Smectic Liquid Crystals from Supramolecular Guanidinium Alkylbenzenesulfonates

Fabrice Mathevet, Patrick Masson,* Jean-François Nicoud, and Antoine Skoulios[a]

Abstract: A homologous series of guanidinium alkylbenzenesulfonates from ethyl to tetradecyl were synthesized and characterised. Their thermotropic polymorphism was investigated by polarizing optical microscopy, differential scanning calorimetry, and dilatometry. The structure of the smectic liquid crystal phases obtained at high temperature with the compounds from octyl to tetradecyl was analysed by X-ray diffraction. The supramolecular assembling of the ionic species inside the smectic layers was investigated by infrared spectroscopy.

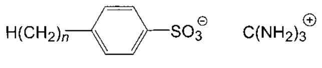
Keywords: amphiphiles · hydrogen bonds · liquid crystals · supramolecular chemistry

Introduction

The crystal structure of a variety of guanidinium alkane- and arenesulfonates has only recently been investigated by X-ray diffraction.[1] Strongly interacting through coulombic forces, the positive and negative ions were, interestingly enough, found to self-assemble into supramolecular two-dimensional networks as a result of "equal numbers of donor and acceptor hydrogen-bonding sites and three-fold topology common to both guanidinium and sulfonate ions". Separated by the organic residues of the sulfonate ions, these networks were, in turn, found to pile up periodically over one another to form lamellar structures. With bulky residues, unable for apparent reasons to sit all on the same side of the supramolecular networks, the ionic sheets are covered by the residues on both sides, and the lamellar structure is single-layered. Inversely, with thin residues, the ionic sheets, covered only on one side are associated in pairs by bracketing together their polar surfaces, and the lamellar structure is double-layered. Figure 1 illustrates the double-layered structure of guanidinium benzenesulfonate, showing the in-layer hydrogen-bonded supramolecular network of the guanidinium and sulfonate ions, the double-layered arrangement of the ionic species, and the interdigitated packing of the benzene rings.

Careful inspection of the crystal structure of the benzene derivative (Figure 1) gives one interesting observation. As deduced from the lattice parameters,[1] the packing area of the interdigitated benzene rings, $\frac{1}{4} ac \sin\beta = 22.6$ Å^2, is large enough to permit the addition of long alkyl chains in the *para* position of the benzene rings without disruption of the ion packing in the crystals (the cross-sectional area of linear paraffins in the crystalline state is of only 18.5 Å^2).[3] In such a *para* alkylated compound, the benzene rings should of course disentangle and the ionic sublayers should be drawn apart in order to make enough room for the alkyl chains to fit into the structure (Figure 1c). More interestingly, the packing area of the benzene rings is large enough even to permit the disordering of the alkyl chains (the cross-sectional area of disordered alkyl chains in smectic liquid crystals generally lies between 21 and 27 Å^2).[3, 4] Taking this last remark as a basis, one may then formulate the conjecture that *para* alkylated guanidinium benzenesulfonate salts should be able to produce smectic liquid crystals after melting of the alkyl chains at high temperature.

The objective of the present work is to check the soundness of the above conjecture. It is also to test whether the strength of the hydrogen bonding of the guanidinium and sulfonate ions is sufficient to maintain the supramolecular architecture of the layers despite the melting of the alkyl chains in the smectic state. For this purpose, a series of guanidinium alkylbenzenesulfonates from ethyl to tetradecyl (abbreviated to GABS-*n*, with *n* even ranging from 2 to 14) were prepared; their thermotropic polymorphism was investigated by polarizing optical microscopy, differential scanning calorimetry, and dilatometry; their structure at high temperature was determined by X-ray diffraction; and their supramolecular architecture was checked by infrared spectroscopy.



GABA-*n*

Results and Discussion

Synthesis: The GABS-*n* compounds were synthesized following the general method described in the literature,[1] by precipitation from solutions of equimolar amounts of guani-

