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PAPER

Quinolinium and isoquinolinium ionic liquid crystals†

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Ionic liquid crystals based on quinolinium and isoquinolinium salts were prepared by quaternization of quinoline and isoquinoline, respectively. In the first place the influence of the alkyl chain on the thermal behaviour was investigated. Two types of (iso)quinolinium salts were synthesized. Long-chained (iso)quinolinium cations (with chain lengths varying from C₁₂H₂₅ to C₂₂H₄₅), with the inclusion of the odd homologues C₁₇H₃₅ and C₁₉H₃₉, were combined with the spherical anions bromide, tetrafluoroborate (BF₄[−]) and hexafluorophosphate (PF₆[−]). Dodecyl sulfate, dioctyl-, dihexyl- and dicyclohexylsulfosuccinate anions allowed the introduction of anions with (long) alkyl chains. It is shown that a subtle balance between strong electrostatic forces and the degree of disorder originating from molten alkyl chains is crucial for mesophase formation. The influence of the anion size on the mesophase behaviour was studied. Smectic A phases were observed for the long chain analogues of the bromide, tetrafluoroborate and hexafluorophosphate salts. The minimum alkyl chain length needed to induce mesomorphism increases when the bromide is exchanged by more voluminous anions, while the transition temperatures are lowered. The introduction of an alkyl chain in the anionic part drastically changes the thermal behaviour. The dodecyl sulfate salts show smectic A phases for cations with much shorter chain lengths than the other anions. For the dioctylsulfosuccinate salts this trend is even more pronounced, as the *N*-methyl(iso)quinolinium dioctylsulfosuccinate salts exhibited enantiotropic smectic A phases at ambient temperature. Structural models for the packing of the quinolinium and isoquinolinium salts in the liquid-crystalline state are presented, as well as the crystal structures of *N*-octylquinolinium dodecyl sulfate and *N*-octylisoquinolinium bromide.

Introduction

Experimental data accumulated over the years give a good insight into the structure–property relationship of ionic liquids.^{1–4} One of the most important properties of ionic liquids is their melting point, because ionic liquids can only be used as solvents above their melting point. In contrast with other physicochemical properties, melting points are more difficult to accurately predict or calculate.^{5–11} Although the melting point can be predicted from the ratio of the calculated values of the melting enthalpy and entropy, differences between the calculated and experimental melting points are about ±25 °C, so that accurate experimental determination of the melting points of new ionic liquids is still of

prime importance.¹² Factors that influence the melting point are the nature of the anion and the cation, and the length of the alkyl chain. In general, the melting point first decreases with increasing chain length and will reach a minimum at a chain length of about four (butyl) to six (hexyl) carbon atoms.^{13,14} The reason for this decrease in melting point is that longer alkyl chains can adopt more different conformations and this hampers efficient packing of the molecules in a crystal lattice. However, the melting point starts to increase for longer alkyl chains, because the contribution of the van der Waals interactions between the alkyl chains becomes more important for the longer alkyl chains. Interestingly, for very long chains the ionic liquids start to exhibit liquid-crystalline behaviour. This means that upon heating, the crystalline solid first melts to give a liquid-crystalline phase (or mesophase). In the liquid-crystalline phase the molecular order is between that of the highly ordered crystalline solid phase and the disordered liquid phase. Liquid crystals are anisotropic fluids. Upon further heating, the molecular order in the liquid-crystalline phase is suddenly lost at the clearing point and one obtains an isotropic liquid. Typically, ionic liquids form layered liquid-crystalline phases (smectic phases). The most common mesophase for ionic liquid crystals is the smectic A phase. In this phase, no correlation exists between the molecules in the layers. The minimum chain length at which an ionic liquid forms a mesophase depends on the nature of the cation, but also on the nature of the

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization of all the compounds; table with transition temperatures and mesophase behaviour of the liquid-crystalline (iso)quinolinium salts; table with melting points of the non-mesomorphic compounds; figures showing the packing of the molecules in the crystal structures; structural model for the quinolinium dodecyl sulfates. CCDC reference numbers 837736 and 837737. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ra21208k

anion. For the 1-alkylimidazolium salts $[C_n\text{mim}][X]$, a mesophase is observed for $[C_{12}\text{mim}][\text{BF}_4]$ and higher homologues,¹³ for $[C_{14}\text{mim}][\text{PF}_6]$ and higher homologues,¹⁵ and for $[C_{16}\text{mim}][\text{TfO}]$ and higher homologues,¹⁶ but no liquid-crystalline behaviour has been reported for the $[C_n\text{mim}][\text{Tf}_2\text{N}]$ series¹⁶ (TfO = triflate, Tf_2N = bis(trifluoromethylsulfonyl)imide). For the liquid-crystalline 1-alkyl-3-methylimidazolium salts, the temperature range of the mesophase widens with increasing alkyl chain length. However, two long chains do not have a stabilizing effect on mesophases.^{17,18} Sometimes, the dependence of the thermal behaviour on the alkyl chain length can be surprising, as in the case of the *N*-alkylpyridinium tetrachlorocuprate(II) salts.¹⁹ The compounds with $C_{12}\text{H}_{25}$, $C_{13}\text{H}_{27}$, and $C_{14}\text{H}_{29}$ chains exhibit a hexagonal columnar mesophase. The derivatives with $C_{16}\text{H}_{33}$, $C_{17}\text{H}_{35}$, and $C_{18}\text{H}_{37}$ chains form a smectic A phase. The compound with a $C_{15}\text{H}_{31}$ chain exhibits a cubic mesophase between the crystalline state and a (partially bilayered) smectic A phase.²⁰ This cubic phase is only observed for the derivative with the pentadecyl chain and not for the derivatives with shorter or longer chains. Highly ordered smectic mesophases have been observed for quaternary ammonium,^{21,22} pyrrolidinium,²³ piperidinium,²⁴ piperazinium,²⁴ morpholinium,²⁴ and 1,10-phenanthroline ionic liquid crystals.²⁵ For an overview of ionic liquid crystals, the reader is referred to the review literature.^{26–29}

