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

Structural study of smectic A phases in homologous series of *N*-alkylpyridinium alkylsulphates

C. Cruz[a]; B. Heinrich[b]; A. C. Ribeiro[ac]; D. W. Bruce[a]; D. Guillon[c]
[a] CFMC-UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal and IST-UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal, [b] School of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, United Kingdom, [c] IPCMS-GMO, 23 rue du Loess, BP 20CR, F-67037 Strasbourg Cedex, France,

To cite this Article Cruz, C. , Heinrich, B. , Ribeiro, A. C. , Bruce, D. W. and Guillon, D.(2000) 'Structural study of smectic A phases in homologous series of *N*-alkylpyridinium alkylsulphates', Liquid Crystals, 27: 12, 1625 — 1631
To link to this Article: DOI: 10.1080/026782900750037185
URL: http://dx.doi.org/10.1080/026782900750037185

LIQUID CRYSTALS, 2000, VOL. 27, NO. 12, 1625–1631

Structural study of smectic A phases in homologous series of *N*-alkylpyridinium alkylsulphates

C. CRUZ†*, B. HEINRICH‡§, A. C. RIBEIRO†‡, D. W. BRUCE§
and D. GUILLON‡

†CFMC-UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa,
Portugal and IST-UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
‡IPCMS-GMO, 23 rue du Loess, BP 20CR, F-67037 Strasbourg Cedex, France
§School of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD,
United Kingdom

(*Received 20 April 2000; accepted 12 June 2000*)

The mesomorphic properties of 27 homologues of the *N*-alkylpyridinium alkylsulphate series were studied by X-ray diffraction and dilatometry. All of these compounds exhibit single smectic A phases whose layer spacings are between 0.64 and 0.8 times the molecular length. Polarizing optical microscopy observation shows that these peculiar layer spacings are not due to the tilting of the molecules; a new packing model is proposed to explain the particular structure of these thermotropic ionic liquid crystal phases.

1. Introduction

It has previously been shown [1] that the homologous series of *N*-alkylpyridinium dodecylsulphates (nPySO$_4m$, see figure 1), with $m = 12$ (the number of carbon atoms of the aliphatic chain connected to the sulphate group), consists of thermotropic ionic liquid crystals.

Each of these compounds exhibit a single smectic A phase, whose temperature range and clearing point are reasonably independent of the chain length, and whose layer spacing is about 0.8 times the molecular length calculated as the simple sum of the lengths of the cation and the anion. As polarizing optical microscopy on the phases shows undoubtedly that they are orthogonal smectic phases, tilting of the molecules cannot be invoked as a reason for the peculiar layer spacing, and so it was supposed that this behaviour would be related to the cross-sectional area of the ionic species which greatly exceeds that of the extended aliphatic tails. From the analysis of powder X-ray diffraction patterns, various models were then discussed, which considered that the alkyl chains would be compelled either to possess large, random tilt or to interdigitate in order to compensate for this difference of bulkiness [1]. Among the different models, one was retained in which the layer is formed by two, single, ionic sublayers where the pyridinium rings sandwich the ionic part of the dodecylsulphate anion; these two sublayers are separated by the aliphatic chains of the anion, which are, on average, standing upright. The two ionic sublayers are covered by the disordered aliphatic chains of the pyridinium rings, which show large random tilting fluctuations to ensure a compatible molecular area between the ionic and aliphatic parts. However, these conclusions were drawn purely from knowledge of the layer spacings without any direct experimental information on the molecular area, which is clearly a key parameter to describe the molecular arrangement within smectic layers [2]. In that previous work, moreover, only the length of the chain attached to the pyridinium ring was changed (n was varied between 8 and 15) while the length of the counteranion chain was kept constant ($m = 12$). A precise discussion of the effect of chain length was therefore not possible.

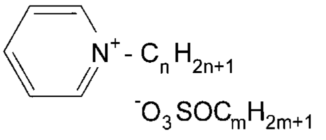


Figure 1. Chemical structure of the studied compounds.

In this paper we present new results associated with the study of 27 new homologues, with $(n + m)$ varying between 20 and 40 and $(n - m)$ varying between -10 and $+8$ (see the table). For the symmetric compounds ($n = m$), dilatometric measurements complement the powder X-ray diffraction measurements. With this extended systematic study we intended to get relevant information in order to understand better the packing characteristics of the smectic A phases exhibited by these

---

*Author for correspondence; e-mail: cruz@alfl.cii.fc.ul.pt

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals

Table. Transition temperatures (°C) obtained from polarizing optical microscopy. The compounds indicated in italics were presented in [1].

