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Liquid-crystalline and thermochromic behaviour of 4-substituted 1-methylpyridinium iodide surfactants

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The mesogenic behaviour of a series of thirty-one 1-alkyl-4-(or 2-)alkylpyridinium salts and of a homologous series of four 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides is described. The occurrence and stability range of the thermotropic phases depend dramatically on the structure of the surfactants. Mesophases are only observed if the 1-alkyl group is methyl. Furthermore, an unusually strong dependence of the mesogenic behaviour on the number of carbon atoms in an unbranched alkyl chain is found. Alkyl chain branching, especially close to the headgroup, in 1-methyl-4-(C_{12}-alkyl)pyridinium iodides lowers the clearing point and, to a lesser extent, the melting point. Apparently, the mesophase is destabilized due to the lack of space to accommodate a protruding side chain. The mesophases of the unbranched as well as the branched compounds are identical to the smectic A phase found for carbohydrate mesogens with one alkyl chain (smectic A_d). The mesophase of the peg-shaped compound 1-methyl-4-(17-tritriacontyl)pyridinium iodide could not be assigned with certainty. Based on molecular shape, textural characteristics and the observed miscibility with the columnar hexagonal phase of a non-ionic carbohydrate amphiphile, the compound most likely exhibits a D_{hd} phase. However, the single reflection, corresponding to a *d*-spacing of just over one molecular length, suggests a smectic phase. It is assumed that all compounds described belong to the general class of amphiphilic mesogens. 1-Methyl-4-*n*-alkoxycarbonylpyridinium iodides are visibly thermochromic, whereas the corresponding 4-alkyl derivatives are not. This probably stems from a shift of the charge-transfer absorption band to higher wavelengths, induced by the presence of the ester group in conjugation with the pyridinium ring. Lyotropic liquid-crystalline phases of some surfactants were also examined. There is no apparent correlation between the occurrence of thermotropic and lyotropic phases in individual compounds. The types of lyotropic phases observed are dependent on the overall shape of the anhydrous molecule, but, surprisingly, it was not always possible to correlate the mesophase behaviour at maximum hydration with the type of aggregate formed in dilute solution.

1. Introduction

Besides the scientific challenge of understanding liquid-crystallinity, the sheer beauty of mesophases stimulated us to start research in this field. The relationship between the structure of the mesogens and the properties of the mesophases are well

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documented for non-amphiphilic mesogens [1]. General requirements for the molecular architecture of such a mesogenic compound, in order to exhibit a certain kind of mesomorphic behaviour (nematic, smectic, etc.), have been described [1]. However, for amphiphilic mesogens this relationship has been much less explored.

Long chain *N*-alkylated pyridinium salts [2–5], recently also with an ω-substituted mesogenic group [6], 1-methyl-3(or 4)-dodecyloxypyridinium salts [7] and their thio analogues [7], 1-methyl-4-*n*-alkylpyridinium salts [8], and 1-methyl-3,5-bis-(*n*-hexadecyloxycarbonyl)pyridinium salts [8] have been found to exhibit mesomorphic behaviour. The nature of these liquid-crystalline phases was assigned as smectic A, except for that of 1-methyl-4-(17-tritriacontyl)pyridinium iodide which was tentatively identified as smectic C [8]. The pyridinium salts clearly belong to the amphiphilic class, but also possess a structural element that may be found in non-amphiphilic mesogens (i.e. the pyridinium ring). These salts might, therefore, be viewed as intermediates between non-amphiphilic and amphiphilic mesogens [9].

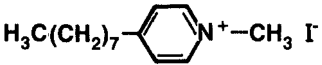
Gray and Harrison [10] have studied the effect of shifting a methyl group progressively to the penultimate carbon of the chain on the mesogenic properties of alkyl 4-(*p*-substituted benzylideneamino)cinnamates. Particularly 1-methylation, and to a lesser extent methyl branching in general, reduces the stability of the mesophase. A similar conclusion was drawn by Malthête *et al.* [11].