Most ionic liquids are based on imidazolium, pyridinium, pyrrolidinium, quaternary ammonium or phosphonium cations. The quinolinium and isoquinolinium ionic liquids have been investigated to a much lower extent, mainly because they are expected to have higher melting temperatures.^{30–40} Nevertheless, these ionic liquids could be of interest as the non-aqueous phase in solvent extraction systems for organic compounds.^{30,31} Although *N*-alkylquinolinium bromides,³⁹ *N*-alkylisoquinolinium hexafluorophosphates³² and *N*-alkylisoquinolinium bis(trifluoromethylsulfonyl)imides,³² with an alkyl chain up to octadecyl ($C_{18}\text{H}_{37}$), have been prepared, no liquid-crystalline phases have been reported for these compounds. Recently, Kato and co-workers described new luminescent liquid crystals based on highly substituted tripodal quinolinium salts.⁴¹

In this paper, we show that mesomorphism can be observed for *N*-alkylquinolinium and *N*-alkylisoquinolinium salts with bromide, tetrafluoroborate, dodecyl sulfate (DOS) and hexafluorophosphate anions, provided that the alkyl chains are long enough, and also that *N*-methyl(iso)quinolinium sulfosuccinate salts are liquid-crystalline. Quinolinium and isoquinolinium compounds with alkyl chains varying between $C_{12}\text{H}_{25}$ and $C_{22}\text{H}_{45}$ have been synthesized. For the long chain lengths, the odd homologues ($C_{17}\text{H}_{35}$, $C_{19}\text{H}_{39}$) have also been prepared. A structural model for the molecules in the smectic A phase (SmA) is presented. The crystal structures of *N*-octylquinolinium dodecyl sulfate and *N*-octylisoquinolinium bromide could be determined by single-crystal X-ray diffraction.

Experimental section

General

Information on the synthesis and characterization of all compounds can be found in the ESI.† Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^1H and at 75 MHz for

^{13}C). Elemental analyses were obtained on a CE Instruments EA-1110 elemental analyzer. Defect textures of the mesophases were observed with an Olympus BX60 polarizing optical microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded with a Mettler-Toledo DSC822e module (heating/cooling rate of $10\text{ }^\circ\text{C min}^{-1}$; helium atmosphere). Powder X-ray diffractograms were recorded with a Bruker AXS D8 Discover diffractometer mounted with a copper X-ray ceramic tube, working at 1.6 kW. The emitted $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) was focused on the sample by a Göbel mirror. All the samples (without a thermal history) were prepared by spreading the compounds on a thin cleaned silicon wafer. Diffractograms were recorded using the Bragg–Brentano reflection geometry ($\theta/2\theta$ setup) at an angular resolution (in 2θ) of 0.03° per step. The deviation between the temperature on the surface of the sample holder and the set temperature was about 3%. The scattering signal was recorded with a one-dimensional detector (LynxEye detector).

Crystallography

Crystals suitable for an X-ray diffraction study of *N*-octylquinolinium dodecyl sulfate **Q8.c** and *N*-octylisoquinolinium bromide **IQ8.a** could be obtained by slowly evaporating a solution of the compound in acetone and dichloromethane, respectively. X-ray intensity data were collected at RT on a Bruker SMART 6000 diffractometer equipped with a CCD detector using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$), using ϕ and ω scans. The images were interpreted and integrated with the program SAINT from Bruker.⁴² Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.^{43,44} Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 times for methyl groups and water molecules). CCDC 837736 and 837737 can be found in the ESI.†

Crystal data for compound Q8.c. $\text{C}_{29}\text{H}_{49}\text{NO}_4\text{S}$, $M = 507.76$, triclinic, $P\bar{1}$ (No. 2), $a = 8.0982(2)$, $b = 8.6854(2)$, $c = 23.0307(5)\text{ \AA}$, $\alpha = 96.8330(10)$, $\beta = 98.6960(10)$, $\gamma = 104.9070(10)^\circ$, $V = 1526.10(6)\text{ \AA}^3$, $T = 293(2)\text{ K}$, $Z = 2$, $\rho_{\text{calc}} = 1.105\text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 1.179\text{ mm}^{-1}$, $F(000) = 556$, crystal size $0.3 \times 0.3 \times 0.1\text{ mm}$, 5214 independent reflections ($R_{\text{int}} = 0.0759$). Final $R = 0.0814$ for 2936 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1885$ for all data. The *N*-octyl chain was found to be disordered and could be modelled in two parts (refined occupancies of 0.418(11) and 0.582(11)).

