecanoate. The d-spacing values are in the ratio $1 : 1/2 : 1/3 \ldots 1/n$. These diffraction peaks correspond to the successive $(0\,0\,l)$ reflections, and indicate the presence of a lamellar structure. The

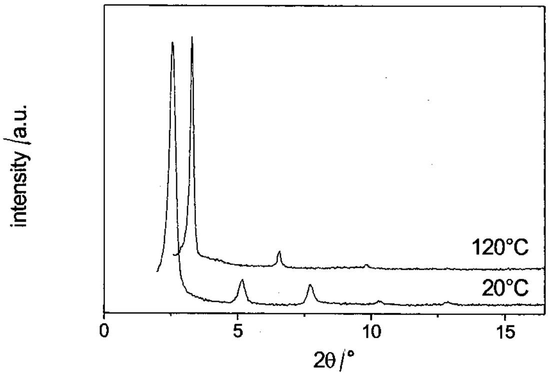

Figure 3. X-ray diffractogram of lanthanum(III) dodecanoate at room temperature and in the smectic A phase.

Table. Transition temperatures of lanthanum(III) alkanoates.

Compound	Transition[a]	Temperature/°C[b]	ΔH/kJ mol^{-1} [c]
$[La(C_3H_7COO)_3]$ H_2O	Cr → I	188.4	13.36
$[La(C_4H_9COO)_3]$ $1/2H_2O$	Cr → M	93.8	n.d.[d]
	M → SmA	139.2	n.d.
	SmA → I	190.2	n.d.
$[La(C_5H_{11}COO)_3]$ $1/2H_2O$	Cr → M	94.4	22.34
	M → SmA	137.9	2.73
	SmA → I	189.9	2.23
$[La(C_6H_{13}COO)_3]$ $1/2H_2O$	Cr → M	97.7	72.66
	M → SmA	133.5	7.32
	SmA → I	189.3	1.98
$[La(C_7H_{15}COO)_3]$ $1/2H_2O$	Cr → M	94.6	n.d.
	M → SmA	122.4	n.d.
	SmA → I	175.9	1.14
$[La(C_8H_{17}COO)_3]$ $1/2H_2O$	Cr → M	98.1	65.09
	M → SmA	121.0	5.24
	SmA → I	179.8	0.79
$[La(C_9H_{19}COO)_3]$ $1/2H_2O$	Cr → M	95.6	41.6
	M → SmA	122.1	8.62
	SmA → I	172.3	0.74
$[La(C_{10}H_{21}COO)_3]$ $1/2H_2O$	Cr → SmA	106.9	91.45
	SmA → I	165.9	0.94
$[La(C_{11}H_{23}COO)_3]$ $1/2H_2O$	Cr → SmA	110.0	63.7
	SmA → I	160.6	1.30
$[La(C_{12}H_{25}COO)_3]$ $1/2H_2O$	Cr → SmA	116.4	26.1
	SmA → I	154.6	1.27
$[La(C_{13}H_{27}COO)_3]$ $1/2H_2O$	Cr → SmA	120.3	35.48
	SmA → I	157.1	1.50
$[La(C_{14}H_{29}COO)_3]$ $1/2H_2O$	Cr → SmA	121.4	29.60
	SmA → I	157.0	1.60
$[La(C_{15}H_{31}COO)_3]$ $1/2H_2O$	Cr → SmA	123.4	57.02
	SmA → I	148.2	1.69
$[La(C_{16}H_{33}COO)_3]$ $1/2H_2O$	Cr → SmA	123.9	46.10
	SmA → I	149.7	1.90
$[La(C_{17}H_{35}COO)_3]$ $1/2H_2O$	Cr → SmA	125.9	46.91
	SmA → I	148.0	1.24
$[La(C_{18}H_{37}COO)_3]$ $1/2H_2O$	Cr → SmA	126.7	78.77
	SmA → I	140.1	1.27
$[La(C_{19}H_{39}COO)_3]$ $1/2H_2O$	Cr → SmA	128.1	89.10
	SmA → I	143.6	1.23

[a] Cr = crystalline phase; M = unidentified smectic phase; SmA = smectic A phase; I = isotropic liquid.

[b] The reported transition temperatures correspond to the peak temperatures in the DSC thermogram and these agree with the values determined by POM.

[c] First heating run.