We have made an extensive study of the aggregation behaviour of 1-alkyl-4-alkylpyridinium salts and 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides in dilute aqueous solutions [12–14]. It became clear that the morphology of the surfactant aggregate (i.e. spherical or rod-like micelle or vesicle) is mainly determined by the shape of the surfactant molecule [12]. In contrast, the properties of spherical micelles are barely dependent upon the structure of the surfactant [13], apart from the packing of the alkyl chains in the core of the micelle [14]. In the course of our studies it was found that many of these surfactants exhibit thermochromic liquid-crystalline behaviour over a distinct temperature range. This range appears to be remarkably dependent upon the precise structure of the surfactant. Furthermore, the large number of compounds available, i.e. thirty-one, gave us the opportunity to study in detail the relationship between the structure of the mesogenic compound and the properties of the mesophase. Finally, attention will be paid to the question as to whether there exists a relationship between the aggregation behaviour in dilute aqueous solutions and thermotropic and lyotropic mesogenic behaviour. The mesogenic behaviour of the relevant surfactants was investigated using optical polarization microscopy, differential scanning calorimetry, and X-ray diffraction on unoriented samples. The following structural features of 1-alkyl-4-alkylpyridinium salt surfactants were varied: (i) the length of the alkyl chain in a series of 1-methyl-4-*n*-alkylpyridinium iodides, **1–6**, and in a series of 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides, **7–10**; (ii) the degree of branching of the alkyl chain in a series of 1-methyl-4-(C_{12}-alkyl)pyridinium iodides, **4** and **11–17**; (iii) the substitution pattern of the pyridinium ring, **4** and **19**; (iv) the counterion type in 1-methyl-4-*n*-dodecylpyridinium salts; and (v) the hydrophobicity of the 1-alkyl group in a series of 1-alkyl-4-*n*-dodecylpyridinium iodides.

2. Results and discussion

2.1. *Thermal behaviour*

The thermal behaviour of the mesogenic compounds was examined using differential scanning calorimetry. The transition temperatures and enthalpy data compiled from the DSC data for a series of 1-methyl-4-*n*-alkylpyridinium iodides, **1–6**,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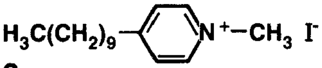
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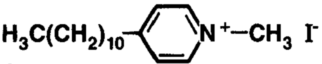
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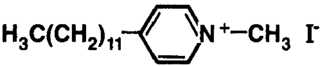
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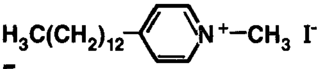
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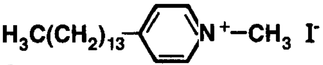
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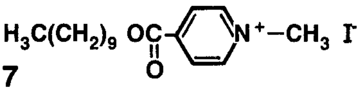
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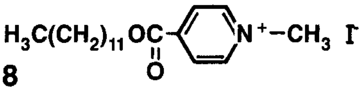
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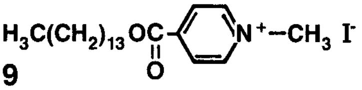
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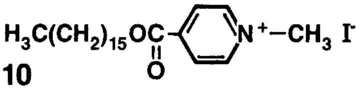
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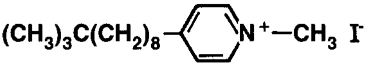
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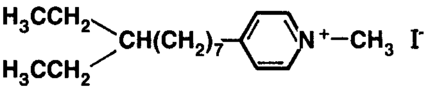
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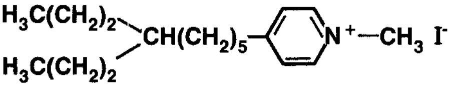
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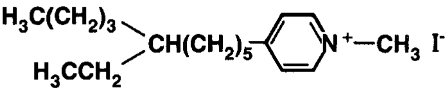
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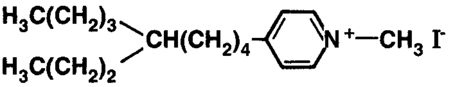
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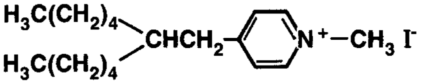
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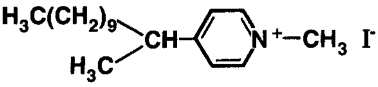
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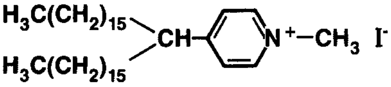
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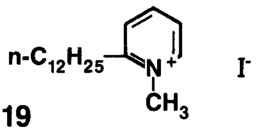
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and for 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides, **7**–**10**, are listed in tables 1 and 2. For various branched 1-methyl-4-(C_{12}-alkyl)pyridinium iodides (**4** and **11**–**17**) as well as for 1-methyl-4-(17-tritriaconyl)pyridinium iodide (**18**) and for 1-methyl-2-*n*-dodecylpyridinium iodide (**19**) the corresponding data are listed in table 3. In contrast to the liquid-crystallinity of 1-methyl-4-*n*-dodecylpyridinium iodide (**4**) no mesophase was found when the substituent on the 1-position in 1-alkyl-4-*n*-dodecylpyridinium iodides was altered from methyl to either hydrogen, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *n*-hexyl, 3-hydroxypropyl, or 2-methoxyethyl. 1-Methyl-4-*n*-dodecylpyridinium bromide, **20**, forms a mesophase at its melting point of 106·1–109·0°C ($\Delta H = 32{\cdot}0\,\mathrm{kJ\,mol^{-1}}$). The clearing point could not be determined because of the onset of decomposition around 198°C.