Crystal data for compound IQ8.a. $\text{C}_{17}\text{H}_{25.26}\text{BrNO}_{0.63}$, $M = 333.59$, monoclinic, $P2_1/n$ (No. 14), $a = 9.8423(5)$, $b = 13.4447(7)$, $c = 13.1983(7)\text{ \AA}$, $\beta = 101.539(2)^\circ$, $V = 1711.19(15)\text{ \AA}^3$, $T = 293(2)\text{ K}$, $Z = 4$, $\rho_{\text{calc}} = 1.295\text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 3.204\text{ mm}^{-1}$, $F(000) = 697$, crystal size $0.6 \times 0.3 \times 0.2\text{ mm}$, 3027 independent reflections ($R_{\text{int}} = 0.0469$). Final $R = 0.0537$ for 2389 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1380$ for all data. The occupancy of the water solvent molecule was refined to 0.628(9).

Results and discussion

Synthesis and characterization

An overview of the quinolinium and isoquinolinium salts is given in Chart 1. The *N*-alkylquinolinium bromides **Qn.a**, the

Chart 1 Overview of the quinolinium and isoquinolinium compounds.

N-alkylisoquinolinium bromides **IQn.a** and the *N*-methyl(iso)quinolinium iodides **Q1.e** and **IQ1.e** were synthesized *via* a quaternization reaction (Menschutkin reaction) of the quinoline or isoquinoline base with the appropriate bromoalkane or iodomethane. The length of the alkyl chain was varied between four (C_4H_9) and twenty-two carbon atoms ($\text{C}_{22}\text{H}_{45}$). The tetrafluoroborate salts **Qn.b** and **IQn.b** were synthesized by means of a metathesis reaction between the bromides **Qn.a** and **IQn.a** and sodium tetrafluoroborate in acetone. The dodecyl sulfate (DOS) salts **Qn.c** and **IQn.c** were synthesized by the reaction of the bromide salt **Qn.a** and **IQn.a** and sodium dodecyl sulfate in water. The hexafluorophosphate salts **Qn.d** and **IQn.d** were synthesized *via* a metathesis reaction of the bromide salt **Qn.a** and **IQn.a** and potassium hexafluorophosphate in a methanol–water mixture (6 : 4). The *N*-alkyl(iso)quinolinium sulfosuccinates **Q1.f–h**, **Q4.f**, **Q8.f** and **IQ.f–h** were synthesized in a similar fashion to the DOS salts using the iodide or bromide salts as starting materials. The purity of the compounds was verified using ^1H NMR and ^{13}C NMR spectroscopy and CHN elemental analysis.

Single crystal X-ray diffraction

In order to study the crystal structure of the quinolinium and isoquinolinium salts, single crystals of two shorter-chain

analogues were grown, namely of *N*-octylquinolinium dodecyl sulfate **Q8.c** and *N*-octylisoquinolinium bromide **IQ8.a**. Compound **Q8.c** crystallized into the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit consists of one *N*-octylquinolinium–dodecyl sulfate cation–anion pair (Fig. 1). The *N*-octyl chain substituent of the quinolinium cation shows a C1–N1–C10–C11 torsion angle of $-97.6(4)^\circ$, orienting most of the staggered chain perpendicular to the quinolinium rings. The end propyl group is found disordered over two positions. Interactions between the dodecyl sulfate anion and the quinolinium cations are observed. Eight close contacts between the sulfate group and five different quinolinium cations are found (in the range 2.35–2.65 Å). In the packing, π – π ring interactions occur between the quinolinium rings. Ring C1–C5/N1 interacts with the symmetry equivalent ring C1–C5/N1 ($1 - x, 1 - y, 2 - z$) and with ring C4–C9 ($1 - x, 1 - y, 2 - z$) (centroid–centroid distances of 3.836(2) and 3.946(2) Å, respectively). Furthermore, layers in the (110) plane are formed by the closely packed hydrophobic alkyl chains of both cations and anions, with their hydrophilic parts pointing outwards. Compound **IQ8.a** crystallized into the centro-symmetric monoclinic space group $P2_1/n$. The asymmetric unit consists of one *N*-octylisoquinolinium–bromide cation–anion pair and one water molecule (Fig. 2). Although there was no water used in the synthesis, nor in the

Fig. 1 ORTEP representation of the molecular structure of compound **Q8.c**, with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. The disorder of the *N*-octyl chain is shown.

crystallization conditions, the observed water molecule is probably due to the highly hygroscopic character of the compound, resulting in binding of residual water molecules present in the solvents used for synthesis and crystallization. The bromide salts with longer alkyl chains are more hydrophobic and have a lower tendency to bind water molecules. The alkyl chain of compound **IQ8.a** shows a C1–N1–C10–C11 torsion angle of 78.0(4)°, with the C10–C11 bond almost perpendicular to the isoquinolinium rings, whereas the rest of the alkyl chain is found staggered and approximately in the same plane as the isoquinolinium rings. C–H⋯Br[−] interactions are observed between the *N*-octylisoquinolinium cation and the bromide anion. Four close contacts between the Br[−] anion and three different isoquinolinium cations are observed (in the range 2.86–2.99 Å). Hydrogen bonds are formed between the water molecule and two Br[−] anion symmetry equivalents ($1/2 - x, -1/2 + y, 1/2 - z$; $-1/2 + x, 3/2 - y, -1/2 + z$), related by an inversion centre (O(H)⋯Br[−] distances of 3.391(7) and 3.171(7) Å, respectively),

creating a cyclic hydrogen bond network. No other structures containing the *N*-octylquinolinium or the *N*-octylisoquinolinium cation were found in the Cambridge Structural Database (CSD).⁴⁵ However, other structures containing quinolinium cations with short linear *N*-alkyl chain substituents were found in the CSD: *N*-pentylquinolinium,⁴⁶ *N*-butylquinolinium,^{47–51} *N*-propylquinolinium,^{46,52,53} *N*-ethylquinolinium,⁵⁴ and methylquinolinium.^{55–57} None of these structures contained a dodecyl sulfate anion. Also, structures containing isoquinolinium cations with linear *N*-alkyl chain substituents were found in the CSD: *N*-butylisoquinolinium,^{32,58} *N*-propylisoquinolinium,⁵⁹ *N*-ethylisoquinolinium,³² and *N*-methylisoquinolinium.⁶⁰ None of these structures contained a bromide anion.