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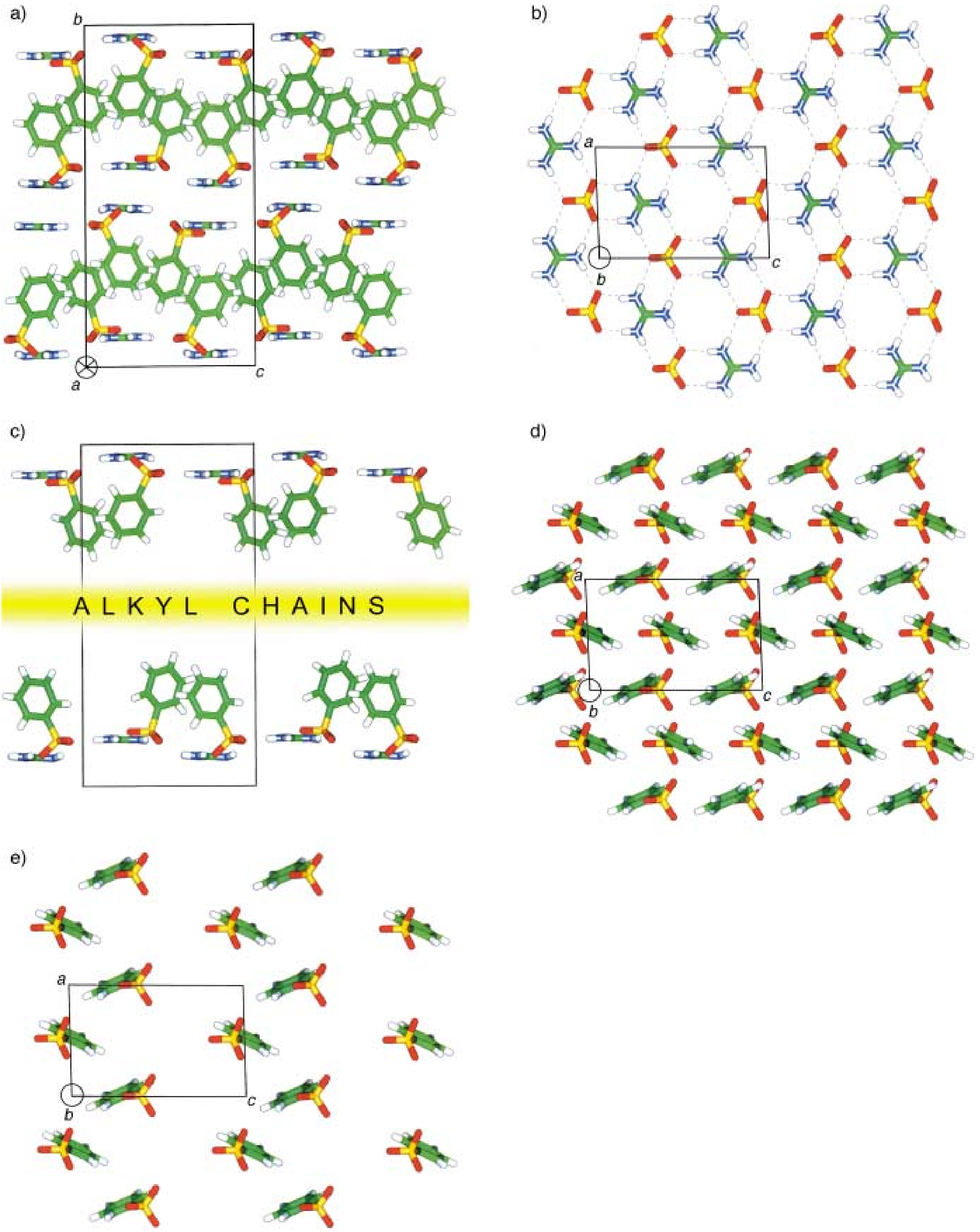

Figure 1. Crystal structure of guanidinium benzenesulfonate drawn by molecular modelling from experimental data of reference:[1] a) projection on *b*, *c* lattice plane of two layers of interdigitated molecules, b) packing mode in *a*, *c* lattice plane of sulfonate and guanidinium ions sitting on upper surface of upper molecular layer (benzene rings are omitted for clarity), c) splitting of the upper molecular layer, the molecules being drawn apart in order to leave enough space for the alkyl chains to be attached to the benzene rings, d) projection on *a*, *c* lattice plane of the upper layer of the interdigitated molecules (guanidinium ions are omitted for clarity), e) projection on *a*, *c* lattice plane of half the upper molecular layer (all guanidinium ions and molecules with sulfonate groups pointing downwards are omitted). Carbon atoms in green, sulphur atoms in yellow, oxygen atoms in red, nitrogen atoms in blue, hydrogen atoms in white. Cell parameters: $a = 7.50$, $b = 23.287$, $c = 12.060$ Å, $\beta = 92.24°$.

dine hydrochloride and sodium 4-alkylbenzensulfonate. To ensure purity, special care was taken to select the appropriate solvent (pure water for $n \leq 8$, or water/ethanol 1:1 *v*/*v* mixture for $n > 8$) and to control its rate and extent of evaporation during the precipitation process. Not commercially available, the sodium 4-alkylbenzensulfonates used were synthesized beforehand by action of chlorosulfonic acid on alkylbenzene and subsequent saponification, a method known to produce *para* isomers exclusively.[5]