Compound	Cr		SmA		I
6PySO$_4$16	•	74	•	150	•
8PySO$_4$14	•	77	•	149	•
8PySO$_4$16	•	81	•	158	•
8PySO$_4$18	•	85	•	163	•
10PySO$_4$10	•	85	•	141	•
10PySO$_4$12	•	86	•	149	•
10PySO$_4$14	•	82	•	159	•
10PySO$_4$16	•	87	•	163	•
10PySO$_4$18	•	86	•	163	•
12PySO$_4$10	•	92	•	150	•
12PySO$_4$12	•	95	•	161	•
12PySO$_4$14	•	97	•	162	•
12PySO$_4$16	•	97	•	163	•
12PySO$_4$18	•	87	•	162	•
14PySO$_4$10	•	96	•	158	•
14PySO$_4$12	•	100	•	163	•
14PySO$_4$14	•	103	•	165	•
14PySO$_4$16	•	102	•	162	•
14PySO$_4$18	•	97	•	161	•
16PySO$_4$10	•	93	•	162	•
16PySO$_4$12	•	101	•	164	•
16PySO$_4$14	•	106	•	163	•
16PySO$_4$16	•	108	•	161	•
16PySO$_4$18	•	106	•	160	•
18PySO$_4$10	•	91	•	163	•
18PySO$_4$12	•	97	•	162	•
18PySO$_4$14	•	106	•	161	•
18PySO$_4$16	•	109	•	160.0	•
18PySO$_4$18	•	111	•	156	•
20PySO$_4$20	•	115	•	147	•

compounds. The study of the influence of the molecular properties—namely the total of the chains' lengths $(n+m)$ and the symmetry or asymmetry of the compounds in terms of the length of the alkylpyridinium and alkylsulphate chains, $(n-m)$—on the structure of the mesophase is particularly important for this purpose.

2. Results

2.1. *Experimental*

X-ray diffraction results were obtained from powder samples, using a Guinier camera or a Debye-Sherrer camera equipped with a bent quartz monochromator (Cu-K$_{\alpha 1}$ radiation) and an electric oven. The temperature was controlled within ±0.05°C and the patterns were registered photographically or using a gas curved counter 'Inel CPS 120' associated with a data acquisition computer system. The dilatometry results were obtained using the Kovacs technique adapted to liquid crystals [3]. For this purpose a high precision computer-controlled, home built device was used. This system includes automatic data acquisition and allows for temperature control within ±0.03°C.

2.2. *Polymorphism*

From polarizing optical microscopy observations we verified that, despite the large variation in $(n+m)$ and $(n-m)$, all the compounds exhibit enantiotropic smectic A phases with a phase range of between 30 and 60°C (see the table).

The maximum clearing temperature is observed for $(n+m)=28$ (165°C), decreasing to minimum values of 141°C and 147°C, respectively, for $(n+m)=20$ and $(n+m)=40$. The variation of the asymmetry of the chains $(n-m)$ (from -10 to $+8$), for a constant total chain length $(n+m)$, has no significant influence on the clearing temperature (the maximum amplitude of the variation never exceeds 3°C). The melting point increases continuously with $(n+m)$, from 85°C to 115°C for $(n+m)=20$ to 40, respectively. Keeping $(n+m)$ constant, the melting point is almost constant for $(n-m)$ values from 0 to $+4$, but decreases continuously with increasing $|n-m|$ beyond these values—up to 18°C for $(n-m)=-10$.

2.3. *X-ray diffraction*

Figure 2 represents the variation of the smectic layer spacing, d, with $n+m$, for symmetric homologues $(n=m)$ at several temperatures. Note that for $(\mathrm{n}+m)=4k+2$ (k being an integer), the values plotted at 120°C correspond to the average d value for both homologues with $(n-m)=\pm 2$. All these experimental data are compared with the expected d spacings calculated from the molecular length.