Thermal properties

The thermal properties of the quinolinium and isoquinolinium salts were investigated by polarizing optical microscopy (POM),

Fig. 2 ORTEP representation of the molecular structure of compound **IQ8.a**, with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.

differential scanning calorimetry (DSC), and also, for compounds **Q18.a**, **IQ18.a**, **Q16.c** and **IQ16.c**, by X-ray powder diffraction at elevated temperatures. In Fig. 3, the DSC traces of compounds **IQ19.b** and **Q22.d** are shown. Due to the complex thermal behaviour and the hygroscopicity of the quinolinium and isoquinolinium salts, the first and second heating runs were not identical for most compounds. The first heating run values were used if no melting peak was observed in the second heating run (the salts did not crystallize on cooling down to $-20\text{ }^{\circ}\text{C}$) and if the second heating showed several unresolved endothermic and exothermic peaks (*i.e.* a sequence of recrystallization processes and crystal-to-crystal transitions) before melting. It must be noted that even though different crystalline conformations were adapted in the first and second heating run, the melting temperature was identical in both cases. Compounds that were heated above $200\text{ }^{\circ}\text{C}$ decomposed slightly. This was observed in the DSC thermogram as a deviation from the baseline at the end of the first heating run and confirmed by POM. In general, the quinolinium and isoquinolinium salts showed up to three different crystalline phases. The occurrence of polymorphism in the solid state is not unusual for ionic liquids.^{61–66} The thermal

behaviour of the quinolinium and isoquinolinium salts is a nice example of the subtle balance between volume effects, electrostatic interactions and separation between ionic and aliphatic parts of the molecules (microsegregation)⁶⁷ that are required for the formation of liquid-crystalline phases.

An overview of the mesophase behaviour of the liquid-crystalline compounds is shown in Fig. 4–7. Tables with the transition temperatures and enthalpy changes for all the compounds are given in the ESI (Tables S1 and S2).† The quinolinium bromides **Qn.a** with tetradecyl and shorter alkyl chain lengths were not liquid-crystalline (Fig. 4). It is not surprising that mesomorphism is observed only for the long chain analogues, since a minimum alkyl chain length of twelve carbon atoms is needed for imidazolium salts and pyridinium salts in order to obtain microphase separation.^{13–16,68} In addition, the ionic head group is extended in (iso)quinolinium salts compared to pyridinium, so that longer alkyl chains are required for the induction of a mesophase. This case is similar to that of the imidazolium and benzimidazolium salts.¹⁷ A monotropic smectic A phase was observed for bromides **Q16.a**

Fig. 3 Top: DSC-trace of **IQ19.b**—second heating run. Bottom: DSC-trace of **Q22.d**—second heating run.

Fig. 4 Schematic representation of the transition temperatures and mesophase behaviour of the quinolinium bromides **Qn.a** (top) and the isoquinolinium bromides **IQn.a** (bottom).

Fig. 5 Schematic representation of the transition temperatures and mesophase behaviour of the quinolinium dodecyl sulfates **Qn.c** (top) and the isoquinolinium dodecyl sulfates **IQn.c** (bottom).

and **Q17.a**. Compounds **Q18.a–Q22.a** showed a smectic A phase over a temperature range 58 to 98 °C. The melting point increases with increasing chain length in the series **Q12.a–Q17.a**. For compounds **Q18.a–Q20.a**, the melting point varies only slightly with the chain length, while the clearing point sharply increases. The mesophase range and transition temperatures of the bromide salt **Q22.a** are similar to those of **Q20.a**. For pyridinium ionic liquid crystals, the same tendency has been observed.⁶⁸ At this point the ionic interactions can no longer efficiently compensate for the large volume that the molten alkyl chain occupies at high temperatures, and no further increase in mesophase stability is observed. Compounds **Q17.a** and **Q19.a** melt at slightly higher temperatures than their analogues with an even number of carbon atoms in the alkyl chain. Such odd–even effects have also been observed for imidazolium and pyridinium salts.^{13,68} It should be mentioned that the *N*-alkylquinolinium bromides with an alkyl chain up to an octadecyl chain have been described in the literature, but their liquid-crystalline behaviour seems to have been overlooked.³⁹

The thermal behaviour of the isoquinolinium bromides **IQ12.a–IQ22.a** resembles that of the corresponding quinolinium bromides (Fig. 4). A smectic A phase was observed for the

Fig. 6 Schematic representation of the transition temperatures and mesophase behaviour of the quinolinium tetrafluoroborates **Qn.b** (top) and the isoquinolinium tetrafluoroborates **IQn.b** (bottom).

bromides with a hexadecyl or longer alkyl chain (**IQ16.a–IQ22.a**). The mesophase temperature range increases with chain length, reaching a maximum of 113 °C for **IQ22.a**. In this series of isoquinolinium salts, the clearing point still rises significantly when going from a $C_{20}H_{41}$ to a $C_{22}H_{45}$ chain, in contrast to the quinolinium bromide salts. This is probably due to better packing of the aromatic cores (see the crystal model presented in Fig. S4 (ESI)†). It is expected that for chain lengths longer than twenty-two carbon atoms, the clearing temperatures and mesophase temperature range will at some point start to level off or to decrease. Unfortunately, 1-bromoalkanes with alkyl chains longer than $C_{22}H_{45}$ are not commercially available or easily accessible *via* synthetic procedures.