[d] n.d. = not determined.

polar groups of the lanthanum(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 lanthanum(III) ions. The fact that the alkyl chains are in all-*trans* conformation is supported by a comparison of the experimental and calculated maximal average d-spacing values ($d_{\max}$). The maximal d-spacing of the bilayer structure was calculated for an all-*trans* conformation of the alkyl chain perpendicular to the metal ion base plane using the formula [19]:

$$d_{\max} = 2d_{\text{C-H}} + 2(n-1)d_{\text{C-C}} \sin 55° + 2d_{\text{C-O}} + 2r_{\text{La}^{3+}} \quad (1)$$

where n = the total number of carbon atoms, $d_{\text{C-H}}$ = 1.09 Å, $d_{\text{C-C}}$ = 1.54 Å, $d_{\text{C-O}}$ = 1.36 Å and $r_{\text{La}^{3+}}$ = 1.356 Å (coordination number = 9) [29]. The calculated and experimental value for a bilayer structure with the alkyl chains in all-*trans* conformation correspond very well. Thus, for $\text{La(C}_{11}\text{H}_{23}\text{COO)}_3$ $d_{\max}$ (calculated) = 34.74 Å, while $d_{\max}$ (experimental) = 34.67 Å.

In the mesophase, the lamellar bilayer structure is retained but a distinct decrease in *d*-spacing is observed. This indicates that the alkyl chains are no longer in all-*trans* conformations and that some kind of folding occurs. In fact, the solid to mesophase transition can be considered as the melting of the alkyl chains. At the clearing point, all structure is lost, and an ionic melt is formed. The temperature dependence of the *d*-spacing corresponds to the characteristic behaviour of a smectic A phase (figure 4).

The low temperature mesophase M, observed for the shorter chain homologues (lanthanum(III) pentanoate to decanoate) has a very high viscosity and can be considered as a phase with partially molten alkyl chains. This can be seen in the X-ray diffractograms at elevated temperatures. Whereas in the crystalline state the alkyl chains are totally extended, a distinct decrease of the *d*-spacing can be seen in the crystal to mesophase M transition. This is an indication for a bilayer structure with partially molten alkyl chains but with restricted motions of the lanthanide ions. A second decrease of the *d*-spacing is observed for the mesophase M to smectic A phase transition. In this phase the alkyl chains are completely molten and the lanthanide ions can rotate freely in the layer. In figure 5 the X-ray diffractograms of $[\text{La(C}_7\text{H}_{15}\text{COO)}_3]$ at room temperature, in mesophase M and in the smectic A phase is given.

The complete series of synthesized compounds exhibits mesomorphism except for the butyrate homologue, although there is a marked influence of the chain length on the transition temperatures. Whereas the melting point increases when the chain length increases, the clearing point decreases. This destabilization of the mesophase is due to less favourable interactions of the alkyl chains on increasing chain length. A second influence of the chain length is the existence of a second mesophase M for the shorter lanthanum(III) alkanoates. In figure 6 the phase diagram of the lanthanum(III) alkanoates is given.

This pattern of thermal behaviour has also been observed for other lanthanide(III) alkanoates [19–23]. The influence of the chain length is the same as we observed here for the lanthanum(III) alkanoates, i.e. increase of the melting point and decrease of the clearing

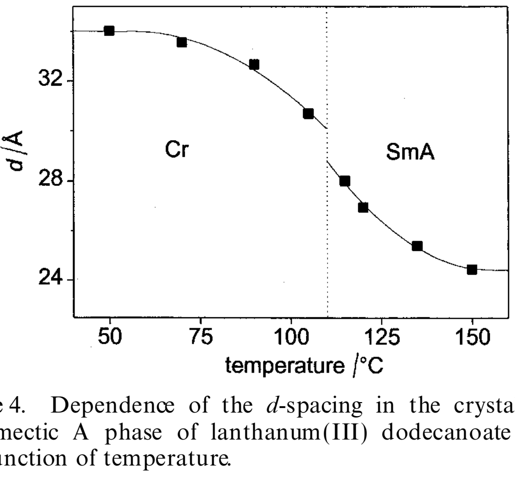

Figure 4. Dependence of the *d*-spacing in the crystal and smectic A phase of lanthanum(III) dodecanoate as a function of temperature.

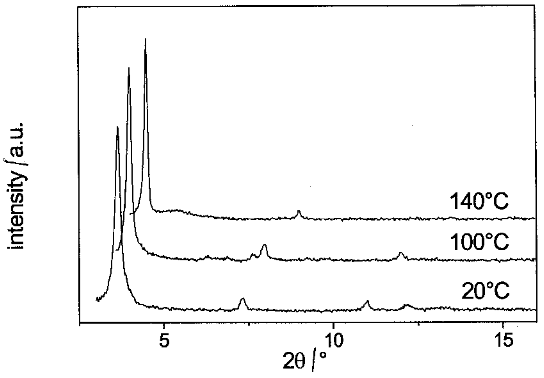

Figure 5. X-ray diffractogram of lanthanum(III) octanoate at room temperature (20°C), in mesophase M (100°C) and in the smectic A phase (140°C).