Thermal and optical studies: Studied by thermogravimetry, the GABS-*n* compounds were all found to be thermally stable up to temperatures of about 320 °C. Examined by polarizing optical microscopy in the temperature range from ambient up to 300 °C, they appeared to melt sharply at the temperatures indicated in Figure 2, transforming either into an isotropic liquid for chain lengths $n \leq 6$, or into a strongly birefringent fluid stable up to the highest temperature explored for chain lengths $n \geq 8$. The focal-conic textures observed (Figure 3) clearly show that the birefringent fluid phases are genuine smectic liquid crystals. With the object of characterising more precisely the crossing over from the isotropic to the smectic state as a function of growing chain length, a set of binary mixtures of GABS-6 and GABS-8 were carefully investigated at high temperature by optical microscopy and X-ray diffraction. Practically independent of temperature, the crossing over was thus found to proceed through a very narrow biphasic region at an average chain length of $n \cong 6.7$.

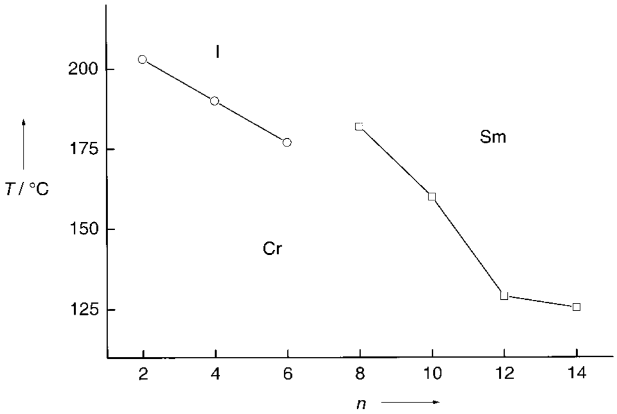

Figure 2. Phase transition temperatures of the guanidinium alkylbenzenesulfonates measured by polarizing optical microscopy and confirmed by differential scanning calorimetry (onset of hottest endotherm) as a function of the number of carbon atoms in the alkyl chains (Cr: crystal, I: isotropic liquid, Sm: smectic).

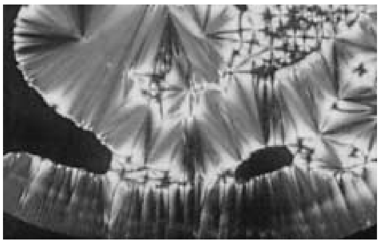

Figure 3. Focal-conic smectic texture of guanidinium octylbenzenesulfonate at 184 °C.

The thermotropic transition from a crystal to a smectic phase was fully confirmed by differential scanning calorimetry. Ranging from 60 to 120 J g^{-1}, the enthalpies measured could not be analysed in detail, particularly as a function of increasing chain length, because of a complex polymorphism in the solid state difficult to control.

Dilatometric investigation of the smectic phases: As stated in the section below, a quantitative interpretation of the smectic structure requires the knowledge of the molecular volumes. Three GABS-*n* compounds, namely GABS-8, GABS-10, and GABS-12, were therefore analysed by dilatometry as a function of increasing, then of decreasing temperature.[6–8] Figure 4 shows the phase transition from the low-temperature crystal to the high-temperature smectic phase in the particular case of GABS-12 taken as an example. In agreement with the results of optical microscopy and differential scanning calorimetry, the molecular volume was found to grow with temperature in the stability range of each one of the phases observed and to jump abruptly at the crystal to smectic phase transition by some 36 Å^3. Upon cooling, the volume decreases quite reversibly in the whole range explored, and the smectic phase supercools, as usual, well below the melting temperature.

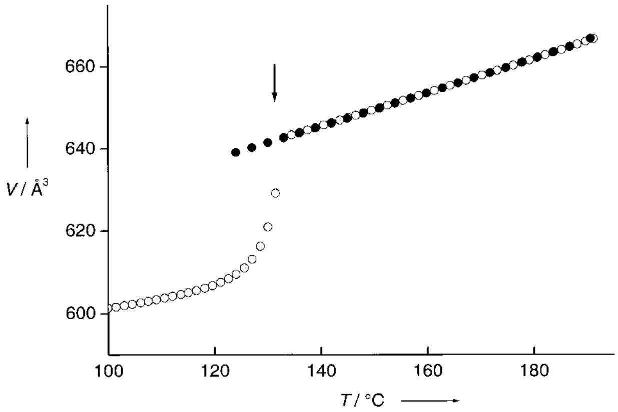

Figure 4. Variation of the molar volume of guanidinium dodecylbenzenesulfonate as a function of increasing (open circles) and decreasing (solid circles) temperature, showing the melting of the crystals and the supercooling of the smectic phase. Arrow indicates the transition temperature detected by optical microscopy.