First, it should be noted that the experimental d spacings are significantly shorter than those expected from the calculated molecular length, ℓ. The ratio d/ℓ

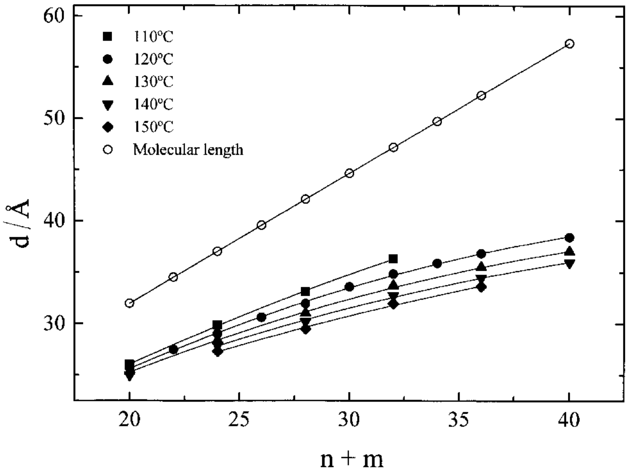


Figure 2. Variation of the smectic A layer spacing, d, of nPySO$_4m$ as a function of the total number of methylene groups per molecule at several temperatures (filled dark symbols) compared with the corresponding molecular lengths (open circles).

ranges from 0.8 for $(n+m)=20$ to 0.64 for $(n+m)=40$. Thus, the dependence of d upon $(n+m)$ is similar to that published previously [1], but the convexity of the variation is now clear as the range of variation in $(n+m)$ is much larger. This convexity implies that the molecular area S ($S = V_{\text{mol}}/d$, where V_{mol} is the molecular volume) increases with increasing $(n+m)$ after taking into consideration the fact that the molecular volume varies linearly with $(n+m)$ as will be shown below. Furthermore, from the decrease of d with increasing temperature, T, we may deduce that S also increases with increasing temperature. It should be pointed out that the influence of T is strongly amplified with increasing $(n+m)$, as indicated in figure 3.

Contrary to $(n+m)$ and T, and crucial to the development of the arguments presented later, the chain length asymmetry, $(n-m)$, has no significant influence on d or consequently on S, as shown in figure 4 for the homologous series and in figure 5 for binary mixtures of symmetric homologues.

Attempts to obtain XRD patterns on an oriented sample were successful with $12\text{PySO}_4 12$. The sample was oriented in a magnetic field perpendicular to the X-ray beam, by crossing the I–SmA phase transition many times before slowly cooling, allowing good alignment of the normal to the planes of the smectic layers along the magnetic field direction. Whereas the diffraction signals corresponding to the smectic layers are concentrated in small sized spots, the diffuse reflection in the wide angle region corresponding to the intermolecular interactions between aliphatic chains is spread over the angular domain. This indicates a pronounced disorganization of the aliphatic medium, as will be confirmed in the next section, with no preferred average direction of the chains. This point is also crucial.

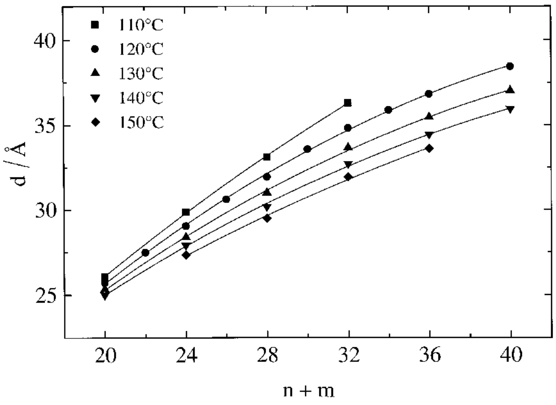


Figure 3. Expanded view of the variation of the smectic A layer spacing, d, of $n\text{PySO}_4m$ as a function of the total number of methylene groups per molecule at several temperatures, in order to show more clearly the larger influence of increasing temperature.

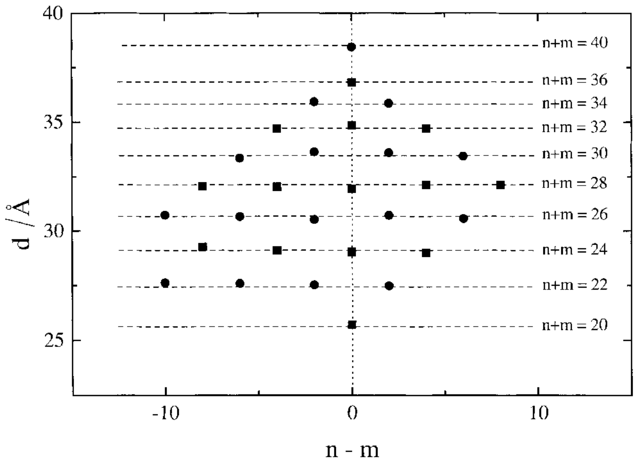


Figure 4. Variation of the smectic A layer spacing, d, of $n\text{PySO}_4m$ as a function of chain length asymmetry $(n-m)$ for different compounds containing the same total number of methylene groups.