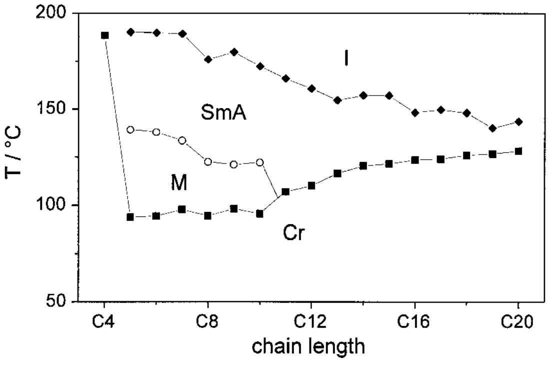

Figure 6. Phase diagram of the series $[\text{La(C}_x\text{H}_{2x+1}\text{COO)}_3]$ $(3 \leqslant x \leqslant 19)$ as a function of chain length. The compounds are labelled with the number of carbon atoms in the alkanoate group (e.g. C12 stands for lanthanum(III) dodecanoate, $x = 11$).

point with increasing chain length and the occurrence of a second high viscous mesophase for the shorter lanthanide soaps. Although this similar influence of the chain length exists for all the lanthanide carboxylates, there is still a marked influence of the lanthanide ion on the thermal properties of these compounds. For lanthanum(III), cerium(III) and praseodymium(III) alkanoates all the homologues with $x = 4$–19 exhibit mesomorphism. This is in contrast to the neodymium(III) series, where no mesophase exists for the neodymium(III) hexadecanoate and longer homologues ($x \geqslant 15$). Also the temperature ranges of the mesophases depend strongly on the lanthanide ion. Whereas the stability range of the SmA phase of [$La(C_{13}H_{27}COO)_3$] is 37°C, this decreases to 20°C for the corresponding cerium compound, to 16°C for the praseodymium compound, and to 13°C for neodymium(III) tetradecanoate. This decrease in the temperature range was also observed for the lanthanide(III) dodecanoate series, where we found that only the light lanthanides with a large ionic radius (La, Ce, Pr and Nd) formed a mesophase [21].

This effect of the lanthanide ion on the thermal behaviour can be explained by taking into account unfavourable electrostatic interactions between the carboxylate groups. As the ionic radius of the lanthanide cation decreases, the distance between the carboxylate groups on either side of the plane containing the lanthanide ions also decreases. The amplitude of the thermal vibrations increases on increasing the temperature and thereby induces unfavourable electrostatic interactions (repulsions) between the carboxylate groups, not only between those of the two opposing layers, but also between adjacent carboxylate groups within the same layer. When the repulsive forces between the negative charges are stronger than the attractive forces between the negative (carboxylate groups) and positive (lanthanide ions) charges, the bilayer structure of the solid metal soaps is no longer stable and breaks down. In this case, a rearrangement of the carboxylate groups and lanthanide ions to obtain a more stable solid state structure (i.e. a crystal–crystal transition) might be expected. However, melting of the compounds is observed. The alkyl chains have sufficient thermal energy for their all-*trans* conformation to be lost when the layer structure breaks down.

On melting, the metal soaps are converted into ionic liquids with a rather low viscosity. This explains the decrease of the melting point within the lanthanide series. The smaller the lanthanide ion, the more unstable the layer structure becomes, and hence less thermal energy is required to break down the solid state structure. A mesophase is formed, when, at the melting point of the alkyl chains, the electrostatic attraction between the lanthanide ions and the carboxylate groups is still sufficiently high to maintain a layer structure. This is the case for the lanthanum(III), cerium(III), praseodymium(III) and neodymium(III) compounds.

The fact that only the first three lanthanides (La, Ce and Pr) exhibit a mesophase across the complete homologous series ($4 \leqslant x \leqslant 19$), and that the neodymium series does not show mesomorphism for the longer chain lengths, can be explained by taking into account both the effect of the lanthanide ion and the chain length. Whereas for lanthanum(III) carboxylates, the ionic radius is sufficiently large to reduce unfavourable electrostatic interactions between the carboxylate groups (and thus the melting of the alkyl chains is the major factor determining the thermal properties of the compounds), for neodymium soaps there is a competition between the stabilization of the ionic layers and melting of the alkyl chains. For the shorter alkyl chains, their melting is the determining factor, whereas for the longer soaps the thermal energy required to melt the alkyl chains is so high that the ionic layer structure breaks down before the alkyl groups are completely molten.

4. Conclusion

Lanthanum(III) carboxylates with the stoichiometry [$La(C_xH_{2x+1}COO)_3$], show either one or two smectic mesophases on heating and cooling. The high temperature mesophase, and the mesophase for compounds with $x \geqslant 10$, was identified as a smectic A phase. The low temperature mesophase is also a lamellar phase, but we were unable to identify the exact molecular organisation within the lamellar planes. The phase behaviour was compared with that of other lanthanide(III) carboxylates. The thermal behaviour of these lanthanide(III) soaps may be rationalized by taking into account the melting of the alkyl chains, unfavourable electrostatic interactions between the carboxylate groups, and the size of the lanthanide(III) ion. In this way we can explain the marked dependence of the transition temperatures on the chain length, and the decrease in mesophase temperature range with increasing ionic radius.