Figure 4 further shows, in agreement with previous observations of liquid crystals, that the molecular volume of the smectic phase increases with temperature in a linear fashion, according to the following Equations (1) – (3) established by a least-squares linear fit of the experimental data ($R > 0.9999$):

$$\text{GABS-8: } V\,[\text{Å}^3] = 480.43_{\pm 0.02} + 0.3196_{\pm 0.0001}\,T\,[^\circ\text{C}] \tag{1}$$

$$\text{GABS-10: } V\,[\text{Å}^3] = 534.21_{\pm 0.03} + 0.3623_{\pm 0.0002}\,T\,[^\circ\text{C}] \tag{2}$$

$$\text{GABS-12: } V\,[\text{Å}^3] = 587.91_{\pm 0.03} + 0.4111_{\pm 0.0002}\,T\,[^\circ\text{C}] \tag{3}$$

The same for the three compounds, the relative thermal expansion coefficient deduced from the equations above, $(\partial V/\partial T)/V \cong 7 \times 10^{-4}\,\text{K}^{-1}$, is equal to that currently given in the literature for organic materials in the molten state.[4] Finally, the molecular volume at 190 °C (where the smectic structure is to be analysed in the section below) increases with the number *n* of carbon atoms in the alkyl chains in a linear fashion (Figure 5), according to the Equation (4) ($R = 0.99999$):

$$V\,[\text{Å}^3] = 291.2_{\pm 1.6} + 31.22_{\pm 0.16}\,n \tag{4}$$

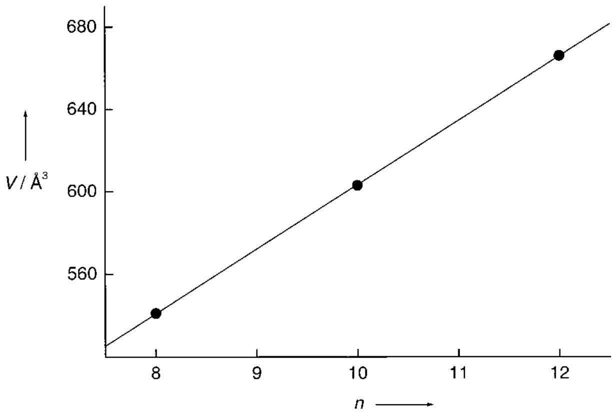

Figure 5. Variation of the molar volume of guanidinium alkylbenzenesulfonates in the smectic state at 190 °C as a function of chain length.

Structural investigation of the smectic phases: The smectic nature of the GABS-n compounds suggested by optical microscopy was fully confirmed by X-ray diffraction. Indeed, the powder patterns recorded at high temperature contain two sharp, equidistant reflections in the small-angle region, related to the smectic layering of the molecules, and a unique diffuse ring in the wide-angle region at about 4.7 Å, related to the liquid-like conformation of the alkyl chains and to the lack of long-range ordering of the ionic species within the smectic layers (Figure 6). With the concept of microphase separation of amphiphiles (with their constituent parts being incompatible with one another) taken for granted,[9, 10] the smectic structure consists of an alternate superposition of nonpolar and polar sublayers, here made respectively of the alkyl chains and the ionic headgroups of the molecules (Figure 7).

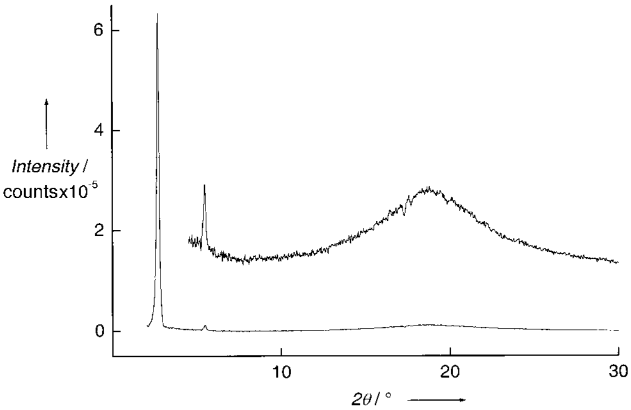

Figure 6. X-ray powder diffraction pattern of guanidinium dodecylbenzenesulfonate in the smectic phase at 190 °C. For clarity, intensity at Bragg angles $2\theta > 4.8°$ is multiplied by 15.