2.1.1. *Variation of alkyl chain length*

Plots of the transition temperatures as a function of the alkyl chain length (n_c) of a series of 1-methyl-4-*n*-alkylpyridinium iodides and of a series of 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides are given in figure 1. For the former type of surfactants a very strong dependence of the clearing point in n_c is found, whereas the melting point is barely dependent on this parameter. This dependence of the clearing point on n_c is much stronger than that for the second series of pyridinium iodides and for other kinds of amphiliphic mesogenic compounds [15–16]. This behaviour is perhaps characteristic for long chain pyridinium halides since Knight and Shaw [2] have found a similar strong dependence for 1-alkylpyridinium halides.

Table 1. Transition temperatures and enthalpic data for a series of 1-methyl-4-*n*-alkylpyridinium iodides.

	Alkyl group	T_{mp}/°C	ΔH/kJ mol^{-1}	T_{cp}/°C†	ΔH/kJ mol^{-1}
1	*n*-octyl	100–103‡			
2	*n*-decyl	111–113‡			
3	*n*-undecyl	113·7–115·6	29·1	< 0§	
4	*n*-dodecyl¶	112·8–113·1	24·2	148–153	0·63
5	*n*-tridecyl	108·4–112·3	32·1	186·5–188·3 (187·3)	1·06
6	*n*-tetradecyl	113·7–115·9	32·7	207·9–208·8 (207·0)	1·10

† Values in parentheses are those observed upon cooling.
‡ Observed with a Kofler hot stage.
§ Estimated from the clearing point of a 3·3 : 1 mixture of **4** and **3**.
¶ Taken from [8].

Table 2. Transition temperatures and enthalpic data for a series of 1-methyl-4-*n*-alkoxycarbonylpyridinium iodides.

	Alkyl group	T_{mp}/°C	ΔH/kJ mol^{-1}	T_{cp}/°C	ΔH/kJ mol^{-1}
7	*n*-decyl	82·8–86·0	31·5	153·4–154·4	0·86
8	*n*-dodecyl	90·9–93·8	40·8	175·7–177·5	1·12
9	*n*-tetradecyl	97·1–98·8	47·6	178·9–181·6	1·11
10	*n*-hexadecyl	101·3–102·9	55·9	179·4–182·1	0·86

Table 3. Transition temperatures and enthalpic data for a series of 1-methyl-4-(C_{12}-alkyl)pyridinium iodides, 1-methyl-2-*n*-dodecylpyridinium iodide, and 1-methyl-4-(17-tritriacontyl)pyridinium iodide.

	Position of branching	T_{mp}/°C	ΔH/kJ mol^{-1}	T_{cp}/°C†	ΔH/kJ mol^{-1}
4‡	12	112·8–113·1	24·2	148–153	0·63
11	9	113·5–115·3	*c*.22·7	142·9–143·2 (143·0)	0·58
12	8	38·3–50·5	8·2	130·3–130·8 (130·5)	0·63
13	6	35·1–51·8	6·0	121·4–122·7 (120·1)	0·85
14	6	91·3–95·2	13·3	132·3–133·0 (132·5)	0·97
15	5	93·9–97·5	16·4	132·9–133·7 (133·3)	0·98
16	2	96–98§			
17	1	69·5–74·4	24·5	(58)	(0·89)
18‡	1	72	43·5	82–83	0·96
19		59·8–61·9	15·8	140·4–145·2 (138·5)	0·55

† Values in parentheses are those observed upon cooling.

‡ Taken from [8].

§ Observed using a Kofler hot stage.