The thermal behaviour of the dodecyl sulfate salts, in which both cation and anion bear a long alkyl chain, is somewhat different from that of the other salts, in the sense that a smectic A phase was already observed for a chain length of twelve carbon atoms or longer (Fig. 5). This is not surprising as the anion is now contributing to the amphiphilicity of the molecule as well. The mesophase stabilities of the dodecyl sulfate salts are lower

Fig. 7 Schematic representation of the transition temperatures and mesophase behaviour of the quinolinium hexafluorophosphates **Qn.d** (top) and the isoquinolinium hexafluorophosphates **IQn.d** (bottom).

than those of the (iso)quinolinium bromide salts. Upon melting, the weak van der Waals interactions between these chains are broken and they no longer adopt an all-*trans* conformation, thus enlarging the aliphatic–ionic interphase area. In other words, the area imposed by the aliphatic chains, which increases with increasing temperature, will no longer fit the area occupied by the ionic head groups. The same reasoning can be applied for the sulfosuccinate salts, although for *N*-methyl-(iso)quinolinium dioctylsulfosuccinates **Q1.f** and **IQ1.f**, only the anion bears alkyl chains, responsible for the fluidity in the system. Both compounds showed thermotropic smectic A phases at room temperature. Elongation of the alkyl chain is not beneficial for mesophase formation, as *N*-butylquinolinium dioctylsulfosuccinate **Q4.f** is not liquid-crystalline. Also, the cyclic sulfosuccinate salts **Q1.g** and **IQ1.g** were not liquid-crystalline, which could be expected. The use of hexylsulfosuccinate as the anion seems to be less effective, since only a monotropic smectic A phase was observed for the quinolinium hexylsulfosuccinate **Q1.h**.

The type of anion has a major influence on the properties of ionic liquid crystals.²⁶ In this paper, the bromide anion was exchanged with the less hydrophilic tetrafluoroborate, hexa-

fluorophosphate anions. The earlier observations that longer alkyl chains are needed to accommodate the voluminous anions in the liquid-crystalline state are confirmed.^{13–16} Enantiotropic mesophases were observed for quinolinium tetrafluoroborates **Q19.b–Q22.b** and isoquinolinium tetrafluoroborates **IQ18.b–IQ22.b** (Fig. 6). Incorporation of the hexafluorophosphate anion requires a chain length of at least twenty carbon atoms to obtain mesomorphic (iso)quinolinium salts (**Qn.d** and **IQn.d**) (Fig. 7). In general, the clearing temperatures and mesophase temperature ranges decrease in the order: $\text{Br}^- > \text{BF}_4^- > \text{PF}_6^-$. All mesomorphic tetrafluoroborate and hexafluorophosphate salts showed a smectic A phase.

The smectic A phases were identified on the basis of their optical defect textures, observed by polarizing optical microscopy (POM). Upon cooling from the isotropic liquid, bâtonnets were formed. These bâtonnets coalesced into fans, giving rise to a fan texture (Fig. 8).

Also, an oily streak texture with pseudo-isotropic domains was observed.

Powder X-ray diffraction (PXRD) and structural models

To obtain a better insight into the ordering of molecules within the smectic A phase, X-ray diffractograms were recorded for compounds **Q18.a**, **IQ18.a**, **Q16.c** and **IQ16.c**. A typical

Fig. 8 Mesophase defect textures observed by polarizing optical microscopy (POM). Top: fan texture of compound **Q16.c** at 132 °C. Bottom: oily streak texture of compound **Q19.a** at 166 °C.

Fig. 9 X-ray diffractogram of the smectic A phase of *N*-hexadecyloquinolinium dodecyl sulfate **IQ16.c** at 90 °C, represented as the logarithm of the scattering intensity (in counts) versus the scattering angle 2θ (Cu-K α radiation). The broad diffraction signal centred at $2\theta \approx 6.5^\circ$ is due to the covering foil used in the experimental setup (marked with *).

diffractogram is shown in Fig. 9. An overview of the Bragg reflections observed for these compounds is given in Table 1. In the small-angle region, one sharp reflection was detected for the smectic A phases of the quinolinium salts **Q18.a** and **Q16.c**, whereas two equidistant reflections were observed for the isoquinolinium salts **IQ18.a** and **IQ16.c**. The fact that only one reflection was observed for compounds that clearly form a smectic A phase is an indication that the smectic layers are ill defined. It is not uncommon for smectic A phases that the second-order reflection has an intensity that is only 1% of that of the first-order reflection.^{69,70} In that case, the second-order reflection often disappears in the background noise. Very weak or missing second-order reflections have also been observed for other types of smectogenic ionic liquid crystals.^{71,72,16} The reflections in the small-angle region are related to the thickness d of the smectic layers. A broad, diffuse peak was observed in the wide-angle region, situated around $4.5 \text{ \AA}$ for the bromide salts (**Q18.a** and **IQ18.a**) and around $4.6 \text{ \AA}$ for the dodecyl sulfate salts (**Q16.c** and **IQ16.c**). This signal is related to the short-range