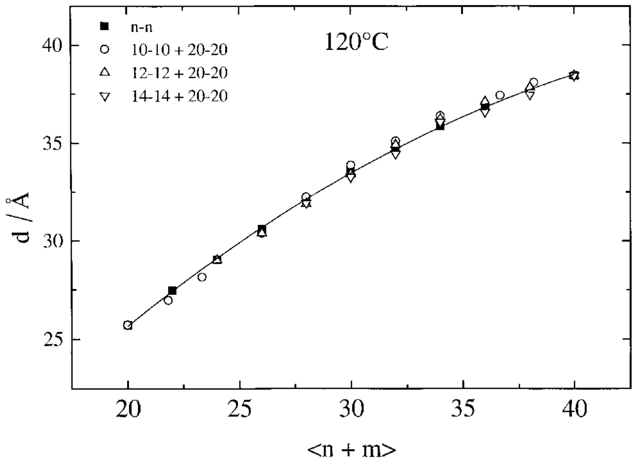


Figure 5. Variation of the smectic A layer spacing, d, as a function of the total number of methylene groups for binary mixtures of symmetric homologues $n\text{PySO}_4m$ at 120°C. Full squares are the d values from figures 2 or 3 for single component systems at 120°C.

2.4. *Molecular volume V_{mol}*

The molecular volume of all symmetric homologues has been measured systematically as a function of temperature; figure 6 shows the variation of the molecular volume, V_{mol}, determined at 120°C, as a function of $(n+m)$. Despite the large range of variation of $(n+m)$, V_{mol} varies linearly. This is consistent with the usual result that the volume of a molten methylene group, V_{CH2}, is constant at a given temperature [4] and confirms also that the volume of the ionic part, V^{c}, is independent of chain length. In other words, the molecular volume V_{mol} at a given temperature, of any homologue, can be

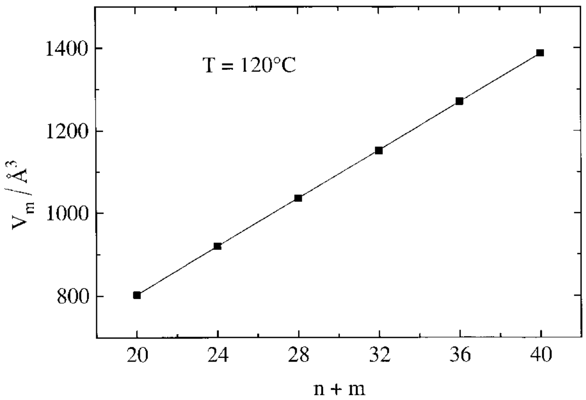


Figure 6. Variation of the molecular volume, V_{mol}, of nPySO$_4m$ as a function of the total number of methylene groups for different symmetric compounds at 120°C.

expressed as:

$$V_{mol} = V^c + (n+m)V_{CH2}. \quad (1)$$

Let us also remark that, according to these results, the variation of V_{CH2} with temperature is very close to that obtained in liquid paraffins [5], where V_{CH2} varies between 28.8 Å^3 at 110°C and 29.6 Å^3 at 150°C. Moreover, V^c (218 ± 1 Å^3 at 110–150°C) is consistent with the sum of the molecular volumes of pyridine and sulphuric acid (222 Å^3 at 20°C [6]).

2.5. *Molecular area, S, and sublayer thicknesses, d^c and d^{ch}*

Figure 7 represents the variation of the molecular area, $S = V_{mol}/d$, as a function of $(n+m)$. It indicates clearly that S has an intermediate value between once and twice the transverse area of an extended aliphatic chain ($V_{CH2}/1.27 = 22.8$–23.6 Å^2 between 110 and 150°C, where 1.27 is the C–C distance in Å along the chain axis).