The smectic periods measured increase linearly with the number n of carbon atoms in the alkyl chains (Figure 8), according to the Equation (5) below, determined at 190 °C by a least-squares linear fit of the experimental data ($R = 0.9996$).

$$d\,[\text{Å}] = 16.87_{\pm 0.15} + 1.228_{\pm 0.015}\, n \qquad (5)$$

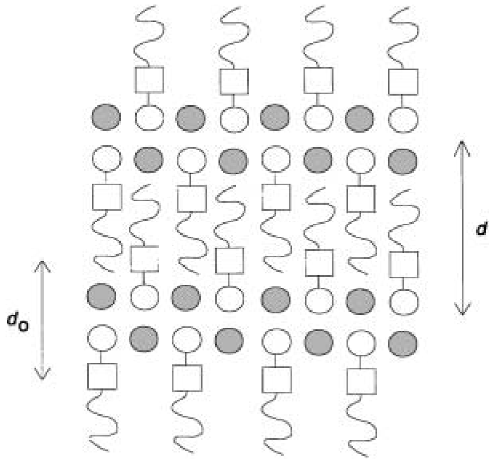

Figure 7. Schematic representation of the structure of the guanidinium alkylbenzenesulfonates in the smectic state: □ benzene rings; ○ sulfonate anions; ● guanidinium cations; wavy lines: molten alkyl chains.

The slope of the d versus n line represents the growth of the thickness of the smectic layers per methylene group added to the molecules. As for its extrapolation down to $n = 0$, it gives an estimate of the thickness of the guanidinium benzenesulfonate polar sublayers ($d_0 = 16.87$ Å), which turns out perfectly consistent with that calculated otherwise by molecular modelling (≈16.1 Å).

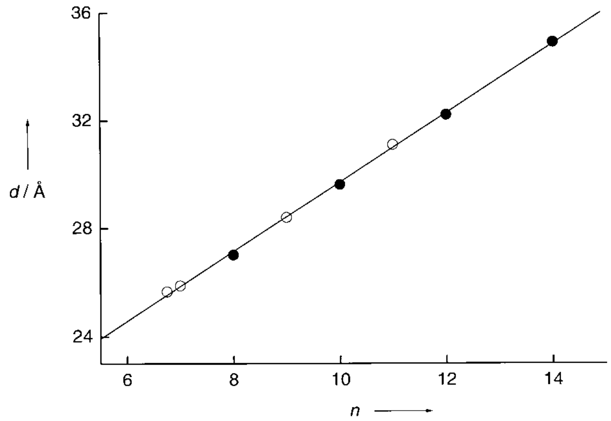

Figure 8. Smectic period of the guanidinium alkylbenzenesulfonates in the smectic state at 190 °C as a function of the (average) number of carbon atoms in the alkyl chains. Solid circles correspond to pure compounds, open circles to hexyl/octyl, octyl/decyl, and decyl/dodecyl binary mixtures.

Considering that a layer of N molecules, occupying a volume $N \cdot V$ and covering an area $N \cdot S$, has a thickness $d = V/S$, one may easily calculate S using the values found experimentally for d and V (except for GABS-14, where the V value was extrapolated from the V versus n equation). It is worth emphasising that parameter S measures the contribution of one molecule to the lateral spreading of the layers and hence represents the cross-sectional area of two molecules coupled end on through their ionic headgroups. As shown in Figure 9, this parameter is not constant but increases slowly with the length of the alkyl chains, so proving beyond question

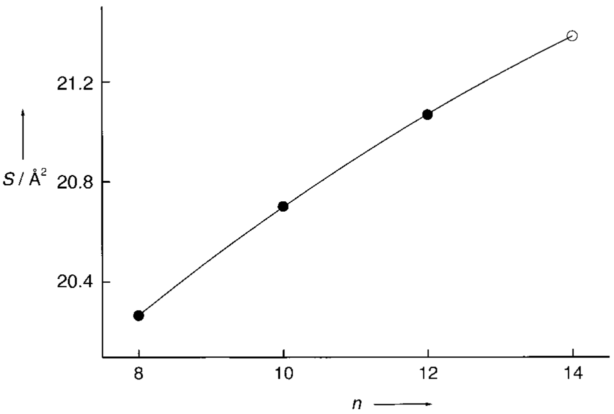

Figure 9. Variation of S with the chain length for guanidinium alkylbenzenesulfonates in the smectic state at 190 °C. Solid circles correspond to volumes measured experimentally, and open circle corresponds to a volume determined by extrapolation.

that the bulkiness of the chains does play an important part in the packing of the ionic species.

It is important to note that the value of S (ranging from 20.3 Å^2 for GABS-8 to 21.4 Å^2 for GABS-14) is actually slightly smaller than that ($ac\sin\beta/4 = 22.6$ Å^2) measured crystallographically for the guanidinium benzenesulfonate crystals.[1] Surprising at first sight, this result is, however, easy to understand—it simply originates in the puckering of the ionic layers, that is, in the distortion of the hydrogen-bonded sheets (by bending of the hydrogen bonds) from strict planarity due to the packing requirements of the bulky residues.[1] As shown in Figure 1a, the ionic species in the puckered sheets are indeed alternately shifted up and down along the c direction, and the interdigitated benzene rings alternately tilted left and right with respect to the layer normal to maximise van der Waals contacts and to accommodate closer packing. Moreover, as often mentioned in the literature,[11] the benzene rings adopt an edge-to-face arrangement in the nonpolar sublayers to satisfy π interactions (Figure 1d). Now, in the presence of long alkyl chains preventing the interdigitation of the benzene rings, the molecules find themselves arranged in double rows oriented along the a direction (Figure 1c and e). Strengthened by the π-interactions and leaving empty spaces between them, these rows have a possibility to draw nearer to one another and so to allow a reduction of the molecular area S by accentuating the puckering of the ionic sheets.