order of the molten alkyl chains. The information obtained from the X-ray diffractograms was used to calculate the molecular volume V_M and the molecular area A_M . The molecular volume was estimated using the relation $V_M = (M/0.6022)f$, where M is the molecular mass (g mol^{-1}) and f is a temperature correcting factor ($f = 0.9813 + 7.474 \times 10^{-4}T$, with T the temperature in °C).⁷³ The molecular area A_M was calculated using the equation $A_M = 2V_M/d$, where d is the smectic layer thickness. As expected, the calculated molecular area is much smaller for the bromide salts ($A_M \approx 48 \text{ \AA}^2$) than for the dodecyl sulfate salts ($A_M \approx 72 \text{ \AA}^2$), because of the large sulfate head groups. From the crystal structures, it can be derived that the aromatic core of the quinolinium salts is oriented almost perpendicularly to the staggered alkyl chain, while the isoquinolinium core lies in the same plane as the major part of the alkyl chain. As a consequence, the molecular area of the quinolinium salts is somewhat larger than the molecular area of the isoquinolinium salts. In Fig. 10 a structural model is proposed for the quinolinium bromides.

Conclusions

Thermotropic liquid crystals are composed of molecules that adopt an anisometric shape, most commonly rod-like or disk-like molecules. At present it is still difficult to predict which type of phase is formed, since several factors have to be taken into account. In this study, we tried to provide a better insight into the driving forces for mesophase formation of (iso)quinolinium salts. Although *N*-alkylquinolinium and *N*-alkyloquinolinium salts with bromide, tetrafluoroborate, hexafluorophosphate, dodecyl sulfate anions and sulfosuccinate exhibit smectic A phases as many other ionic liquid crystals,²⁶ the thermal behaviour of these ionic liquid crystals is atypical, in the sense that these compounds only exhibit liquid-crystallinity when their alkyl chain is very long. It had been observed for 1-alkyl-3-imidazolium salts that the temperature range of the mesophase widens with increasing alkyl chain length,¹³ but it is uncommon that mesophases are formed only in the case of very long chains. After all, the long-chain compounds have relatively large aliphatic parts compared to the ionic parts, while the ionic part is responsible for the formation of the layer structure and thus

Table 1 Bragg reflections collected from the X-ray diffractograms of the enantiotropic mesophases (Cu-K α radiation)

Compd.	$d_{\text{meas}}/\text{\AA}^a$	I^b	hkl^c	$d_{\text{calc}}/\text{\AA}^a$	Parameters of the mesophase at temperature $T^{d,e,f}$
Q18.a	32.62	S	001	32.62	SmA: $T = 120^\circ\text{C}$
	4.53	br	h_{ch}		$V_M = 823 \text{ \AA}^3$ $A_M = 50.4 \text{ \AA}^2$
IQ18.a	34.50	S	001	34.60	SmA: $T = 111^\circ\text{C}$
	17.35	M	002	17.30	$V_M = 817 \text{ \AA}^3$
	4.51	br	h_{ch}		$A_M = 47.3 \text{ \AA}^2$
Q16.c	29.14	S	001	29.14	SmA: $T = 111^\circ\text{C}$
	4.68	br	h_{ch}		$V_M = 1096 \text{ \AA}^3$ $A_M = 75.2 \text{ \AA}^2$
IQ16.c	30.63	S	001	30.78	SmA: $T = 90^\circ\text{C}$
	15.47	W	002	15.39	$V_M = 1080 \text{ \AA}^3$
	4.67	br	h_{ch}		$A_M = 70.1 \text{ \AA}^2$

^a d_{meas} and d_{calc} are the measured and calculated diffraction spacings, respectively. ^b I is the intensity of the reflections: S, strong; M, medium; W, weak; br, broad reflection. ^c hkl are the Miller indices of the reflections and h_{ch} is the periodicity corresponding to the liquid-like order of the molten aliphatic chains. ^d T is the temperature at which the X-ray diffractogram is recorded. ^e V_M is the molecular volume and A_M the molecular area. ^f Abbreviation: SmA = smectic A phase.

Fig. 10 Structural model for the smectic A phase of compound **Q18.a**. The smectic layer thickness is indicated by d (at 120 °C, $d = 32.62 \text{ \AA}$, and $A_M \approx 50.4 \text{ \AA}^2$).

for the occurrence of the smectic mesophases. It is not true that just increasing the alkyl chain length leads to more stable mesophases in the case of ionic liquid crystals, as illustrated by the disappearance of liquid-crystallinity in the case of the lanthanide(III) alkanooates with very long alkyl chains.^{74,75} There exist only very few studies on liquid crystals with alkyl chains longer than $C_{20}H_{41}$,^{76,77} because the required long-chain 1-bromoalkanes are very expensive or even not commercially available. This study shows that liquid-crystalline behaviour can be observed for ionic liquids with very long alkyl chains as well as for their short-chained analogues, dependent on the choice of anion. The key factor for mesophase formation in these ionic

liquid crystals is a delicate equilibrium between microphase segregation and the relative size of areas occupied by incompatible units (aliphatic/ionic) at the interface, rather than the number of carbon atoms present in the alkyl chain.