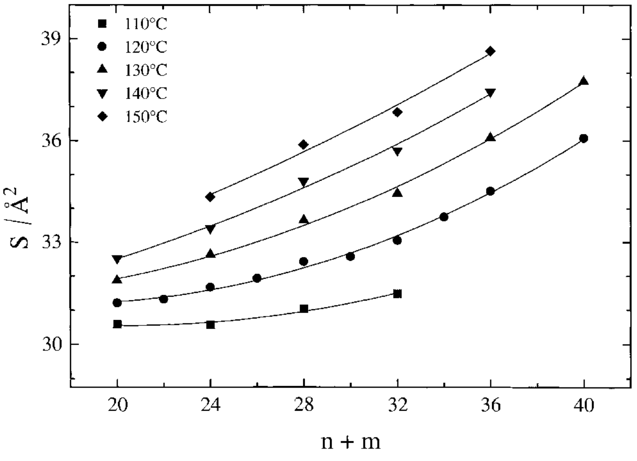


Figure 7. Variation of the molecular area, S, of nPySO$_4m$ as a function of the total number of methylene groups at several temperatures.

It also reveals a very important increase in S with increasing temperature and total chain length (S increases from 29.1 Å^2 for $(n+m) = 20$ at 90°C up to 38.6 Å^2 for $(n+m) = 36$ at 150°C), this behaviour being reversible on cooling. The corresponding ionic sublayer thickness, $d^c = V^c/S$, decreases with increasing temperature and total chain length by more than 20% from $(n+m) = 20$ at 110°C to $(n+m) = 36$ at 150°C (see figure 8). As V^c is independent of $(n+m)$ and increases very slightly with temperature, the mean distance between neighbouring cations and anions remains the same and the d^c and S variation must result from an evolution in the packing structure within the ionic sublayer.

As for the aliphatic sublayer, d^{ch} is directly deduced from the difference between the total layer spacing, d, and the aromatic sublayer spacing, d^c, calculated above. Its variation as a function of $(n+m)$ is represented

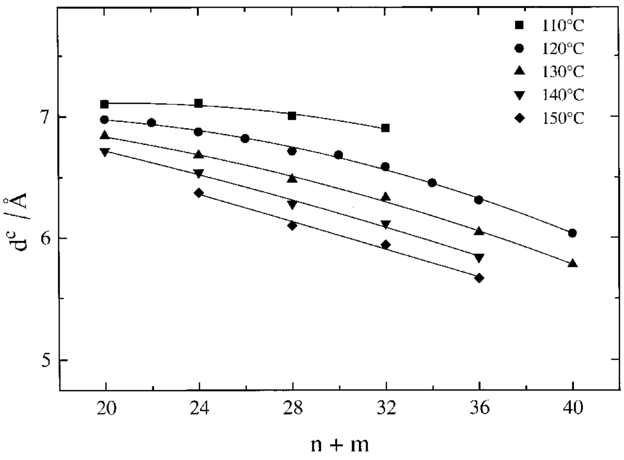


Figure 8. Variation of the ionic sublayer spacing, d^c, as a function of the total number of methylene groups at several temperatures.