Infrared spectroscopy: Since the smectic phases described belong to the class of the so-called disordered smectic phases, in which the in-layer ordering extends over only a few molecules, the question immediately arises of whether the hydrogen bonding that holds the molecules together in the crystal survives at high temperature in the liquid crystal. In a search of specific information about this bonding, one of the compounds, namely GABS-12, was carefully investigated by infrared spectroscopy.

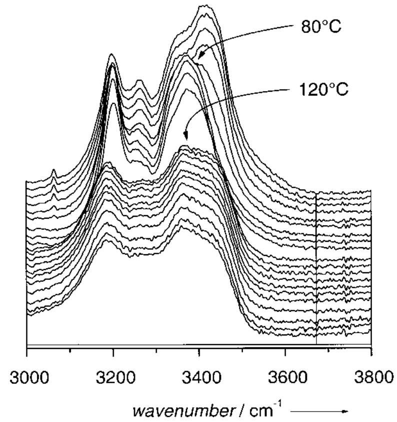

Figure 10. IR absorption spectra of guanidinium dodecylbenzenesulfonate in the 3000–3600 cm^{-1} N–H stretching region, recorded as a function of increasing temperature in the range from 30 °C (upper curve) to 220 °C (lower curve) with steps of 10 °C.

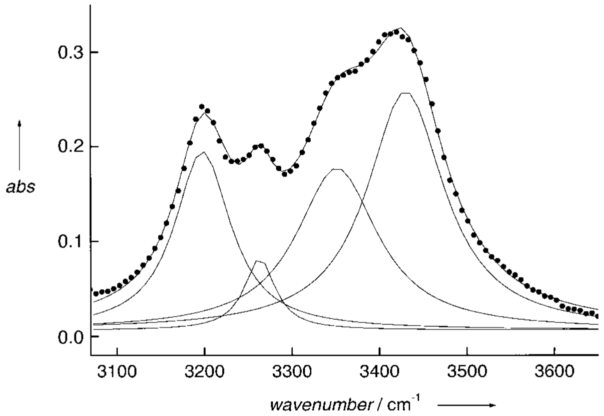

Figure 11. Deconvolution of the IR absorption spectrum of guanidinium dodecylbenzenesulfonate in the crystalline state at room temperature.

The spectra recorded as a function of increasing temperature, particularly in the 3000–3600 cm^{-1} N–H stretching region where the hydrogen bonding shows up most clearly (Figure 10), permit the detection of the phase transitions quite clearly: One transition at about 80 °C between two crystal forms and one other at about 120 °C between a crystal and the smectic phase. In the crystalline state at room temperature, the spectra contain four absorption bands (3198, 3263, 3351 and 3430 cm^{-1}, as determined by a least-squares multiple-Lorentzian fit of the experimental data, see for instance Figure 11) that are very close to those reported in the literature for GABS-0 (guanidinium benzenesulfonate) (3186, 3258, 3341 and 3341–3400 cm^{-1}).[1] Evidently, the hydrogen-bonding pattern of the molecules in both GABS-12 and GABS-0 is essentially the same. In the smectic phase at high temperature, on the other hand, the absorption bands, which are lower but wider, have basically the same position (3186, 3282, 3369 and 3442 cm^{-1}) and the same area (84 cm^{-1} at 150 °C, instead of 101 cm^{-1} at 30 °C) as in the crystal. The number of hydrogen bonds is therefore little affected by the melting process—even though disorderly assembled within the smectic layers, the molecules continue to be extensively hydrogen-bonded to form rather large two-dimensional supermolecules. This result may appear surprising at first

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sight on account of the disordering that takes place inside the layers at the crystal to smectic phase transition; it is, however, easy to understand because the acquisition time of the spectra ($\approx 10^{-3}$ s) is way larger than the characteristic time ($\approx 10^{-9}$ s) of the local-order fluctuations in the smectic layers.