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References

- 1 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 2 T. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3773–3789.
- 3 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- 4 P. Wasserscheid and T. Welton (ed.), *Ionic Liquids in Synthesis*, 2002, Wiley-VCH, Weinheim.
- 5 M. Deetlefs, K. R. Seddon and M. Shara, *Phys. Chem. Chem. Phys.*, 2006, **8**, 642–649.
- 6 L. Glasser and H. D. B. Jenkins, *Chem. Soc. Rev.*, 2005, **34**, 866–874.
- 7 A. R. Katritzky, A. Lomaka, R. Petrukhin, R. Jain, M. Karelson, A. E. Visser and R. D. Rogers, *J. Chem. Inf. Model.*, 2002, **42**, 71–74.
- 8 I. Billard, G. Marcou, A. Ouadi and A. Varnek, *J. Phys. Chem. B*, 2011, **115**, 93–98.
- 9 P. Eiden, S. Bulut, T. Kochner, C. Friedrich, T. Schubert and I. Krossing, *J. Phys. Chem. B*, 2011, **115**, 300–309.
- 10 U. Preiss, V. N. Emel'yanenko, S. P. Verevkin, D. Himmel, Y. U. Paulechka and I. Krossing, *ChemPhysChem*, 2010, **11**, 3425–3431.
- 11 C. Q. Yan, M. J. Han, H. Wan and G. F. Guan, *Fluid Phase Equilib.*, 2010, **292**, 104–109.
- 12 U. Preiss, S. Bulut and I. Krossing, *J. Phys. Chem. B*, 2010, **114**, 11133–11140.
- 13 J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133–2139.
- 14 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.
- 15 C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627–2636.
- 16 A. E. Bradley, C. Hardacre, J. D. Holbrey, S. Johnston, S. E. J. McMath and M. Nieuwenhuyzen, *Chem. Mater.*, 2002, **14**, 629–635.
- 17 K. M. Lee, C. K. Lee and I. J. B. Lin, *Chem. Commun.*, 1997, 899–900.
- 18 X. J. Wang, F. W. Heinemann, M. Yang, B. U. Melcher, M. Fekete, A. V. Mudring, P. Wasserscheid and K. Meyer, *Chem. Commun.*, 2009, 7405–7407.
- 19 F. Neve, O. Francescangeli, A. Crispini and J. Charmant, *Chem. Mater.*, 2001, **13**, 2032–2041.
- 20 F. Neve and M. Imperor-Clerc, *Liq. Cryst.*, 2004, **31**, 907–912.
- 21 J. Przedmojski and P. Dynarowicz-Latka, *Phase Transitions*, 1999, **70**, 133–146.
- 22 E. Alami, H. Levy, R. Zana, P. Weber and A. Skoulios, *Liq. Cryst.*, 1993, **13**, 201–212.
- 23 K. Goossens, K. Lava, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Driesen, C. Gortler-Walrand, K. Binnemans and T. Cardinalaels, *Chem.-Eur. J.*, 2009, **15**, 656–674.
- 24 K. Lava, K. Binnemans and T. Cardinalaels, *J. Phys. Chem. B*, 2009, **113**, 9506–9511.
- 25 T. Cardinalaels, K. Lava, K. Goossens, S. V. Eliseeva and K. Binnemans, *Langmuir*, 2011, **27**, 2036–2043.
- 26 K. Binnemans, *Chem. Rev.*, 2005, **105**, 4148–4204.
- 27 T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38–68.
- 28 I. J. B. Lin and C. S. Vasam, *J. Organomet. Chem.*, 2005, **690**, 3498–3512.
- 29 K. V. Axenov and S. Laschat, *Materials*, 2011, **4**, 206–259.