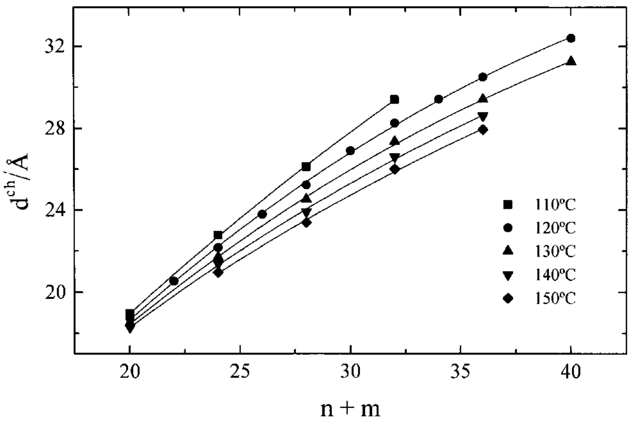
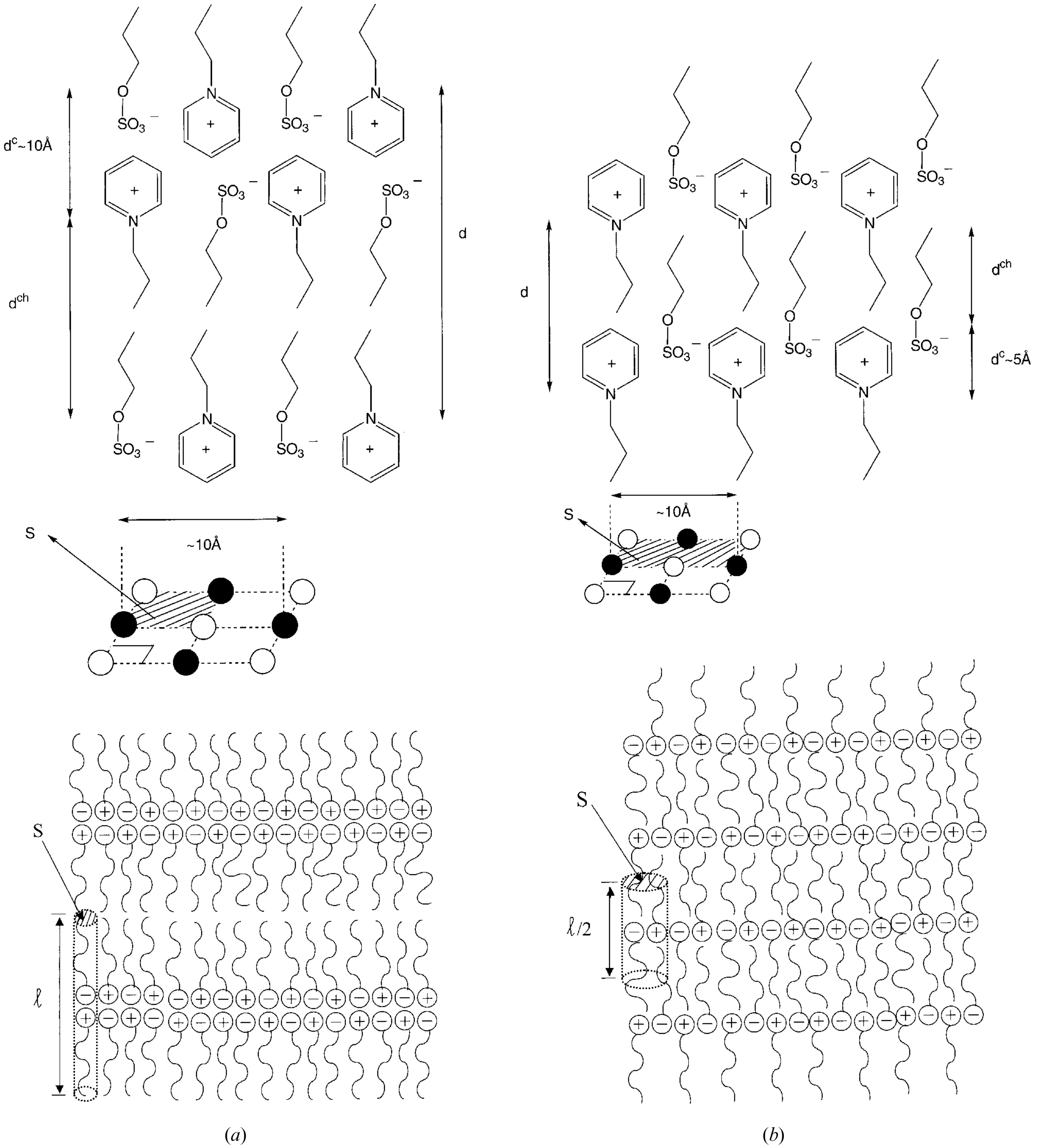


Figure 9. Variation of the aliphatic sublayer spacing, d^{ch}, as a function of the total number of methylene groups at several temperatures.

in figure 9 at different temperatures. If at 110°C the variation is practically linear, it becomes more and more convex with increasing temperature.

This indicates that the spreading of the aliphatic chains between the ionic sublayers becomes progressively more pronounced. Such a behaviour is in agreement with the variation of the molecular area as a function of temperature (see figure 7) and is consistent with the results of the X-ray measurements on the aligned sample. It is also worth noting that the linear fit of the data at



(a) (b)

Figure 10. Molecular arrangement in the smectic A phase of $n\mathrm{PySO}_4m$ with (a) a double ionic sublayer and no interdigitation, (b) a single ionic sublayer and a complete interdigitation of the aliphatic chains.

110°C leads to an increase of the aliphatic sublayer of 0.86 Å per CH_2, much smaller than the value of 1.27 Å per CH_2 expected for a stretched chain normal to the plane of the layers.