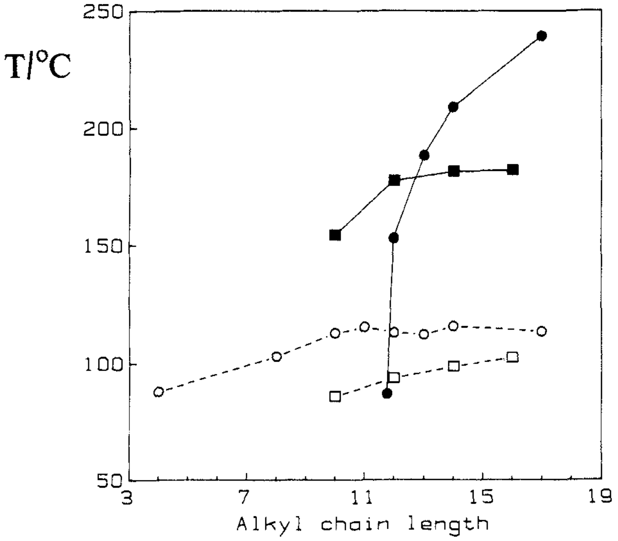


Figure 1. The transition temperatures of a series of 1-methyl-4-*n*-alkylpyridinium iodides (○ melting; ●, clearing points and a series of 1-methyl-4-*n*-alkoxy-carbonylpyridinium iodides □, melting; ■, clearing points) as a function of the number of carbon atoms in the alkyl chain.

2.1.2. *Effect of alkyl chain branching*

A plot of the transition temperatures of a series of 1-methyl-4-(C_{12}-alkyl)-pyridinium iodides as a function of the position of branching is shown in figure 2. The clearing points are shifted to lower temperatures when the position of branching is shifted towards the headgroup. For 1′-methylation (**17**) and 2′-alkylation (**16**) the liquid-crystalline behaviour is strongly reduced, but **17** is still monotropic, the mesophase only being observed upon cooling the isotropic liquid. The melting points are less strongly affected by branching. The much lower melting points of **12** and **13** may originate from a different packing in the crystal lattice. The mesophases of **1–17** were all assigned as smectic A (*vide infra*). Branching increases the width of the molecule, which usually destabilizes the mesophase, provided that the headgroup is kept unchanged [9]. In a smectic phase the molecules are packed side by side. Especially near the headgroups there is no space to accommodate a protruding side chain. Therefore, the stability of the mesophase is affected most when the alkyl chain is branched near the headgroup. When the alkyl chain is branched at positions farther away, the alkyl chain can adapt its conformation in such a way that the effect of the increase in width is spread out, leading to a smaller destabilization of the mesophase.

Malthête *et al.* [11] have studied the mesophorphic properties of branched derivatives of fluorene. The mesophases were assumed to be smectic A, with the branched alkyl chain ends interdigitated. Interestingly, the stability of these mesophases depends on the position of branching in a similar way to that of the 1-methyl-4-(C_{12}-alkyl)pyridinium iodides.

2.1.3. *Variation of the 1-alkyl group*

The effect of variation of the 1-alkyl group in 1-alkyl-4-*n*-dodecylpyridinium iodides on the liquid-crystalline behaviour indicates how subtle the properties of a mesophase depend on the detailed molecular structure of the mesogenic compound. Only in the case of a 1-methyl group is a mesophase observed. The absence of

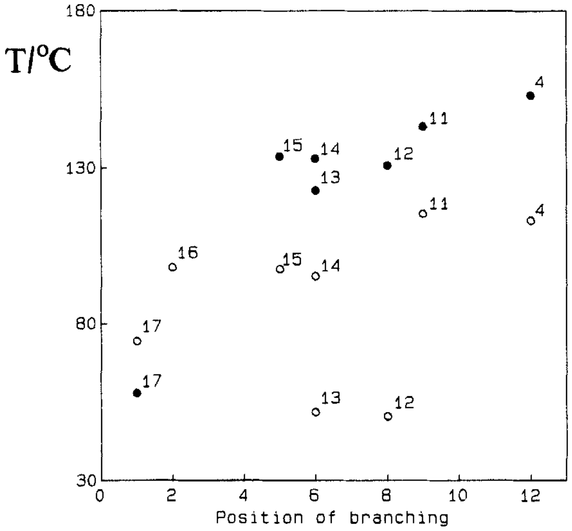


Figure 2. The transition temperatures of a series of 1-methyl-4-(C_{12}-alkyl)pyridinium iodides as a function of the position of branching. ○, melting; ●, clearing points.

mesophases for other substituents at the 1-position such as ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *n*-hexyl, 3-hydroxypropyl, or 2-methoxyethyl may originate from the introduction of an apolar section at the outside of the molecule, thus interrupting the interlayer attractive forces necessary for stabilizing the mesophase [17]. Mesophases were also absent for 4-*n*-dodecylpyridinium iodide which may be due to a particularly favourable lattice energy, as is apparent from the high melting point. Mesophases may again emerge when the 4-alkyl chain is elongated.