Conclusion

To conclude, it is appropriate to emphasise the main result of the present work, namely, the production of supramolecular smectic liquid crystals from guanidinium alkylbenzenesulfonates. The idea that prepared the way for this venture—and that proved perfectly valid—originated in the simple remark that the packing area of the ionic species in the layers of guanidinium benzenesulfonate crystals is large enough, not only to permit the introduction of long alkyl chains in the *para* position of the benzene rings without disruption of the supramolecular hydrogen-bonded association of the ions, but also to permit eventually their melting at high temperature, leading to the formation of smectic liquid crystals. The disordered nature of the smectic phases obtained, implying that the ordering of the molecules inside the layers is not extending over long distances, could at first sight be taken to suggest that the supramolecular self-assembly of the ions vanishes completely in the smectic state. In fact, this is definitely not the case as proven by infrared spectroscopy. The supramolecular organisation described is all the more satisfying as the smectic phases, rather fluid, reach their thermodynamic equilibrium easily.

Experimental Section

General: ^{1}H NMR spectroscopy: Bruker spectrometer at 200 MHz in [D$_6$]DMSO, 25 °C. Elemental analysis: performed at Institut Charles Sadron, Strasbourg. Thermogravimetry: Setaram TGA 92, argon flow, heating rate of 10 °C min^{-1}. Polarizing optical microscopy: Leitz-Orthoplan, Mettler FP82 hot stage. Differential scanning calorimetry: Perkin–Elmer DSC7, heating-cooling rates of 10 °C min^{-1}. Dilatometry: home-made computer-driven dilatometer, 1 g of carefully degassed sample immersed in about 10 mL of mercury, heating and cooling steps of 0.1 °C every 2 min. X-ray diffraction: Guinier focusing camera, $\mathrm{Cu_{K\alpha 1}}$ radiation, powder samples in Lindemann capillaries, INSTEC hot stage, INEL CPS-120 curved position-sensitive detector. Molecular modelling: MSI Insight II software, Silicon Graphics. Infrared spectroscopy: ATI Mattson FTIR spectrometer, resolution of 4 cm^{-1}, samples in KBr pellets heated in a home-made temperature-controlled hot stage.

Synthesis of tetradecylbenzene: Tetradecylbenzene, which is not commercially available, was synthesized by Kumada's cross-coupling reaction.[12] A Grignard reagent was prepared under argon by slow addition of 1-bromotetradecane (0.2 mol) to magnesium (0.2 mol) in dry ether (100 mL) and heating at reflux for 2 h. Chlorobenzene (0.16 mol) and $\mathrm{NiCl_2(dppp)}$ (0.4 mmol) used as a catalyst were dissolved in diethyl ether (60 mL) and added with the ether solution of the Grignard reagent; the mixture, turning from red to pale green, was then heated at reflux overnight. After cooling to 0 °C, the mixture was hydrolysed with aqueous 2 N HCl (100 mL). The organic layer was washed with water and a saturated aqueous solution of $\mathrm{NaHCO_3}$, the organic layer was dried over $\mathrm{MgSO_4}$ and evaporated to dryness. The liquid tetradecylbenzene obtained was finally purified by distillation at 164–166 °C (7 mmHg) (71 % yield). ^{1}H NMR: $\delta = 7.18$ (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 5H, Ar-*H*), $\delta = 2.59$ (t, $^3J(\mathrm{H,H}) = 7.6$ Hz, 2H, $\mathrm{Ar\text{-}C\mathit{H_2}CH_2)_{12}CH_3}$), 1.57 (m, 2H, $\mathrm{Ar\text{-}CH_2C\mathit{H_2}(CH_2)_{11}CH_3}$), 1.26 (m, 6H, $\mathrm{Ar\text{-}CH_2CH_2(C\mathit{H_2})_{11}CH_3}$), 0.88 (t, $^3J(\mathrm{H,H}) = 6.35$ Hz, 3H, $\mathrm{Ar\text{-}(CH_2)_{13}C\mathit{H_3}}$)]; elemental analysis calcd (%) for $\mathrm{C_{20}H_{34}}$ (274.49): C 87.52, H 12.45; found C 87.60 H 12.45.