3. Discussion and structural model

To describe the molecular arrangement within the smectic A layers, it is necessary first to take into account that two cationic pyridinium rings presumably sandwich the sulphate part of the anion, as described previously [1, 7]. Let us now consider the transverse area of the ionic moiety, i.e. the area occupied by the ionic moiety in the plane of the layers. From the value of its volume $V^c = 218 \pm 1\,\text{Å}^3$ deduced from the data represented in figure 6, and from its thickness (evaluated at 4.9 Å by the BIOSYM software), a transverse area σ^c of about $45\,\text{Å}^2$ is calculated. It should be pointed out here that this value is fully consistent with the monolayer area before collapse is reached in a Langmuir trough for the homologues with large $(n+m)$, about $50\,\text{Å}^2$ [8]. In other words, if the smectic layers were completely flat, one should observe an experimental value of S of about $45\text{–}50\,\text{Å}^2$ for smectic layers with interdigitated chains or half of this for smectic layers with a double ionic sublayer; see figures 10(*a*) and 10(*b*). Both situations should be consistent with the molecular area of a molten aliphatic chain of around $25\,\text{Å}^2$. Surprisingly, the experimental molecular area S found in the present work ranges from 30 to $40\,\text{Å}^2$, corresponding to an intermediate situation between the two models represented in figure 10. Let us also recall that the layer spacings observed are between half and one molecular length (figure 2).

This behaviour is similar to that observed in the case of unsymmetrical and highly polar smectogens exhibiting smectic polymorphism with single and double layers or partial bilayering [9]. In particular, a molecular model of organization invoking a mixture of single molecules and pairs of head to head associated molecules has been proposed to describe the structural behaviour of the partially bilayered smectic A_d phases [10]. By analogy, a structural model invoking a mixture of both models represented above is quite appropriate to fit all the experimental data reported in the present work (see figure 11).

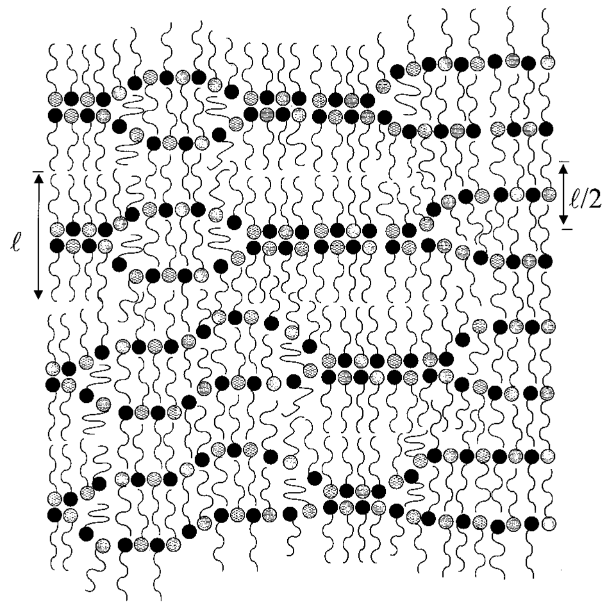


Figure 11. Molecular arrangement in the smectic A phase of $n\text{PySO}_4m$ with a combination of figures 10(*a*) and 10(*b*). Black circles are for pyridinium rings and grey circles for sulphate moieties.

Let us consider one smectic layer containing N molecules, N_1 molecules engaged without any interdigitation, figure 10(*a*), and N_2 molecules engaged with complete interdigitation, figure 10(*b*). If $N_1 = \tau N$, then $N_2 = (1-\tau)N$ and the area of the smectic layer, Σ, is:

$$\Sigma = \tau N\sigma + 2(1-\tau)N\sigma = (2-\tau)N\sigma \tag{2}$$

with σ being the average lateral molecular area of the cation or the anion and τ the fraction of molecules in the non-interdigitated arrangement. This leads to a molecular area $\Sigma/N = (2-\tau)\sigma$. The total maximum theoretical volume of such a smectic layer is $\Phi = N\ell\sigma$, with ℓ being the molecular length. Then the layer spacing observed can be expressed as:

$$d = \Phi/\Sigma = \ell/(2-\tau). \tag{3}$$

The values of τ deduced from such expressions are represented in figure 12. They indicate a clear tendency for the molecules to organize more and more in an interdigitated structure as the aliphatic chain length