2.1.4. *Variation of the counterion*

Sudhölter *et al.* [8] have presented melting points and clearing points for 1-methyl-4-*n*-dodecylpyridinium chloride and the corresponding perchlorate. It appears that the stability of the mesophase exhibits a complex dependence on the nature of the counterion of 1-methyl-4-*n*-dodecylpyridinium salts. Knight and Shaw [2] have found similar effects for 1-*n*-alkylpyridinium halides.

In summary, it is evident that the occurrence and range of the mesophase depend dramatically on subtle variations in the structure of the mesogenic compound. First, liquid-crystalline behaviour is only observed when the 1-alkyl group is methyl. Secondly, this behaviour is strongly dependent upon the length of the (unbranched) alkyl chain. Thirdly, the presence of an ester group between the alkyl group and the pyridinium ring alters the stability of the mesophase. Furthermore, the counterion also plays an important role. Finally, alkyl chain branching, while keeping the number of carbon atoms constant, influences the width of the temperature range over which a mesophase is observed.

2.2. *Characterization of the mesophases*

The mesophase textures of **4–15** and **19** are very much alike. All of the evidence points towards a smectic A phase. Upon cooling the samples from the isotropic phase on untreated microscope slides, bâtonnets are formed at the clearing point, which coalesce to fan-like focal conic structures and large pseudo-isotropic domains. Oily streaks are invariably observed. The enthalpy of the mesophase to isotropic transition is relatively small (see table 1–3), which is also in agreement with the assignment of a smectic phase with liquid layers [9].

Südholter *et al.* [8] concluded that the mesophase of compound **4** is most likely smectic A_d. Powder X-ray data of **4** reveal a single sharp reflection at a low angle and a diffuse band at a much higher angle, which is consistent with a smectic phase with liquid layers. For **4** a layer spacing of 29 Å can be calculated from the Guinier photograph. This layer spacing corresponds to approximately 1·25 times the length of a fully extended molecule of **4**. The authors proposed a bilayer structure with interdigitated alkyl chains and the polar headgroups on the outside of each layer (for an illustration see figure 4 of [8]). This proposed structure is of course very similar to that of the lyotropic L_α phase. The powder pattern of compound **15** reveals a layer spacing of 26 Å. The length of a fully extended molecule as calculated from the CPK model is approximately 19 Å to which 2·15 Å for the contribution of the iodide anion should be added. As the textures are not indicative of a tilted phase, a S_{Ad} phase is suggested. More evidence was found from a miscibility experiment of compound **8** with 1-undecylamino-1-deoxy-D-glucitol [15–16]. Mono-alkylated carbohydrate derivatives are now generally believed to display S_{Ad} phases [17]. The mesophases of both compounds are miscible in all proportions. In a contact preparation (see figure 4) no

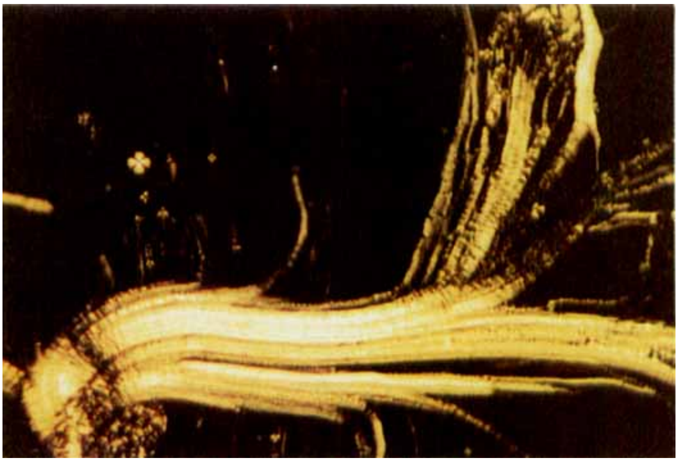


Figure 3. The oily-streak texture of the smectic A_d phase of **4** (crossed polarizers, 116°C).