- 30 J. D. Holbrey, I. Lopez-Martin, G. Rothenberg, K. R. Seddon, G. Silvero and X. Zheng, *Green Chem.*, 2008, **10**, 87–92.
- 31 A. E. Visser, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, 2001, 2484–2485.
- 32 A. E. Visser, J. G. Huddleston, J. D. Holbrey, W. M. Reichert, R.P. Swatloski and R. D. Rogers, *ACS Symp. Ser.*, 2007, **975**, 362–380.
- 33 C. M. Lee, *J. Korean Chem. Soc.*, 1972, **16**, 205–207.
- 34 U. Domanska, M. Zawadzki, M.M. Tshibangu, D. Ramjugernath and T. M. Letcher, *J. Chem. Thermodyn.*, 2010, **42**, 1180–1186.
- 35 U. Domanska, M. Zawadzki, M. Krolikowska, M.M. Tshibangu, D. Ramjugernath and T. M. Letcher, *J. Chem. Thermodyn.*, 2011, **43**, 499–504.
- 36 U. Domanska, M. Zawadzki and M. Zwolinska, *J. Chem. Thermodyn.*, 2011, **43**, 775–781.
- 37 U. Domanska and M. Zawadzki, *J. Chem. Thermodyn.*, 2012, **48**, 276–283.
- 38 U. Domanska, M. Zawadzki, M.M. Tshibangu, D. Ramjugernath and T. M. Letcher, *J. Phys. Chem. B*, 2011, **115**, 4003–4010.
- 39 A. Busetti, D. E. Crawford, M. J. Earle, M. A. Gilea, B. F. Gilmore, S. P. Gorman, G. Laverty, A. F. Lowry, M. McLaughlin and K. R. Seddon, *Green Chem.*, 2010, **12**, 420–425.
- 40 M. Zawadzki and U. Domanska, *J. Chem. Thermodyn.*, 2011, **43**, 989–995.
- 41 K. Tanabe, Y. Suzui, M. Hasegawa and T. Kato, *J. Am. Chem. Soc.*, 2012, **134**, 5652–5661.
- 42 *SAINT, Manual Version 5/6.0*, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, 1997.
- 43 *SHELXTL-NT, Manual Version 5.1*, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, 1997.
- 44 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- 45 F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388.
- 46 H. H. Li, Z. R. Chen, L. C. Cheng, M. Feng, H. D. Zheng and J. Q. Li, *Dalton Trans.*, 2009, 4888–4895.
- 47 G. Menczel, J. Kurti and R. Lehoc, *Acta Chim. Hung.*, 1984, **116**, 335–344.
- 48 C. M. Zhong, Y.J. Zuo, H. S. Jin, S. Q. Liu and T. C. Wang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, o5050–5051.
- 49 H. H. Li, Z. R. Chen, Y. Liu, K. N. Ding, J. Q. Li, C. C. Huang and L. Q. Guo, *J. Cluster Sci.*, 2007, **18**, 817–829.
- 50 H. H. Li, Z. R. Chen, L. Q. Guo, K. N. Ding, J. Q. Li, C. C. Huang and Z. L. Cai, *Aust. J. Chem.*, 2007, **60**, 595–602.
- 51 Y. J. Zuo, C. M. Zhong, H. S. Jin, Z.H. Su and T. C. Wang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, o3561–o3562.
- 52 G. Rindorf, N. Thorup and K. Kamaras, *Synth. Met.*, 1988, **25**, 189–195.
- 53 Y. J. Wang, H. H. Li, C. C. Chen and J. B. Liu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m2736–u963.
- 54 M. Sokolov, A. Virovets, V. Nadolnnyi, K. Hegetschweiler, V. Fedin, N. Podherezskaya and V. Fedorov, *Inorg. Chem.*, 1994, **33**, 3503–3509.
- 55 T. M. Bockman and J. K. Kochi, *J. Am. Chem. Soc.*, 1989, **111**, 4669–4683.
- 56 J. P. Cornelissen, E. J. Creyghton, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta*, 1991, **185**, 97–102.
- 57 J. L. Zuo, R. G. Xiong, X. Z. You and X. Y. Huang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 46–48.
- 58 H. Xue, Z. F. Tong, F. Y. Wei and S. G. Qing, *C. R. Chim.*, 2008, **11**, 90–94.
- 59 E. O. Lykova, M. S. Chernov'yants, O. N. Kazheva, A. N. Chekhlov and O. A. D'yachenko, *Russian J. Phys. Chem.*, 2004, **78**, 1785–1789.
- 60 A. S. Kumbhar, S. B. Padhye, A. A. Kelkar, R. P. Patil, R.V. Chaudhari, V. G. Puranik, N. N. Dhaneshwar and S.S. Tavale, *Polyhedron*, 1996, **15**, 1931–1935.
- 61 D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164–4170.
- 62 J. Golding, S. Forsyth, D. R. MacFarlane, M. Forsyth and G. B. Deacon, *Green Chem.*, 2002, **4**, 223–229.
- 63 D. R. MacFarlane, S. A. Forsyth, J. Golding and G. B. Deacon, *Green Chem.*, 2002, **4**, 444–448.
- 64 A. Triolo, A. Mandanici, O. Russina, V. Rodriguez-Mora, M. Cutroni, C. Hardacre, M. Nieuwenhuyzen, H. J. Bleif, L. Keller and M. A. Ramos, *J. Phys. Chem. B*, 2006, **110**, 21357–21364.
- 65 J. D. Holbrey, R. M. Reichert, M. Nieuwenhuyzen, S. Johnston, K. R. Seddon and R. D. Rogers, *Chem. Commun.*, 2003, 1636–1637.
- 66 A. V. Mudring, *Aust. J. Chem.*, 2010, **63**, 544–564.
- 67 C. Tschierske, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 355–370.
- 68 G. A. Knight and B. D. Shaw, *J. Chem. Soc.*, 1938, 682–683.
- 69 J. Stamatoff, P. E. Cladis, D. Guillon, M. C. Cross, T. Bilash and P. Finn, *Phys. Rev. Lett.*, 1980, **44**, 1509–1512.
- 70 W.R. Krigbaum, J. C. Poirier and M. J. Costello, *Mol. Cryst. Liq. Cryst.*, 1973, **20**, 133–163.
- 71 P. H. J. Kouwer and T. M. Swager, *J. Am. Chem. Soc.*, 2007, **129**, 14042–14052.
- 72 J. M. Suisse, S. Bellemin-Laponnaz, L. Douce, A. Maise-Francois and R. Welter, *Tetrahedron Lett.*, 2005, **46**, 4303–4305.
- 73 K. Goossens, P. Nockemann, K. Driesen, B. Goderis, C. Görller-Walrand, K. Van Hecke, L. Van Meervelt, E. Pouzet, K. Binnemans and T. Cardinaels, *Chem. Mater.*, 2008, **20**, 157–168.
- 74 K. Binnemans and C. Görller-Walrand, *Chem. Rev.*, 2002, **102**, 2303–2345.
- 75 K. Binnemans, L. Jongen, C. Bromant, D. Hinz and G. Meyer, *Inorg. Chem.*, 2000, **39**, 5938–5945.
- 76 K. Binnemans, R. Van Deun, B. Thijs, I. Vanwelkenhuysen and I. Geuens, *Chem. Mater.*, 2004, **16**, 2021–2027.
- 77 Y. Wang, N. Archambault, A.M. Belcher, D. Busse, D.B. Damon, A. Mills, A.E. Riddle, I.J. Samardjiev, B.L. Lucht and W.B. Euler, *Macromolecules*, 2008, **41**, 7115–7121.