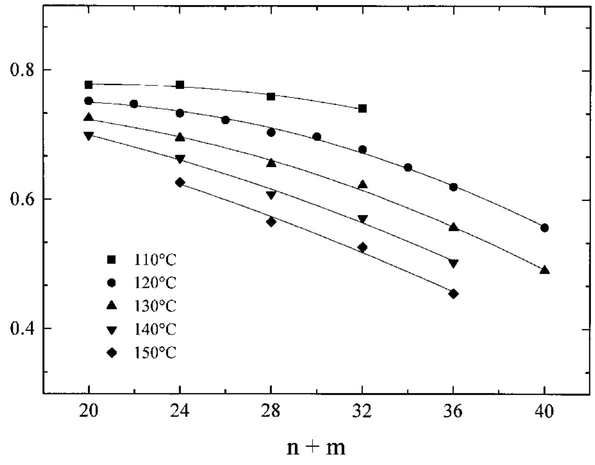


Figure 12. Variation of the fraction of non-interdigitated molecules as a function of the total number of methylene groups per molecule at several temperatures in the smectic A phase.

increases. The same tendency is observed for an increase of temperature. This behaviour seems quite reasonable from an entropic point of view. The structural model thus proposed agrees with all the experimental data reported in the present work. It certainly reflects the predominant role of the ionic interactions, which favour the continuity of the ionic sublayer structure, but also shows the role of the density of the paraffinic medium which can disturb the structure of the ionic sublayer, going from a double ionic layer to a single one. It should be emphasized also that the picture represented in figure 11 is only a static view of the real structure which will be strongly dynamic, with undulations ensuring the continuity between the microdomains where the molecules are completely interdigitated and those where molecules are not interdigitated. However, the size of these undulation wavelengths cannot be predicted directly from our experimental data in the scope of the present model. In fact, considering equations (2) and (3), one can easily verify that different wavelengths would produce the same results in terms of layer spacings and molecular areas, providing that the volumic proportions of monolayer and bilayer regions are the same. Nevertheless, one can predict that the wavelengths of these undulations are not macroscopic, otherwise there would appear a biphasic regime involving regions where the layer spacing is close to one molecular length, and regions where it is close to half of it; moreover, the variation in the layer spacings and molecular areas would not be reversible with temperature as we found. This behaviour would then correspond to different macrodomains, and not to microdomains as in the model proposed in figure 11. Further, such macrodomains would be observable by XRD, in contradiction with our experimental results which clearly show the existence of one unique smectic A phase. We may also state that, contrary to what is observed in the smectic $\tilde{\mathrm{A}}$ phase [9], the predicted undulations must be incoherent, otherwise an extra spot would appear in the oriented sample X-ray pattern, corresponding to the periodicity in the plane of the layers. This was definitely not observed in our case.

C. C. and B. H. thank the European project ERBCHRX CT 390161 for financial support; A. C. R. wishes to thank the University Louis Pasteur of Strasbourg for financial support; and D. G. wishes to thank Praxis XXI for a fellowship under the project 3/3.1/MMA/1769/95.

References

[1] Bruce, D. W., Estdale, S., Guillon, D., and Heinrich, B., 1995, *Liq. Cryst.*, **19,** 301.
[2] Guillon, D., and Skoulios, A., 1977, *Mol. Cryst. liq. Cryst.*, **38,** 31; Ibn-Elhaj, M., Coles, H., Guillon, D., and Skoulios, A., 1993, *J. Phys.*, **3,** 1807.
[3] Kovacs, A. J., 1955, *Ric. Sci. Suppl.*, **25,** 668; Guillon, D., and Skoulios, A., 1977, *Mol. Cryst. liq. Cryst.*, **39,** 139.
[4] Guillon, D., and Skoulios, A., 1976, *J. Physique*, **37,** 797; Poeti, G., Fanelli, E., Torquati, G., and Guillon, D., 1983, *Il nuovo Cimento, 1*, **2D,** 1335.
[5] Doolittle, A. K., 1951, *J. appl. Phys.*, **22,** 1471.
[6] *Handbook of Chemistry and Physics*, 67th Edn, 1986-87 CRC Press Inc. (Boca Raton: CRC Press).
[7] Navarro-Rodriguez, D., Frère, Y., Gramain, Ph., Guillon, D., and Skoulios, A., 1991, *Liq. Cryst.*, **9,** 321.
[8] Cruz, C., Gallani, J. L., Guillon, D., Heinrich, B., and Bruce, D. W., 1999, *Mol. Cryst. liq. Cryst.*, **330,** 1395.
[9] Hardouin, F., Levelut, A. M., Achard, M. F., and Sigaud, G., 1983, *J. Chim. Phys.*, **80,** 83; Prost, J., and Barois, Ph., 1983, *J. Chim. Phys.*, **80,** 83.
[10] Guillon, D., and Skoulios, A., 1984, *J. Physique*, **45,** 607.