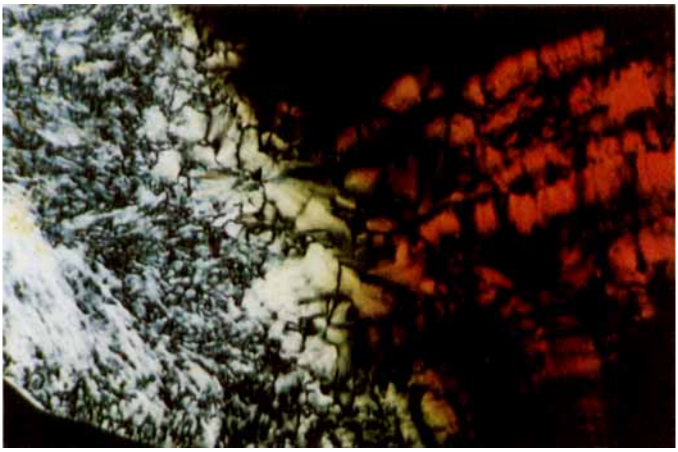
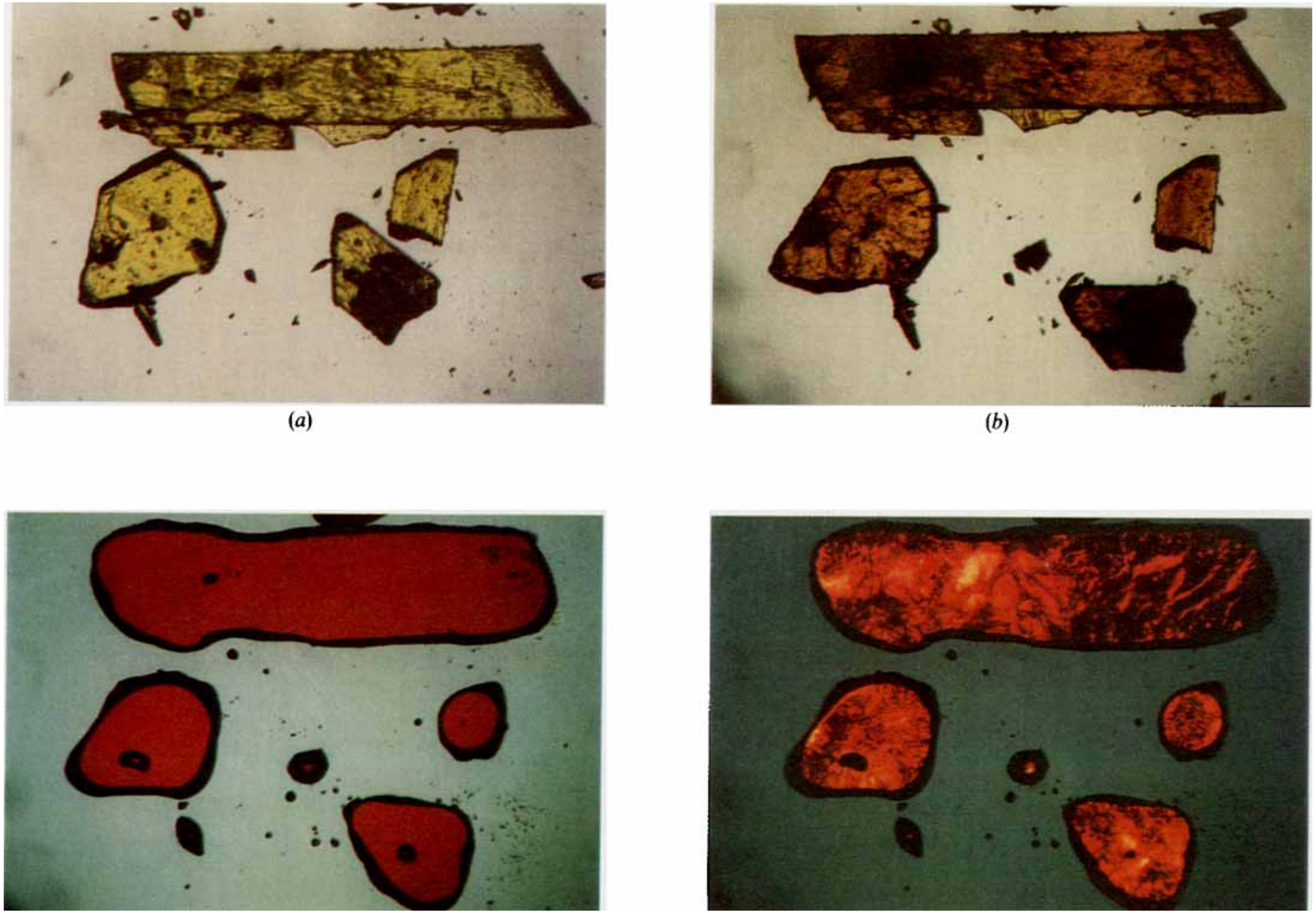


Figure 4. Contact preparation of **8** (left; orange) and 1-undecylamino-1-deoxy-D-glucitol (right; white) showing complete miscibility (crossed polarizers, 130°C).