Synthesis of sodium 4-alkylbenzenesulfonates: The synthesis of the decyl derivative, taken as an example, is as follows. Decylbenzene (from Aldrich) (40 mmol) in dichloroethane (30 mL) was added dropwise at room temperature with chlorosulfonic acid (40 mmol) in dichloroethane (10 mL). After stirring overnight, 4-decylbenzenesulfonic acid was isolated as a yellow viscous liquid (occasionally crystallising at room temperature) by evaporation to dryness. It was carefully added under stirring with NaCl (5 g) in water (85 mL). The sodium 4-decylbenzenesulphonate formed as a white precipitate was filtered off and recrystallized in water (90 % yield). The whole set of sodium 4-alkylbenzenesulfonates synthesized (yields growing from 55 % for ethyl to 90 % for higher than octyl) were characterised by ^{1}H NMR: $\delta = 7.48$ (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H, Ar-*H ortho* $\mathrm{SO_3}$), 7.10 (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H, Ar-*H meta* $\mathrm{SO_3}$), 2.53 (t, $^3J(\mathrm{H,H}) = 7.3$ Hz, 2H, $\mathrm{Ar\text{-}C\mathit{H_2}(CH_2)_{\mathit{n}-2}CH_3}$), 1.52 (m, 2H, $\mathrm{Ar\text{-}CH_2C\mathit{H_2}(CH_2)_{\mathit{n}-3}CH_3}$), 1.22 (m, $(2n-6)$H, $\mathrm{Ar\text{-}CH_2CH_2(C\mathit{H_2})_{\mathit{n}-3}CH_3}$), 0.83 (t, $^3J(\mathrm{H,H}) = 6.3$ Hz, 3H, $\mathrm{Ar\text{-}(CH_2)_{\mathit{n}-1}C\mathit{H_3}}$).

Synthesis of GABS-*n*: Salts with $n \leq 8$ were prepared in pure water. For example, GABS-2 was synthesized by dissolving guanidine hydrochloride (used as received from Aldrich) (3.1 mmol) and sodium 4-ethylbenzenesulfonate (prepared as described above) (3.1 mmol) in hot water (10 mL). Precipitating as transparent crystals by simple cooling, the expected product was filtered off, dried in vacuum, and controlled by ^{1}H NMR (70 % yield). On the other hand, salts with $n > 8$, were prepared in water/ethanol mixtures. For example, GABS-10 was synthesized by dissolving guanidine hydrochloride (3.1 mmol) and sodium 4-decylbenzene-sulphonate (3.1 mmol) inhot water/ethanol 1:1 *v*/*v* mixture (20 mL). Precipitating by cooling to room temperature and partial evaporation of the solvent, the product was filtered off, dried, and controlled by ^{1}H NMR (82 % yield). Following this procedure, the whole set of GABS-*n* compounds from $n = 2$ to 14 were synthesized. To make up the shortage in guanidinium of the long-chained compounds, due to co-crystallisation with small amounts of unreacted sodium 4-decylbenzenesulphonate, the products obtained were redissolved in hot water/ethanol 1:1 *v*/*v* mixture (20 mL), treated with additional guanidine hydrochloride (0.3 mmol), and isolated by precipitation and evaporation as previously. The final compounds were characterised by ^{1}H NMR: $\delta = 7.48$ (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H, Ar-*H ortho* $\mathrm{SO_3}$), 7.10 (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 2H, Ar-*H meta* $\mathrm{SO_3}$), 6.95 (s, 6H, $[\mathrm{C(N\mathit{H_2})_3}]^+$), 2.53 (t, $^3J(\mathrm{H,H}) = 7.2$ Hz, 2H, $\mathrm{Ar\text{-}C\mathit{H_2}(CH_2)_{\mathit{n}-2}CH_3}$), 1.52 (m, 2H, $\mathrm{Ar\text{-}CH_2C\mathit{H_2}(CH_2)_{\mathit{n}-3}CH_3}$), 1.22 (m, $(2n-6)$H, $\mathrm{Ar\text{-}CH_2CH_2(C\mathit{H_2})_{\mathit{n}-3}CH_3}$), 0.83 (t, $^3J(\mathrm{H,H}) = 6.3$ Hz, 3H, $\mathrm{Ar\text{-}(CH_2)_{\mathit{n}-1}C\mathit{H_3}}$)]; elemental analysis calcd (%) for GABS-2 (245.08): C 44.07, H 6.16, N 17.13; found C 43.88, H 6.21, N 17.13; elemental analysis calcd (%) for GABS-4 (273.11): C 48.33, H 7.01, N 15.37; found C 48.27, H 7.02, N 15.33; elemental analysis calcd (%) for GABS-6 (301.15): C 51.81, H 7.69, N 13.94; found C 51.66, H 7.73, N 13.82; elemental analysis calcd (%) for GABS-8 (329.18): C 54.69, H 8.26, N 12.75; found C 54.61, H 8.30, N 12.75; elemental analysis calcd (%) for GABS-10 (357.21): C 57.11, H 8.75, N 11.76; found C 57.28, H 8.80, N 11.75; elemental analysis calcd (%) for GABS-12 (385.24): C 59.19 H 9.15, N 10.90; found C 59.60, H 9.26, N 10.79; elemental analysis calcd (%) for GABS-14 (413.27): C 60.98, H 9.50, N 10.16; found C 60.90, H 9.54, N 10.22.

Acknowledgement

The authors wish to thank Dr. B. Heinrich for skilled assistance and helpful discussions in the dilatometry experiments.

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Received: October 4, 2001 [F3593]