L.J. is indebted to the Flemish Institute for the Encouragement of Scientific and Technological Research in Industry (IWT) for financial support. K.B. is Postdoctoral Fellow of the F.W.O.-Flanders (Belgium); financial support by the K. U. Leuven (GOA 98/03) and by the F.W.O.-Flanders (G.023.99) is gratefully acknowledged. L.J. and K.B. wish to thank Prof. C. Görller-Walrand for providing laboratory facilities.

References

[1] Misra, S. N., Misra, T. N., and Mehrotra, R. C., 1963, *J. inorg. nucl. Chem.*, **25,** 195.

[2] Misra, S. N., Misra, T. N., and Mehrotra, R. C., 1963, *J. inorg. nucl. Chem.*, **25,** 201.

[3] Ducros, P., 1985, *J. less-common Met.*, **111,** 37.

[4] Sauvion, G. N., Bains, M. S., and Gothi, J. S., 1969, *Indian J. Chem.*, **7,** 514.

[5] Hussain, R., and Mahmood, F., 1994, *J. chem. Soc. Pak.*, **16,** 225.

[6] Mahmood, F., and Hussain, R., 1995, *J. chem. Soc. Pak.*, **17,** 147.

[7] Zhang, Q., Ming, H., and Zhai, Y., 1996, *Polym. Int.*, **41,** 413.

[8] Zhang, Q., Ming, H., and Zhai, Y., 1996, *J. appl. polym. Sci.*, **62,** 887.

[9] Lin, Y., 1997, *J. appl. polym. Sci.*, **63,** 811.

[10] Dobetti, L., Esposito, P., and Boltri, L., 1994, *Eur. J. Pharm. Biopharm.*, **40,** 161.

[11] Oehme, A., Gebauer, U., Gehrke, K., and Lechner, M. D., 1996, *Angew. makromol. Chem.*, **235,** 121.

[12] Mehrotra, R. C., Misra, T. N., and Misra, S. N., 1966, *J. Indian chem., Soc.*, **43,** 61.

[13] Zaitseva, M. G., Stepanyan, S. A., Kravchenko, V. V., and Petrov, K. I., 1976, *Russ. J. inorg. Chem.*, **21,** 1820.

[14] Mehrotra, K. N., Chauhan, M., and Shukla, R. K., 1989, *Monatsh. Chem.*, **120,** 1063.

[15] Mehrotra, K. N., Chauhan, M., and Shukla, R. K., 1997, *Tenside Surf. Det.*, **34,** 124.

[16] Mehrotra, K. N., and Upadhyaya, S. K., 1991, *Pol. J. Chem.*, **65,** 1035.

[17] Mehrotra, K. N., and Sharma, N., 1996, *Monatsh. Chem.*, **127,** 257.

[18] Upadhyaya, S. K., and Sharma, P. S., 1993, *J. Indian chem. Soc.*, **70,** 735.

[19] Marques, E. F., Burrows, H. D., and da Graça Miguel, M., 1998, *J. chem. Soc., Faraday Trans.*, **94,** 1729.

[20] Binnemans, K., Heinrich, B., Guillon, D., and Bruce, D. W., 1999, *Liq. Cryst.*, **26,** 1717.

[21] Binnemans, K., Jongen, L., Görller-Walrand, C., d'Olieslager, W., Hinz, D., and Meyer, G., 2000, *Eur. J. inorg. Chem.*, 1429.

[22] Binnemans, K., Jongen, L., Bromant, C., Hinz, D., and Meyer, G., 2000, *Inorg. Chem.*, **39,** 5938.

[23] Jongen, L., Binnemans, K., Hinz, D., and Meyer, G., *J. mater. Sci. Eng. C.* (in the press).

[24] Jongen, L., Binnemans, K., Hinz, D., and Meyer, G., 2001, *Liq. Cryst.* **28,** 819.

[25] Nakamoto, K., 1963, *Infrared Spectra of Inorganic and Coordination Compounds* (New York: Wiley).

[26] Deacon, G. B., and Philips, R. J., 1980, *J. coord. Chem. Rev.*, **33,** 227.

[27] Jongen, L., Meyer, G., and Binnemans, K., 2001, *J. Alloys Compd.*, **323,** 142.

[28] Mirnaya, T. A., Prisyazhnyi, V. D., and Shcherbakov, V. A., 1989, *Russ. Chem. Rev.*, **58,** 821.

[29] Shannon, R. D., 1976, *Acta Cryst.*, **A32,** 751.