Figure 5. Contact preparation of D-ribose-di-*n*-decyl-S,S-acetal (right) and **18** (left) suggesting complete miscibility (crossed polarizers, 55°C).



(*a*) (*b*)

(*c*) (*d*)

Figure 6. Thermochromicity of **8** at (*a*) 25°C, (*b*) 85°C, (*c*) 93°C, and (*d*) mesophase texture (crossed polarizers).

discontinuity of the texture is observed. We therefore submit that the surfactants **4–15** and **19** also form S_{Ad} mesophases. This is also the most common phase for other long chain pyridinium salts [5].

Praefcke *et al.* [18] have shown that a columnar hexagonal phase (D_{hd}) instead of a S_{Ad} phase arises in non-ionic amphiphilic mesogens which are branched close to the polar headgroup (peg-shaped). Therefore, a D_{hd} phase was also expected for the highly branched **16**. Unfortunately, **16** shows no liquid-crystalline behaviour, which may be caused by the decreased length of the fully extended molecule. The mesophase of **18**, which is also branched near the headgroup, has previously been assigned as smectic C [4]. Based on considerations of molecular shape, a D_{hd} phase would be predicted. Upon reexamination, the texture of **18** strongly resembles that of a D_{hd} phase (see figure 2 of [8]). Moreover, microscopic examination of an uncovered droplet of **18** reveals well-defined hexagonal domains and no evidence of stratification. The mesophase of D-ribose-di-*n*-decyl-S,S-acetal has been identified as D_{hd} [18]. Although a contact preparation of this ribose derivative and **18** (see figure 5) shows little spontaneous diffusion, a homogeneous mesophase with a hexagonal texture was obtained after mixing the two compounds in several ratios. This suggests that the mesophase of **18** could also be columnar hexagonal. However, the Guinier photograph of **18** does not support this conclusion; only one sharp reflection is observed, which corresponds to a *d*-spacing of 30·4 Å, with very little change as a function of temperature. This value is slightly more than the length of one fully extended molecule (28 Å, with parallel alkyl chains). We cannot be sure that this is, in fact, the only reflection, because the Guinier camera that is available to us does not provide any information on *d*-spacings higher than 35 Å. Therefore, we cannot give a definite assignment of the mesophase of **18**.

The finding that the mesophase of the ionic pyridinium salts is compatible with the mesophase of non-ionic carbohydrate derivatives was somewhat unexpected. Goodby [19] tried, unsuccessfully, to identify the mesophase of alkyl glucopyranosides by miscibility experiments. Since then carbohydrates were considered to form a separate class [20], incompatible with other mesogens due to the abundant presence of hydrogen bonds. Our results indicated that (i) we should probably consider all amphiphilic mesogens to be in one class after all and (ii) the observed mesophases formed are governed by molecular shape and they are very similar, if not identical, to common lyotropic phases such as L_α, H_I, H_{II} [17].

2.3. *Thermochromic behaviour*

1-Methyl-4-alkoxycarbonylpyridinium iodides are thermochromic. Upon heating, changes in colour are observed at (i) a crystal–crystal transition (see figures 6 (*a*) and (*b*)) (ii) the melting point (see figures 6 (*b*) and (*c*)). The colour actually deepens with increasing temperatures. This increasing effect is not observed in visible light, but is not necessarily absent (*vide infra*), for 1-methyl-4-alkylpyridinium iodides. Bazuin *et al.* [21] have reported thermochromicity for 1-*n*-hexadecyl-4-cyanopyridinium iodide.

A strongly electronegative group in conjugation with the pyridinium ring appears to be of paramount importance for the observation of this effect. These electronegative substituents either shift the charge-transfer absorption band [22] to higher wavelengths which makes the colour change visible to the human eye, or induce a special kind of sandwich-like orientation of the pyridinium ring and the iodine anion necessary for charge transfer. We favour the former explanation since in dilute aqueous solution the charge-transfer absorption bands of **7–10** are indeed shifted to longer wavelengths

[13] compared to those of **1–5** [12]. This implies that possible thermochromic behaviour of other long chain pyridinium iodides may be veiled to the human eye as well.

Upon melting of **7–10** a red-shift is found (see figure 6). This shift may be caused by a reduction of the micropolarity near the pyridinium ring due to a change in packing of the molecule. At the melting point the packing of the molecules changes from a monolayer of 20 Å width into an interdigitated bilayer of 28 Å width.

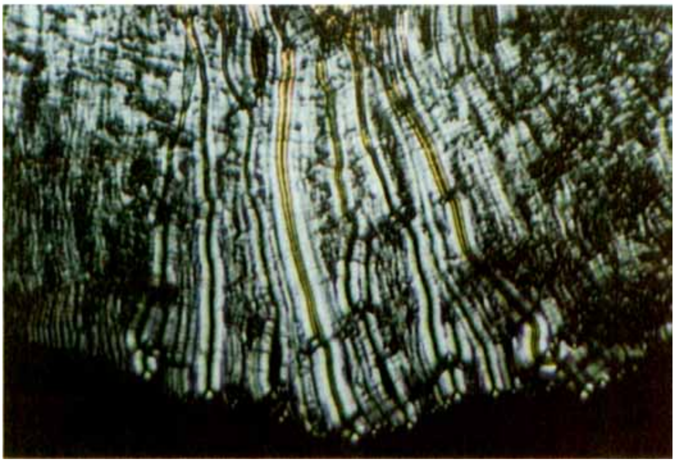
2.4. *Lyotropic liquid-crystallinity*

In this section preliminary results of the lyotropic behaviour [23] of several of the long chain 4-alkylpyridinium salts are presented and these results are compared with the aggregation behaviour of these surfactants in dilute aqueous solution. There appears to be no correlation between the occurrence of thermotropic and lyotropic behaviour in individual compounds as several of the non-mesogenic derivatives with a substituent on nitrogen other than methyl, for example 1-ethyl-4-dodecylpyridinium iodide and 1-(2′-methoxyethyl)-4-dodecylpyridinium iodide do form lyotropic liquid crystal phases in water.

Figure 7 (*a*) shows a photograph of the different phases of **4** in a contact experiment with water. As a function of increasing surfactant concentration a hexagonal, a cubic, and a lamellar lyotropic liquid-crystalline phase can be identified as 328 K. For **11** a similar sequence of phases has been found. For **15** and **16** a lamellar mesophase (so-called myeline figures [24]) is observed at the surfactant–water interface (see figure 7 (*b*)). Compound **18** does not form lyomesophases at ambient temperature, but upon heating to 50°C a (presumably inverted) hexagonal mesophase is formed at the surfactant–water interface.

In dilute aqueous solutions at ambient temperatures monomers of **4** and **11** aggregate, above a critical concentration, into spherical micelles which grow into rod-like or worm-like micelles (no stiffness is implied) at increasing surfactant concentration [12, 13]. In contrast, monomers of **15** and **16** associate into bilayers [13]. Interestingly, the first lyotropic liquid-crystalline phase is hexagonal for surfactants which associated into rod-like micelles. A lamellar mesophase is the first liquid-crystalline phase found for surfactants aggregating into bilayers. It is evident that the aggregation behaviour in dilute aqueous solutions and the lyotropic liquid-crystalline behaviour are strongly linked, an observation in agreement with the work of Hoffmann [25] and Tiddy [26]. The balance of forces, determined by the shape of the surfactant molecule, which governs the morphology of a surfactant aggregate in dilute aqueous solutions also determines the morphology of the lyotropic mesophases. A contact preparation on a microscope slide constitutes, therefore, a very simple determination of the type of aggregates that a surfactant will most likely form in aqueous solution. However, things are seldom as simple as they seem. Electron microscopic studies [12, 27] have revealed that compounds **7–10** form vesicles in dilute solution. Therefore, we would expect a lamellar lyophase (myelin figures) to arise at the surfactant–water interface, but this is not the case. The first lyophase to form in all four cases is cubic, whereas a lamellar phase is formed in a ring closer to the anhydrous bulk, i.e. at lower water concentrations. Several types of cubic lyophases are known, all of them optically isotropic and therefore difficult to distinguish by means of a contact preparation. The behaviour of **7–10** in dilute solution can be correlated with the first non-cubic phase, but this may be coincidental. Further research is required to be able to describe the lyotropic phase behaviour of our compounds in more detail.

(*a*)



(*b*)

Figure 7. (*a*) Textures of various lyotropic liquid-crystalline phases of **4** (crossed polarizers 56°C). (*b*) Myelin figures of **16** (crossed polarizers, room temperature).

3. Experimental

The preparation of **1–20** and of the 1-alkyl-4-*n*-dodecylpyridinium iodides have been described previously [8, 13]. Liquid-crystalline behaviour was determined visually with a Mettler FP 82 hot stage mounted on a Nikon polarization microscope and quantitatively with a Perkin–Elmer Delta Series DSC 7 apparatus. Mr F. van der Horst (Department of Solid State Physics, University of Groningen) kindly performed temperature dependent powder X-ray measurements (Guinier-Simon camera).

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